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SPECIAL ISSUE ON GAS-PHASE KINETICS & DYNAMICS



Guest Editor P. Mathi

A Publication of Indian Society For Radiation and Photochemical Sciences

Message from the President and Secretary, ISRAPS

Dear ISRAPS Members,

Greetings from the ISRAPS Executive Council!

We take this opportunity to acknowledge all the ISRAPS Life Members and other researchers who have contributed in organizing various activities of ISRAPS at different institutes across the country.

The new executive council assumed office in March 2021. On behalf of the executive council, we thank the members for their support in its formation, and expect continued support and guidance for future activities. We made a good start by announcing ISRAPS Discussion Meeting on Gas-Phase Kinetics & Dynamics on April 10th, 2021, to felicitate a senior member Prof. Sanjay Wategaonkar, who was to superannuate in April 2021 at the age of 65 years after his meritorious service. Around the same time, the second wave of COVID-19 pandemic struck. Considering the ongoing travel restrictions and health advisories, the ISRAPS executive council decided to conduct the discussion meeting online. Prof. Wategaonkar, TIFR has contributed significantly in the area of Supersonic Jet Spectroscopy. The meeting focused on the state-of-the-art research in the area of Gas-Phase Kinetics & Dynamics, undertaken by various research groups in the country. This bulletin is a collection of articles on some of the topics discussed in the meeting. The Executive Council of ISRAPS takes this opportunity to thank all the speakers and contributors to this discussion meeting, and acknowledge Dr P. Mathi for meticulously organizing and Guest Editing this issue.

It is our continuous endeavor to find new ways, in these challenging times, to stay connected scientifically and disseminate the knowledge of Radiation and Photochemical Sciences among young researchers in the country. With this spirit, recently we could successfully conduct the National Symposium on Radiation & Photochemistry (NSRP 2021) on virtual platform at IIT Gandhinagar and BARC, Mumbai.

On behalf of the ISRAPS council, we convey our sincere gratitude to all life members for their constant support and encouragement. The council looks forward to your valuable suggestions and active participation in the forthcoming events of ISRAPS, such as hosting symposia, quarterly thematic scientific meetings at different institutes/universities, publication of ISRAPS Bulletins, etc. The next important event is Trombay Symposium on Radiation & Photochemistry (TSRP-2022) being organized online during Jan. 12-15, 2022.

We wish all the members excellent health and satisfying scientific career.



Dr. Awadhesh Kumar President, ISRAPS



Dr. Jyotirmayee Mohanty Secretary, ISRAPS

ISRAPS Bulletin



A Publication of Indian Society for Radiation and Photochemical Sciences

Editor's Desk...

It is a great honor to be involved as the guest editor of this special issue of ISRAPS bulletin dedicated to "Gas-Phase Kinetics & Dynamics". This bulletin is a collection of articles based on some of the topics covered in the ISRAPS Discussion Meeting on Gas-Phase Kinetics & Dynamics held on April 10th, 2021. Investigation of elementary chemical reactions, energy transfer processes, and kinetics, under chemically isolated conditions and more complex conditions, is essential for fundamental understanding of gas-phase chemistry in a wide range of disciplines.

In the first article, the authors have investigated the factors affecting π -stacking interactions at the molecular level in model systems, using gas-phase IR spectroscopic method in conjunction with quantum chemical calculations. The second article focuses on gas phase reactivity of atmospheric interest; here, the authors propose the gas-phase thermal reaction between nitrogen dioxide and phenol, to be an important contributor to the atmospheric HNO₃. Microhydration of acids is discussed in the third article. The fourth article provides an account of the diverse photochemistry exhibited by clusters under the influence of intense laser pulses. Studies on the gas phase reaction of the OH radical with volatile organic compounds are discussed in the last article.

I hope that our esteemed readers would find this issue interesting and get a glimpse of the research and developmental activities in the field of gas phase kinetics and dynamics in the country. I thank the authors for their sincere cooperation and efforts in writing the articles in extremely short notice. I am also grateful to Prof. S. Wategaonkar for writing a wonderful forward to this issue of ISRAPS bulletin. Finally, I would like to thank the Executive council of ISRAPS for entrusting me with this responsibility.

Dr. P. Mathi (Guest editor)



Dr. P. Mathi joined BARC in 2001, received PhD from University of Mumbai in 2009 and carried out postdoctoral research at Institute of Atomic and Molecular Sciences, Taipei, from 2009-2011. Currently her research efforts are related to iodine aerosol chemistry and application of femtosecond laser induced breakdown spectroscopy in high energy materials and paleoclimate reconstruction.

A Foreword to the ISRPAS Bulletin on the GAS PHASE KINETICS and DYNAMICS

It is my privilege and pleasure to write a foreword to this special issue of ISRAPS bulletin on Gas-Phase Kinetics and Dynamics. Gas phase investigations of a variety of molecular phenomena are of immense importance from the point of view of understanding the fundamental microscopic details of the mechanisms/ kinetics of the reactions, transition states, the energy disposal to the products, the intrinsic binding energies of weak interactions, etc. I personally thank ISRAPS for bringing out this issue that consists of five articles that covers diverse topics such as the molecular properties that govern stacking interactions among aromatic molecules to the complex reactions in clusters under intense laser fields. All the contributions are from the research groups of eminent scientists in India working in the experimental and theoretical aspects of the gas phase kinetics and dynamics. The article by Patwari et al. elucidates the importance of dipole moments in stabilizing the pi-stacked structures of aromatic compounds. These structures are very weakly bound and the binding potential well is very shallow which renders investigating such structures, which are abundant and very influential in day to day life, very difficult. An article by Tapas Chakraborty categorically shows that the nitrous acid, HONO, is not observed as one of the products of the reaction between the NO₂ and phenol, although it has been predicted theoretically. Prof Maity dwells on how many of solvent molecules would be required for a weak acid to dissociate in its hydrated cluster. He has shown that there is linear relationship between the number of water molecules and the pKa of the acid. An article by Prof Pramod Sharma shows that the large clusters have profound influence on the fragmentation/ionization dynamics of the species under the influence of intense laser fields. Finally, the last article by Prof Awadhesh Kumar et al. presents the temperature dependent kinetic studies of OH radical with volatile organic compounds in the gas phase. These data are very important from the point of view of determining their average lifetime in the troposphere and also determining their global warming potential. It was pleasure to peruse all the articles and I am sure the readers would also enjoy reading them.

Prof. Sanjay Wategaonkar



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Dipole Moment Assisted π -Stacking in Phenylacetylenes

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Abstract

The low stabilization energies of π -stacking interactions are challenging to investigate, even though various molecular systems have shown the significance of such interaction. Investigating the factors affecting π -stacking interactions at the molecular level requires a representative system without much perturbation to the aromatic electron cloud. Herein, we review dimers of phenylacetylene and mono-fluoro substituted phenylacetylenes investigated using gas-phase IR spectroscopic method combined with quantum chemical calculations. Interactions present in small gas-phase dimers of phenylacetylene and mono-fluorophenylacetylenes are very well described by their enhanced ability to π -stack which is proportional to increased dipole moment.

1. Introduction

A variety of intermolecular interactions present in nature play significant roles in determining structures and reactivity in a wide range of phenomena starting from simple proton transfer reaction to three-dimensional systems of macromolecules in biology and material sciences.¹⁻³ Interactions between π electron densities of two molecules, known as π -stacking, is one of the most important interactions which is least understood at the molecular level. Relatively low stabilization energy (about 10 kJ mol⁻¹) and the shallowness of the potential energy surfaces of π -stacking interaction lead to rapid interconversion to structures that are close in energy and to those which are not necessarily π -stacked, making its investigation difficult experimentally as well as theoretically. Although these interactions are relatively weak, they significantly influence many chemical and biological processes. Hence, a molecularlevel understanding of factors affecting such interactions is necessary further to explore its implementation in many chemical and biological events.

The π -stacking interaction refers to an attractive, non-covalent interaction between

aromatic rings of two molecules, benzene and other substituted aromatic molecules serve as prototypical models for molecular-level investigations of π -stacking interaction. Even though both the parallel displaced π -stacked and the T-shaped structures of benzene dimer have been reported to almost isoenergetic using high-level *ab initio* calculations,⁴⁻⁸ however, experimental gas-phase studies have revealed only the presence of T-shaped benzene dimer.9-12 On the other hand, several π -stacked dimers are reported for aromatic molecules with heteroatoms or substituents on the ring.^{13,14} A model proposed by Hunter and Sanders^{15,16} on π -stacking of substituted aromatic rings suggests that an electron-donating substituent on one of the interacting molecules should increase the negative charge of the π electron cloud, leading to an increase in the repulsion between the two stacked aromatic rings and electronwithdrawing substituent should inverse the behaviour. However, in sharp contrast, highlevel calculations based on dimers of substituted aromatic compounds revealed that all the substituted benzenes bind stronger than the unsubstituted benzene, irrespective of the nature of the substituent.7,17-19 Recent DFT calculations and some experimental results have suggested

that substitution on phenyl ring increases the dipole moment and electrostatic contribution to the interaction, enhancing the stability of substituted benzene dimers by increasing the interaction between polar substituents and apolar benzene rings. In the gambit of these pieces of information, the role of dipole moment in the π -stacking ability of substituted aromatic molecules needs to be addressed systematically for rigorous understanding of such interaction.

Phenylacetylene (PHA), in the absence of any heteroatom or group, incorporates minimal perturbation on the benzene ring.²⁰ Additionally, the mildly electron-withdrawing nature of ethynyl increases the polarizability and dipole moment of the molecule. Position dependent F atom substitution in mono-fluoro substituted phenylacetylenes (mFPHAs) viz., 2-fluorophenylacetylene (2FPHA), 3-fluorophenylacetylene (3FPHA), and 4-fluorophenylacetylene (4FPHA) further increase the dipole moment without significantly altering the system of interest. The absence of heteroatom based functional groups renders PHA and mFPHAs to exhibit multiple weak H-bonding sites as shown in Figure 1. The number of polymorphic forms is reported for PHA and mFPHA incorporating different combinations of possible interactions based on these weak H-bonding sites present in the system. Thus, PHA and mFPHAs serve as model systems to investigate π -stacking interaction with minimal perturbation to the benzene ring and gradual increase in the dipole moment without any strong H-bonding interaction sites. This article reviews



Figure 1. Various weak H-bonding interaction sites in PHA.

the structures of homo- and hetero- dimers of PHA and mFPHAs investigated using gas-phase IR spectroscopic measurements in combination with quantum chemical calculations.²¹⁻²³

2. Methods

The formation of molecular complexes in the gas phase is the first step towards the structural investigation which is achieved by the supersonic jet expansion method. This method produces a molecular beam consisting of gas-phase clusters in which molecular entities are bound by weak intermolecular non-covalent interactions. In our experiments, the desired molecular complexes/ clusters were formed in a supersonic free-jet expansion of a mixture of the reagents in the helium buffer gas. Vibrations spectroscopy has been long realized as a convenient spectroscopic tool in the investigation of intermolecular hydrogen bonding. The spectra in the acetylenic $C-H(Ac)_C-H$ and aromatic $C-H(Ar)_C-H$ stretching region of molecules are sensitive to the hydrogen bonding and show a characteristic shift in the vibrational frequencies upon hydrogen bonding. Hence infrared spectroscopy using population labelling of target species with electronic transition has been used for structural investigation.^{24,25} Laser induced fluorescence (LIF) and/or resonant two-photon ionization (R2PI) techniques are used to monitor the electronic transition. The LIF excitation spectra were recorded by collecting the total fluorescence perpendicular to both the gas and the laser pulses using a 50 mm focal length f/1 lens and detected using a photomultiplier tube (PMT-9780SB+ 1252-5F, Electron tubes Limited) and a Filter (WG305/WG320) combination.²⁶ On the other hand, the ion detection was carried out using a time-of-flight mass spectrometer based on the Wiley-McLaren design.²⁷ The electronic excitation of bare molecules and various clusters was achieved by the frequency-doubled output of a dye laser (Narrow Scan GR, Radiant Dyes) pumped with the second harmonic of a Nd:YAG laser (Surelite I-10; Continuum). The choice of

LIF and/or R2PI is primarily based on the signalto-noise (S/N) ratio for the given experiment. The infrared spectra of bare molecules and molecular clusters in their electronic ground state can be recorded using the IR-UV doubleresonance spectroscopic technique. IR spectra were recorded by introducing an IR laser 100 ns prior to the introduction of UV laser with the help of a digital delay generator (DDG 555; Berkeley Nucleonics Corporation) which results in population depletion of the ground state under vibrational resonant conditions. Ground state population depletion lowers the ion signal due to UV laser, which yields the ion dip IR (IDIR) spectrum as a function of IR frequency. The tunable IR light was generated by LiNbO3 OPO (Custom IR OPO; Euroscan Instruments), as an idler component, pumped with an injectionseeded Nd:YAG laser (Brilliant-B; Quantel).

Vibrational spectroscopy serves as an excellent tool to explore local interactions present in the molecular assemblies,²⁸ however



Figure 2. IR spectra of (A) PHA and (B) PHA dimer in the {Ac}_C-H stretching region (panel-I) and the {Ar}_ aromatic C-H stretching region (panel-II). Inset shows the calculated global minimum for the PHA dimer. See Ref [21] for details.

only provides qualitative information about the possible structures. Hence experimental observations need to be verified with the help of quantum chemical calculations which act as supplementary to the experimental results. Details of the conformational search and energy calculations carried out for the structural confirmation of molecular clusters are given in the corresponding literature.²¹⁻²³ Further, stabilization energy decomposition analysis of dimers was carried out using SAPT (Symmetry adapted Perturbation Theory) method, allowing the separation of interaction energies into physically well-defined components, such as those arising from electrostatic, induction, dispersion and exchange.²⁹ Energy decomposition analysis helps in determining the factors responsible for π-stacking interactions.

3. Results and Discussion

3.1 A π -stacked dimer of PHA

The IR spectra of PHA monomer and dimer in {Ac} C-H and {Ar}_C-H stretching region are shown in Figure 2. Detailed analysis of spectral characters is given in literature based on PHA dimer. IR spectrum of PHA monomer in {Ac}_C-H region shows the presence of two intense bands at 3326 and 3343 cm⁻¹ accompanied by several weaker transitions which have been attributed to the Fermi resonance couplings. However, with a marginal redshift of 2-3 cm⁻¹ and the overall appearance of PHA dimer spectra is very much similar to that of monomer in the {Ac}_C-H as well as in the {Ar}_C-H stretching region. This observation is in correspondence to hardly any perturbation to {Ac}_C-H and {Ar}_C-H oscillators. Along with experimental results, conformational search and energy calculations of PHA dimers were carried at different levels of theory. Five lower energy structures obtained from conformational search are reported as π -stacked structures with varying orientations of constituent monomers. The antiparallel π -stacked structure shown in the inset of Figure 2 remains the global minima among all the other structures obtained from conformational search irrespective of the level of theory.

Results from the spectral analysis and conformational search indicate the fact that the interaction among both the phenylacetylene molecules is restricted to the π electron density of the benzene ring without any involvement of {Ac}_C-H and {Ar}_C-H oscillators in the interaction. Thus, all these spectral features in {Ac} C-H and {Ar} C-H stretching regions along with stabilization energy favour the formation of anti-parallel π -stacked structure for PHA dimer. The DFT-SAPT interaction energy decomposition calculation for the phenylacetylene-dimer shows that the most stable anti-parallel π -stacked dimer maximizes both the electrostatic and the dispersion contributions.²¹ This result indicates that the alignment of dipole moments and interaction between the extended π electron densities play an important role in stabilizing the anti-parallel π -stacked form of the complex.

3.2 Enhanced *π*-stacking in mFPHA dimers

Results in the earlier section indicate the significance of dipole moment, which increases the electrostatic component of the interaction energy of the anti-parallel π -stacked dimer of PHA.²¹ In view of such observations, the role of the dipole moment of π -stacking interaction needs to be investigated further with appropriate model systems. Substitution of F atom on PHA increases the dipole moment of the system and expected to increase electrostatic contribution to the interaction. Therefore, hetero-dimers of Phenylacetylene (PHA) with four fluorophenylacetylenes (mFPHA) 2FPHA, 3FPHA, 4FPHA and 2,6-difluorophenylacetylene (DFPHA) and homo-dimers of mFPHAs were investigated using electronic and vibrational spectroscopic techniques in the gas phase and the results were interpreted using the electronic structure and SAPT calculations.^{22,23}



Figure 3. Panel-I: IR spectra in the {Ac}_C-H stretching region for (A) 2FPHA, (A') 2FPHA-PHAD (B) 3FPHA, (B') 3FPHA-PHAD, (C) 4FPHA, (C') 4FPHA-PHAD, (D) DFPHA, and (D') DFPHA-PHAD. Also shows the IR spectrum of the PHA (X) monomer for the sake of comparison. Panel-II: IR spectra in the {Ac}_C-H stretching region of (A) 2FPHA, (B) 2FPHA-dimer, (C) 3FPHA, (D) 3FPHA-dimer, (E) 4FPHA and (F) 4FPHA-dimer. See Refs [22] and [23] for details.

The IR spectra of hetero-dimers of PHA with mFPHAs and DFPHA along with homodimers of mFPHAs in the {Ac}_C-H stretching region are shown in Figure 3 panels I and II, respectively. Details of spectral analysis has been reported elsewhere.^{22,23} These spectra indicate that the extent of Fermi resonance coupling is modulated by fluorine substitution in the case of mFPHA as compared to PHA.³⁰ Spectra of hetero-dimers are complicated to interpret due to the overlap of resulting bands from two different constituent monomers. To deconvolute the IR spectra in the {Ac}_C-H stretching region, the PHA monomer was replaced with its monodeuterated isotopomer PHA-D1 (PHAD) in the hetero-dimers, wherein the {Ac}_C-H group is substituted with C-D group, which results in removing the bands due to PHA in the IR spectra. This procedure allows a direct comparison of the IR spectra of the hetero-dimers with corresponding mFPHA monomers. The IR spectra of the hetero-dimer (Figure 3, panel-I) show marginal (2-9 cm⁻¹) red-shifts relative to the corresponding monomers along with some changes in the intensity distribution pattern, which can be attributed to the redistribution of



Figure 4. Five lowest energy calculated structures of hetero-dimers of PHA with 2FPHA (row-1), 3FPHA (row-2), 4FPHA (row-3) and DFPHA (row-4) calculated stabilization energies are given in parenthesis for each structure. See Ref [23] for details.

Fermi resonance coupling due to shifts in the position of the fundamental bands. Similarly, a comparison of the IR spectra of homo-dimers of mFPHAs with that of the corresponding monomers (Figure 3 panel II) once again show marginal red-shifts (2-6 cm⁻¹) suggesting that the monomer units in the dimer are marginally perturbed relative to the corresponding monomer.

In an effort to assign the structures responsible for the observed spectra, DFT calculations were carried out for all the sets of hetero-dimers and homo-dimers resulting in 15 to 20 different structures for each set of dimers. Optimized structures for all the dimers can be categorized into different sets on the basis of different types of possible interactions present in the complex.

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Figure 5. Five lowest energy calculated structures of homo-dimers of 2FPHA (row-1), 3FPHA (row-2), 4FPHA (row-3) and PHA (row-4). Calculated stabilization energies are given in parenthesis for each structure. See Ref [22] for details.

However, for all the cases of hetero-dimers and homo-dimers, the lowest energy structures were found to be π -stacked structures differing in the relative orientation of the two monomer units shown in Figures 4 and 5, respectively. Based on the characteristics of IR spectra observed, inferences on possible structure can be made. The marginal changes in the IR spectra of {Ac} C-H stretching region of heterodimers and homodimers as compared to the corresponding monomers indicates the fact that the {Ac}_C-H group of the monomer is weakly perturbed and rules out the formation of structures that involve {Ac}_C-H group as hydrogen bond donor (either to π or F) in both the cases. The observed spectra suggest the possibility of dimer with either C-H… π interaction involving {Ar} C-H groups, or structures with C-H…F hydrogen bonds, or those which are π -stacked. While none of these structures can be ruled out based on the appearance of the spectra, the energetics of the dimers readily favour the π -stacked structures compared to the other structures. Therefore, the observed dimers can be logically assigned to the π -stacked structures.

Energy decomposition analysis of net stabilization energy carried out for homodimers and hetero-dimers indicates maximum stabilization by dispersion component and destabilization by dispersionless interactions, suggesting π -stacking is mainly driven by dispersion. However, the contribution of the electrostatic component is substantial. Figure 6 shows a linear correlation between the electrostatic components of the dimers and the average (computed) dipole moments of the constituent monomers. This correlation indicates the assistance of the dipole moment to form π -stacked structures by maximizing the electrostatic interaction even though the dispersion contributes predominantly. In the case of PHA hetero-dimers, the ratio of the dispersion to to the electrostatic component is maximum for the π-stacked structures with 60-70% contribution from the dispersion and 30-40% contribution from the electrostatics. Furthermore, in the case of FPHA homo-dimers electrostatic component of 2FPHA dimer is about 20% larger than in the case of PHA dimer in the order 2FPHA > 3FPHA > 4FPHA \approx PHA, which is the same as the stabilization energy order. On the other hand, the corresponding increase in the dispersion component is about 11% in the same order. Therefore, it can be inferred that substitution of fluorine does lead to an increase in the electrostatic component to a larger extent



Figure 6. The plot of the electrostatic component of the interaction energy average computed dipole moment for homo- and hetero- dimers of mFPHAs. The straight line is a linear fit to the data points with an R2 value of 0.966 and residuals are within 0.5 kJ mol⁻¹. The data points corresponding to PHA homo-dimer and DFPHA-PHA hetero-dimer (open squares) were omitted in the linear fitting.

than dispersion (on a relative scale). Thus, the substitution of fluorine enhances the ability of substituted benzenes to π -stack which can be attributed to the increased dipole moment.

4. Conclusions

In this report, the role of dipole moment on II-stacking ability for the gas-phase dimers of phenylacetylene and fluorophenylacetylenes is reviewed. Structures of gas-phase homoand hetero- dimers of PHA and mFPHAs were explored with the help of the gas-phase IR spectroscopic method in combination with quantum chemical calculations. Results indicate that the dispersion component dominates in all the cases, however, the ability to II-stack increases with the dipole moment, concurrent with the increase in the electrostatic component of the interaction energy.

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Gas-phase Reaction of phenol with NO₂

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Abstract

A recent study on the gas-phase thermal reaction between nitrogen dioxide and phenol is presented here. The reaction was carried out in an anaerobic dry nitrogenous environment in a glass reactor, and the products formed were identified by infrared spectroscopy. Our analysis reveals that the major reaction products are nitric acid, nitric oxide and o-nitrophenol. On the other hand, in contrast to the prediction of the electronic structure calculation, no trace of HONO has been identified. The kinetic analysis reveals that the likely reaction stoichiometry is 3NO₂ + PhOH ® HNO₃ + NO + o-nitrophenol, and the reaction enthalpy is $\Delta_{\rm p}$ H⁰= -44.82 kcal/mol. The reaction shows a pseudo first-order kinetic behavior with respect to phenol in the presence of excess NO₂, and the corresponding rate constant is 6.67 ± 0.12) x 10^{-3} s⁻¹. The analysis also reveals that the dimerization of NO₂ to N₂O₄ is the key process for the occurrence of the reaction with phenol, and this has been established by monitoring the development of the infrared signal corresponding to HNO₃ as a function of increasing concentration of NO $_3$ in the reaction mixture. The increase of HNO $_3$ signal is observed to be linearly correlated with the effective concentration of nitrogen dioxide dimer (N_2O_4) produced in the reaction mixture. It is also observed that the overall reaction of N_3O_4 and phenol follows a 2nd order kinetic behavior. The estimated 2nd order rate constant value at 298 K is (3.53 ± 0.56) × 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹. Electronic structure calculation predicts multiple conformational structures for the N₂O₄-phenol collisional complex, and in the lowest energy conformer of the complex the orientation of the two NO, molecules about the phenolic-OH group is similar to that of the charge-separated asymmetric dimer of NO₂. We have ruled out the possibility of a radical mechanism for the reaction because HONO has not been identified as a product.

1. Introduction:

Phenol is the simplest aromatic alcohol and belongs to the category of the volatile organic compounds (VOCs) present in the earth's atmosphere. VOCs play a very key role in the chemistry of the earth's lower atmosphere (troposphere) and are directly involved in the pathway of tropospheric ozone formation and secondary organic aerosols. Aromatic compounds belongs to an important sub-group of VOCs present in the atmospheres of urban and semi-urban areas, and benzene, toluene, xylenes, styrene and their oxidation products are the typical examples of aromatic VOCs.¹⁻³ According to RCP data base, the contribution of anthropogenic emission of aromatics is » 23 TgCyear⁻¹. The contribution of bio-mass burning according to GFAS inventory is ≈ 5 TgC year⁻¹. Volatile organic compounds in the urban atmosphere are produced by means of fossil fuel burning, spillage of gasolines and solvents in laboratories and industries. Aromatic alcohols are produced via atmospheric oxidations of the aromatic hydrocarbons by OH radicals followed by reactions with NO₃. Nitrophenols are toxic for humans and plants. An important atmospheric significance of *o*-nitrophenol is the photochemical formation of atmospheric nitrous acid (HONO) which accounts for nearly 60% of the daytime production of OH radical.⁴⁻⁶

Nitrogen dioxide (NO_2) is also an abundant trace gas in the urban atmosphere, and the

primary atmospheric source of NO, is the different anthropogenic activities like emission of the vehicle exhausts, industrial fossil fuel burning, thermal power plant, etc., and a small fraction by the biogenic activities. NO₂ is a pollutant and hazardous for human health and affects terrestrial plant growth. Its transportation from the urban to pristine environment occurs primarily in the form of peroxyacetylnitrate (PAN). Reaction of NO₂ with O₃ generates important atmospheric oxidants like nitrate radical (NO₂) and N_2O_5 . Two important atmospheric acids, nitrous (HONO) and HNO₃ acids are produced by hydration of NO₂. According to the observed experimental evidences the hydration is a heterogeneous surface-induced reaction.

The atmospheric abundance of HNO_3 is high $(1 \times 10^{12} \text{ molecules/cm}^3)$ and which is 4-7 orders of magnitude larger as compared to that of sulfuric acid. Production of HNO_3 occurs via the oxidation of NO_2 to HNO_3 by the atmospheric OH radical. There are other anthropogenic sources like fossil fuel burning and natural processes like forest fire and lightning that contribute to the atmospheric nitric acid concentrations. Like sulfuric acid, the role of HNO_3 for the formation of the atmospheric particulate matters involving the formation of hydrogen-bonded clusters with ammonia and amines as the seeds were also reported earlier.⁷

In this report, we present the findings of our recent investigation of a thermal reaction between NO_2 and phenol in the gas phase.⁸ Several reports are there concerning the reactions of different substituted phenols with NO_2 in liquid phases, but to our knowledge, no gasphase study has been reported till the date. As NO_2 is an efficient one-electron oxidant ($E^0 = 0.79$ Volt) and phenol is known to be an H atom donor, the general expectation is HONO as a likely product. In contrast, it is shown here that nitric acid is the major product of the reaction and no evidence for the formation of the former has been observed. The finding is likely to be significant from the atmospheric viewpoint,

especially in the polluted air where both nitrogen dioxide and phenol concentrations are high. The other important product that has been identified is *o*-nitrophenol, and which is also significant from the atmospheric viewpoint, because, it has been reported recently that photochemically *o*-nitrophenol produces OH radical.⁶

2. Experimental details:

2.1 Preparation of pure NO₂

A key requirement for the experimental investigation of reactions with NO_2 is to have this gas in pure form. The following arrangement was made to prepare pure $NO_{2'}$ and the same is shown schematically in Figure 1.

Step 1: The salt sodium nitrite $(NaNO_2)$ was allowed to react with ferrous sulphate heptahydrate (FeSO₄, 7H₂O) to produce NO by mixing at 1:2 ratio in a vacuum sealed 1 l glass (Borosil) round bottom flask. The mixture was slightly heated by monitoring the pressure inside the flask by a high-pressure capacitance gauge.

Step 2: Nitric oxide (NO) so formed was mixed with excess ultrahigh pure (99.9%) oxygen acquired from Indian Refrigeration Stores, and the gas mixture was kept for 15 minutes until the color of the mixture turns deep brown indicating NO₂ production.

Step 3: NO₂ produced by this process contains a number of impurities like nitric oxide, nitrogen trioxide (N₂O₃), nitrous acid, nitric acid and a little of water vapor, etc. Less volatile impurities like water vapor, nitrous and nitric acid vapors were removed by partial condensation method by passing gas mixture formed in step 2 through a thermostatic trap cooled at -20°C.

Step 4: The gas exiting the -20 °C trap was sent to a second trap maintained at -60°C and at this temperature NO_2 is solidified, and other volatile gaseous impurities viz. NO, N_2O_3 and excess oxygen were taken out slowly by an evacuating pump.





Step 5: The solidified NO_2 is sublimed to a mixture of NO_2 vapor and its dimer dinitrogen tetra oxide (N_2O_4) on increasing the temperature to -20°C, and this vapor was then mixed with ultrahigh pure N_2 gas in a glass mixing chamber where the molecules remain distributed as monomer and dimeric forms.

To obtain phenol vapor in quantitative amounts, solid phenol was evaporated by heating at 40 $^{\circ}$ C and the vapor was mixed with dry high-pure nitrogen (purity 99.99%). The gas mixture was collected in an evacuated round

bottom flask at a total pressure of ~900 mbar, which was treated as the stock. Phenol vapor from the aforesaid stock was transferred in quantitative amounts into the reactors by a mass flow controller (MKS).

2.2 Reactors and reaction monitoring:

The reaction has been carried out in both ex-situ and in-situ modes of operation as shown schematically in Figure 2. In the ex-situ mode, a spherical Borosil glass vessel of volume 10 liter was used as the reactor, whose surface-to-



Figure 2: Schematic diagram for the reaction kinetics study by infrared monitoring

volume (S/V) ratio was 0.24 cm⁻¹. The reaction between phenol and NO₂ was monitored by recording the FTIR spectra mid-infrared region (400-4000 cm⁻¹) with an instrumental resolution of 0.5 cm⁻¹ (Bruker Optics, model no. IFS 66S). For concentration monitoring, the reaction mixture was transferred into a multi-pass White type cell (Bruker Optics, Model: I 26005 ECL01) of variable path lengths (0.8 to 8 m). The reaction vessels were evacuated using an oil-free root pump and the gas pressures of the reactors were monitored by a high-pressure capacitance gauge (model no. CMR 361 Pfeiffer Vacuum, Germany). Highquality teflon tubing was used for transferring gases and mixtures and after the completion of each reaction set the reactors were flushed with dry UHP nitrogen.

The in-situ mode of reaction arrangement was used for monitoring the reaction kinetics. Typical concentrations of the reactants for such arrangement were $\sim 10^{15}$ - 10^{16} molecules cm⁻³. Such higher concentrations were needed to increase the detection sensitivity of FTIR

monitoring. However, it has been assumed that the concentrations will not have much effect on the reaction kinetics.

3. Results and discussion:

3A. Identification of the products:

Depicted in Figure 3 are the infrared spectral signatures for the occurrence of the reaction between phenol and NO₂ in the gas phase. The traces I and II depict the spectra of pure PhOH vapor and NO₂ gas, respectively, and trace III correspond to the reaction mixture after allowing the reaction to occur for about ten minutes. The reaction was monitored following the changes of the intensities of the 1176 cm⁻¹ band of phenol vapor and 2918 cm⁻¹ band of nitrogen dioxide. The infrared absorption cross-section values of these bands are known to be 8.96×10⁻¹⁹ cm²molecule⁻¹ and 7.05×10⁻²⁰ cm²molecule⁻¹, respectively. The spectra were recorded by transferring small fractions of the reaction mixture into a multi-pass gas absorption cell after allowing the reaction to occur for specific time periods. In the reaction



Figure 3: FTIR spectra of PhOH vapor (trace-I), NO_2 (trace-II), and the mixture of PhOH and NO_2 (trace-III) after allowing the reaction to occur for 10 minutes in the dark at 25° C. The bands corresponding to the three major products are labeled by A, B and C.⁹⁻¹¹

vessel, 60 mbar of NO_2/N_2 mixture and 170 mbar of PhOH/ N_2 mixtures were introduced, and the total pressure was made 1 bar by introducing an additional amount of dry UHP nitrogen. The temperature of the reactor was 22 °C and reaction vessel was shielded to avoid light exposure that can initiate photochemical reaction.

The three major products of the reaction, HNO₃, o-nitrophenol, and NO are identified by corresponding their characteristic midinfrared bands. The bands at 1711, 1325, and 878 cm⁻¹ correspond to the N-O anti-symmetric stretching, N-O symmetric stretching, and NO₂ deformation modes of HNO₃, respectively. An important product, o-nitrophenol has been identified observing the bands at 748 and 3250 cm⁻¹, labeled B, which correspond to the O-H bending and O-H stretching vibrations of the molecule, respectively, which agree well with our recorded gas-phase infrared spectra of the molecule. o-Nitrophenol production in a gas phase reaction between phenol and NO₂ is observed in our study for the first time to our knowledge. NO is also identified as an important product of the reaction and its characteristic rovibrational bands associated with N-O stretching fundamental appear within the frequency range of 1850-1950 cm⁻¹, labeled here with C. It has been ascertained also that the infrared signature of an expected product HONO, which characteristic frequency is 1263 cm⁻¹, is completely absent in the spectrum of the reaction product trace, and the finding contrasts the prediction of a recent theory. The mechanism of the overall reaction has been discussed based on the following additional observations.

3B. Reaction stoichiometry:

The stoichiometry of the reaction has been established by monitoring the temporal behavior of the lowering in concentrations of NO_2 and phenol with the progress of the reaction, which are shown in Figure 4. It is seen that within ten minutes of the reaction, the concentration of NO_2 is lowered by nearly three times as large

as that of phenol. It implies that the reaction occurs in 1:3 stoichiometry (equation 1), and the corresponding reaction enthalpy, $\Delta_r H^o = -44.82$ kcal/mol.

$PhOH+3NO_2 \rightarrow HNO_3 + NO + o-nitrophenol,$
$\Delta_{\rm r} {\rm H}^{\rm o}$ = -44.82 kcal/mol (1)
$\Delta_{\pm} H^{\circ} = \Sigma \Delta_{\pm} H^{\circ} (Products) - \Sigma \Delta_{\pm} H^{\circ} (Reactants)$

The temporal characteristics of the accumulation of the two products (NO and HNO₃) are calculated using the known values of the absorption cross-sections as shown in Figure 4. It is interesting to note that while the behavior of NO correlates well with the disappearance of the reactants, the concentration of HNO₂ after an initial increase, shows a sharp decrease as shown in inset of figure 5 (the points are denoted with blue squares), and we have noted that this happens because of the adsorption of HNO₂ vapor on the inner glass surfaces of the reaction cell. In order to make a correction, the adsorption kinetics of HNO₃ vapor in the same cell has been monitored separately, and adsorption correction has been done using the method reported earlier by our group¹². The adsorption-corrected accumulation curve of HNO₃ is presented with red circles, which nicely correlates with that of nitric oxide (NO). This correlation is consistent with the equivalence of formation of the two products as shown in equation 1. It also demonstrates that the reaction occurs only in the gas phase. If the reaction would have occurred on the inner surfaces of the container, owing to the sticking tendency of HNO₃ very little of it would have desorbed into the gas phase.

In the case of *o*-nitrophenol, the absorption cross-section values of its infrared absorption bands are not known, and in the present study those have been estimated in the following way. Phenol and *o*-nitrophenol are solids at room temperature having very low vapor pressures (less than 1 mbar). Therefore, they were heated and their vapours were mixed with UHP nitrogen and the gas mixture was kept in a container for sufficiently longer time to allow deposition on



Figure 4: Concentration lowering of the two reactants with the progress of the reaction. The concentrations of phenol and NO₂ were probed using the absorption cross-section values of their infrared bands at 1176 and 2918 cm⁻¹, respectively.



Figure 5: *Growth in concentrations of the major products in the reaction cell.*



Figure 6: FTIR spectra of the reaction mixture at three different NO₂ concentrations (I) $[NO_2] = 12 \times 10^{15}$ molecules/cm³, (II) $[NO_2] = 6.97 \times 10^{15}$ molecules/cm³, (III) $[NO_2] = 3.12 \times 10^{15}$ molecules/cm³. Panel (a) and (b) represent the spectra recorded in absence and in presence of PhOH (at a concentration of 5.68 $\times 10^{14}$ molecules/cm³), respectively.

the surface walls. A mass flow controller was used to ensure taking similar concentrations of the two species in the multi-pass gas absorption cell. From the measured absorbance value and absorption cross-section of phenol, the same for o-nitrophenol has been estimated.

3C. Mechanistic details of the reaction:

In the reaction mixture, as NO₂ exists both in monomer as well as dimeric forms, a key issue here is to determine the actual species that react with phenol. In order to throw additional light on this matter, the infrared spectra of the reaction mixture have been recorded for different initial concentrations of NO₂ for a fixed concentration of phenol vapour. As depicted in Figure 6 (parts-a and -b) that the signal corresponding to the prove IR peak of HNO₃ is correlated with the formation of NO₂ dimer in the reaction mixture. Part-a of the figure depicts the concentrationdependent changes of the IR spectrum of NO₂ in the absence of phenol, and the band for the dimer of NO₂ (N₂O₄) appears at 1264 cm⁻¹. The spectra trace in part-b indicates that the HNO₃ band at 878 cm⁻¹ could be identified only when the concentration of NO, in the reaction cell is enough that allows the occurrence of dimerization. Thus, the findings indicate clearly that N_2O_4 is the key



Figure 7: A plot of $ln([PhOH]_0/[PhOH]_t)$ against t appears linear, which indicates that PhOH-NO₂ reaction follows pseudo first-order kinetics.

reactive species for the reaction of NO_2 with phenol.

Concerning the kinetic issue, it is shown first that the reaction follows a pseudo firstorder kinetics with respect to phenol. A plot of $ln([PhOH]_0/[PhOH]_t)$, where $[PhOH]_0$ and $[PhOH]_t$ are the concentrations of phenol vapours in the reaction mixture at the initiation of the reaction and at time t, against t, where the concentration of NO₂ was about ten times larger compared to that of phenol is shown in Figure 7.

From the slope of the plot, the pseudo 1st order rate constant is estimated to be (6.67±0.12) $\times 10^{-3}$ s⁻¹. The opposite process, i.e., measuring the reaction order taking large excess of phenol vapour compared to NO₂ could not be done because of relatively smaller vapor pressure of phenol. Therefore, the reaction order with respect to NO₂ has been estimated in the following way.



Figure 8: The two plots depict the variation of $ln([PhOH]_0 / [PhOH]_1)$ with time for the use of two different NO₂ concentrations. The plot indicated with black square corresponds to $[NO_2] = 11.27 \times 10^{15}$ molecules/cc and red circles $[NO_2] = 13.58 \times 10^{15}$ molecules/cc (set II).

Similar plots as in Figure 7 are generated for use of different NO_2 initial concentrations, and two such cases are shown in Figure 8.

The slope of the linear plot corresponds to $k[NO_2]_1^n$, where n is the reaction order and k is

the rate constant. The slopes for the two plots are 0.33 and 0.50, and using the values of two different concentrations of NO₂, our estimated value of $n = 2.14 \gg 2$

Finally, in order to verify further the possibility that a bimolecular second-order type reaction between N_2O_4 and phenol is the key step in the reaction mechanism, a plot corresponding to the integrated form of the bi-molecular reaction kinetics is depicted in Figure 9a. It is known that for a prototypical A + B ® P type reaction, a plot of $ln\{([A]_0[B]_t)/([A]_t[B_0])\}$ versus t is expected to be linear and the slope of the plot is $k([B]_0-[A]_0)$, k is the second-order bimolecular rate constant.

The concentration changes of N₂O₄ has been estimated noting the time dependent changes of NO₂ concentration and the known value for the equilibrium constant of the reaction, $2NO_2\hat{U}$ N₂O₄ (k_{eq} = 4.67 atm⁻¹).¹³ As shown in Figure 9a, the plot is fairly linear, which validates the proposed mechanism. The second order rate constant value estimated from the slope is 3.53 ± 0.56) × 10⁻¹⁸ cm³ molecule⁻¹ s⁻¹. This implies that effectively the reaction between PhOH and NO₂ should follow third order kinetics, and the same is also apparent from the plot shown in Figure 9b, and the corresponding rate constant value



Figure 9a: Plot for the integrated form of bimolecular second-order rate equation for the reaction between PhOH and N_2O_4 . The rate constant of the reaction estimated from the slope is $(3.53\pm0.56) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

has been estimated to be (7.62 \pm 0.52) x10⁻³⁵ cm⁶ molecule⁻² s⁻¹.

The reaction mechanism that we propose is shown Figure 10 and the formation of a binary collisional complex of N_2O_4 with phenol has been proposed. Electronic structure calculations carried out at *MP2/aug-ccpvdz* level predicts multiple geometric structures for the binary complex, and the one shown in Figure 11a has the largest binding energy. In this conformer the two NO₂ molecules are oriented about the phenolic O-H group in a highly charge-



Figure 9b: Here $Y = (ln (([NO_2]_t [PhOH]_0) / ([NO_2]_0 [PhOH]_t)) + (2([PhOH]_0 - [PhOH]_t)(2 [PhOH]_0 - [NO_2]_0))/([NO_2]_0 [NO_2]_t)$. The estimated value of the rate constant for the third order rate equation between PhOH and NO_2 is (7.62± 0.52) x10⁻³⁵ cm⁶ molecule⁻² s⁻¹.



Figure 10: Proposed reaction mechanism



Figure 11a: The optimized geometries, for calculation at MP2/aug-ccpvdz level, of the asymmetric dimer, N_2O_4 (trans-ONONO₃) (I), 1:1 complex of N_2O4 with water (trans-ONONO₃-H₂O) (II) and phenol (trans-ONONO₃-PhOH) (III).

separated asymmetric dimeric configuration. The geometries of the bare asymmetric dimer and its 1:1 complex with a water molecule optimized by the same method are also shown in Figure 11a.

The depicted geometric parameters and partial charges reveal a number of interesting features.¹⁴ First, the N $\cdot \cdot$ O distance between NO and NO₃ segment is the largest (1.88 Å) in the phenyl complex and shortest in the bare dimer (1.71 Å) and has an intermediate value of 1.78 Å for the water complex.

This might imply that the collisional complex formation with phenol induces the splitting of N_2O_4 into NO and NO₃ components. Secondly,

with respect to Mulliken charge distribution, the PhOH-N₂O₄ complex is also different compared to the other two. In bare N₂O₄, the charges on NO and NO₃ components are +0.483 and -0.483, respectively. Although this charge distribution is altered upon complexation with a water molecule, the total charge on N₂O₄ remains conserved. In contrast, in the PhOH-N₂O₄ complex, the charge conservation on N₂O₄ is lost and the phenolic O-H bond is largely polarized as depicted in Figure 11a. Furthermore, the O-H...O hydrogen bond length in the phenol complex (1.71 Å) is significantly shorter compared to that of the water complex (2.00 Å). All these features indicate that the proton transfer from the phenolic O-H



Figure 11b: Potential energy profile for the proton transfer reaction in PhOH- N_2O_4 complex that results in the formation of HNO₃ and phenyl nitrite. The calculation has been performed at MP2/aug-ccpvdz level.

group to the negatively polarized NO₃ segment should be easier compared to that of the H₂O- N_2O_4 complex. In fact, the electronic structure calculation predicts that the proton transfer in the former case is indeed an extremely lowbarrier process as shown in Figure 11b, and the adduct is stabilized to a configuration consisting of nitric acid and phenylnitrite. Phenylnitrite is unstable under ambient conditions and tends to undergo dissociation into nitric oxide and phenoxy radical, and the latter can react readily with NO₂ to produce o-nitrophenol. The infrared spectrum of phenyl nitrite vapor is not available in the literature, but the spectrum was recorded only under a matrix trapped condition followed by an in-situ method of preparation.¹⁵

A few remarks about the feasibility of the formation of the collisional complex shown in Figure 11a are deemed worthy. Although, the asymmetric form of N_2O_4 is unstable in the gas phase and does not have a chemically significant lifetime to be probed by the steadystate FTIR spectroscopy under the ambient conditions, the collisional complex with the asymmetric structure of N2O4 could be produced via the following pathway.¹⁶ The fact is, under the ambient conditions in the gas phase, N_2O_4 (dimer) remains in the dynamic equilibrium with NO₂ (monomer), and for this to happen, a significant fraction of the dimer must remain populated at the higher vibrational levels near the dissociation threshold of the intermolecular stretching potential. Binary collision of such dimer population with phenol is likely to allow easy structural rearrangement. Therefore, although many of the recent theoretical studies have reported that the direct interconversion barrier from the stable centrosymmetric (O₂NNO₂) to asymmetric (ONONO₂) structure of N_2O_4 is

large in the gas phase¹⁷, the actual reactivity is determined by the dimeric fraction populated at the higher vibrational levels of the O₂N-NO₂ stretching potential.

Summary:

We have demonstrated that in the gas phase the reaction of NO₂ with phenol occurs with a low energy barrier, and the major products are nitric acid, o-nitrophenol and nitric oxide. The stoichiometry of the reaction has been established observing directly the disappearance rate of the reactants, which appears as $3NO_2$ + PhOH ® HNO₃ + NO + *o*-nitrophenol, and the corresponding reaction enthalpy, $\Delta_{\rm r} {\rm H}^0$, is - 44.82 kcal/mol. With respect to kinetic parameters, it has been shown that the reaction follows a pseudo 1st order kinetics with respect to phenol and but the reaction order with respect to NO₂ is two, and the rate constant value estimated for the former case is $(6.67 \pm 0.12) \times 10^{-3} \text{ s}^{-1}$. Using an IR spectroscopic probe, we have shown that HNO₃ formation is directly correlated with NO₂ dimerization. The estimated bimolecular 2^{nd} order rate constant between N2O4 and phenol is $(3.53 \pm 0.56) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K},$ and the corresponding termolecular rate constant considering the reaction of phenol with two NO₂ at the rate determining step is (7.62 \pm 0.52) x10⁻³⁵ cm⁶ molecule⁻² s⁻¹.

According to the electronic structure calculation, in the preferred geometry N_2O_4 -phenol collisional complex, N_2O_4 assumes an asymmetric conformation about the phenolic O-H group, which significantly polarizes the latter to facilitate intermolecular proton transfer, and the overall energy barrier for HNO₃ formation appears low. The production of *o*-nitrophenol in the gas-phase reaction between phenol with NO₂ is reported here for the first time to our knowledge. This could be produced by the reaction of phenoxy radical with NO₂. Alternatively, this could also be produced via a low-energy molecular mechanism involving a collision of NO₂ with energized phenyl

nitrite or the precursor activated complex. We propose that this gas-phase reaction could be an important contributor to the atmospheric $\text{HNO}_{3'}$ particularly in polluted urban atmospheres, where the abundances of phenol and NO_2 are high.

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Theoretical studies on hydrated clusters of acid molecules

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Abstract

Hydrated clusters of an acid molecule can be generated by adding solvent water molecules to an acid molecule successively. Finding most stable structure of a large size hydrated cluster can be a challenging task as traditional gradient based optimization methods always lead to local minima. An alternative simple route will be discussed to find the structures of large-sized molecular clusters ensuring that the global minimum structure is not missed out. In addition, certain characteristic molecular properties of hydrated acid clusters will be presented. Present discussions are mainly focused on carboxylic acids.

Introduction

Microhydration studies of acids can help in comprehending many biological, physical and environmental phenomena; from acid rain to proton transport and protein folding. During the process of hydration of an acid molecule in a pool of water molecules, hydrogen bonded solvent water molecules break its hydrogen bonding network to accommodate the solute acid molecule. Solute acid molecule does form hydrogen bonds with the solvent water molecules present in the immediate neighborhood. As a result of intermolecular interactions between the acid molecule and solvent water molecules, weakening of O-H bond of the acid molecule (carboxylic acid) happens and proton transfer from the acid molecule to solvent water molecules occurs leading to dissociation of the acid molecule. Studies based on size selected hydrated clusters of the acid molecule are very useful to understand intermolecular interactions between the solute acid and solvent water molecules leading to dissociation of the acid molecule. Explicit hydration studies of acid molecules can help in correlating hydration, dissociation of acid and reactivity under different chemical environment. Hygroscopic molecules, and among them dicarboxylic acids, play an important role in water uptake by organic aerosol, and thus affect equilibrium supersaturations at which aerosol particles grow large enough to become cloud condensation nuclei.

Studies of molecular clusters have gained popularity as it helps in bridging the gap between a single molecule and the bulk material.¹ Growth of systems from molecule to bulk is expected to be reflected in many properties of the molecular clusters. The study of molecular interactions, structure and properties of clusters has wide range of implications in physical, chemical and biological areas. Complementing experimental measurements, ab initio calculations are very useful in exploring structure-property correlations and energetics of molecular clusters. However, application of post Hartree-Fock methods, incorporating electron correlation, like Møller-Plesset second order (MP2) theory and coupled cluster singles and doubles with perturbative triples (CCSD(T)), for the calculation of large molecular clusters are often beyond the scope due huge computational cost. Moreover, non-covalent interactions provide flexibility to the systems, making ab initio geometry optimization of molecular clusters very challenging. The most common algorithm for finding the equilibrium geometry of a molecular system applying electronic structure theory is Newton-Raphson method. The problem with this procedure is that the geometry converges to the nearest local minimum. Hence, the choice of initial guess structures is very important. The number of possible initial input geometries increases with the size of the system. The huge computational cost limits the number of initial guess structures that can be tried for large clusters. Morever, there is always a possibility of missing important input structures.

Different approaches have been reported to study theoretically the structure and properties of large size molecular clusters. They include semiempirical methods, reduced scaling methods and fragmentation methods. Molecular tailoring approach (MTA), a fragmentation method has been proposed for estimating molecular electrostatic potential (MESP) of zeolites. The large system is fragmented into smaller systems in MTA. The properties of the original system are obtained by combining the corresponding properties of all the smaller systems. This can affect the accuracy of the energy obtained for the system. In addition, there is a chance to miss an important structure as this one has also initial value problem. Recently, significant efforts are also put in stochastic search techniques and these can be separated into two broad categories. One deals with a single solution and during evolution the solution is subjected to be updated according to certain criteria as wanted eg. Simulated Annealing (SA) technique. The other types of stochastic search techniques deal with multiple solutions and these solutions need to be handled in parallel. Genetic Algorithm (GA), Parallel Tempering techniques etc. belong to this category. However, accuracy of these techniques depends on interaction potentials and often these potentials are either empirical or not available in the literature. Thus, these methods are not so popular in calculation of molecular clusters.

A simple method to ensure a thorough scan of the potential energy surface is presented and a few large hydrated clusters of oxalic acid is considered for the studies. The geometries of hydrated clusters of oxalic acid, (COOH)2.nH2O, n=9-12, clusters are studied, first applying cost effective MD simulations at lower level of theory. The low energy equilibrium conformers obtained from the MD simulations are fine tuned applying more accurate level of theory following DFT based electronic structure theory with suitable functional. Several molecular properties are examined if any characteristic feature showing breaking of O-H bond in carboxylic acid could be predicted on successive addition of water molecules. Existence of any correlation with pKa of an acid and the number of water molecules needed to ionize an acid is also examined.

Theoretical Methods

Initial input guess geometries are generated applying Atom centered Density Matrix Propagation (ADMP) MD model², at B3LYP/6-31G(d) level of theory. ADMP based molecular dynamics is an extended Lagrangian approach that makes use of Gaussian basis functions and propagates the density matrix. Under this framework, fictitious masses for the electronic degrees of freedom are set to be small enough that thermostats are not required for good energy conservation in the simulations. This also allows one to retain hydrogen atoms in the system and not substitute heavier isotopes. Other advantages of this method include: i) the freedom to rigorously treat all electrons in the system or to use pseudopotentials; ii) the ability to use reasonably large time steps; iii) the freedom to employ a wide variety of accurate and effective exchange-correlation functionals; iv) the ability to treat charged molecular systems in a simple and easy way; and v) good computational efficiency. The simulations are allowed to run for 400 steps with step size of 0.2 fs and extended even upto 2000 steps for (COOH), 9H,O to examine the effect of simulation for longer time. However,

no new input structures with lower energy are predicted for this cluster on extending simulations time upto 4 ps. The minimum energy geometry and all the geometries within 5.0 kcal/mol of this minimum energy geometry are selected and further optimized at ω B97XD/ aug-cc-pVDZ level of theory in this two-level approach. This level of theory has been reported to describe hydrated clusters of carboxylic acid well. Hessian calculations are carried out to confirm that the equilibrium structures thus obtained are true minima and to simulate IR spectra. All calculations are carried out using general quantum chemistry software package, Gaussian 16.³

Results and discussion

Of all the structures obtained from the ADMP-MD simulations considering micro-

canonical ensemble, a set of structures are selected based on total energy of the hydrated cluster calculated at B3LYP/6-31G(d) level of theory. The set of geometries consists of the most stable one and those are within 0.008 a.u. (5.0 kcal/mol) of energy of the most stable structure. This set of structures is further optimized applying a more accurate level of theory, namely, ω B97XD/augcc-pVDZ. Hessian calculations are performed to ensure that the structures of each size of hydrated oxalic acid cluster ((COOH), .nH, O, n=9-12) thus obtained are true minimum. In all the simulation studies, it is confirmed based on calculated total energy of the system that MD simulations are equilibrated. Figure 1 displays the variation of calculated total energy for (COOH),.nH,O (n=9-12) systems over all the simulation steps.⁴ The most stable minimum energy structure of nona-hydrate of oxalic acid, (COOH),.9H,O is a



Figure 1. The plots show the variation in total energy calculated at B3LYP/6-31G(d) level of theory as a function of simulation steps for the hydrated cluster of oxalic acid, $(COOH)_2.nH_2O$ (n=9-12). These plots suggest that simulations are equilibrated under the micro-canonical ensemble condition

solvent-separated ion pair where solvent water molecules are present between deprotonated oxalic acid and the proton of one of the two carboxylic groups.

Nine structures of nona-hydrated cluster of oxalic acid with relative energy within 5.0 kcal/ mol of the minimum energy structure obtained from MD simulations are considered as the input structures for geometry optimization. The most stable structure is shown in Fig. 2a. One can see that the solvent water molecules form a closed cage-like motif consisting of four and five member rings on one side of the acid molecule. None of these structures shows breaking of both the O-H bonds of the acid molecule and transfer



Figure 2. The most stable equilibrium structure of a) $(COOH)_2.9H_2O$; b) $(COOH)_2.10H_2O$; c) $(COOH)_2.11H_2O$ and d) $(COOH)_2.12H_2O$ clusters. Geometry optimization is carried out at $\omega B97XD/aug$ -cc-pVDZ level of theory with input structures from the results of ADMP-MD simulations. The red, grey and blue balls represent oxygen, carbon and hydrogen atoms respectively.

of both the carboxyl protons to the neighboring solvent water molecules.

In case of $(COOH)_2.10H_2O$ system, 23 input structures predicted from simulations are considered for the search of the most stable structure. The minimum energy conformer (see

Fig 2b) shows transfer of one the carboxylic protons of the acid molecule to the solvent water molecules while the other is retained by the acid molecule. The minimum energy structure of undeca-hydrated cluster of oxalic acid molecule, (COOH),.11H₂O has one of the carboxylic protons of the oxalic acid molecule transferred to the neighboring solvent molecule as shown in Fig. 2c. This structure is obtained based on 17 input structures as suggested by the results of MD simulations. In case of dodeca-hydrate of oxalic acid, (COOH), 12H, O, the most stable equilibrium structure has cage-like hydrogen bonded motifs formed by solvent water molecules, as shown in Figure 3d. In this structure, one of the protons of this dibasic acid molecule is transferred to the solvent water molecule while the other proton is retained by the acid molecule. A degenerate equilibrium structure is also obtained for the dodeca-hydrate of oxalic acid molecule, where the water molecules are distributed uniformly around the acid molecule. In this structure also, one of the protons of this dibasic acid molecule is transferred to the solvent water molecule while the other proton remains with the acid molecule. Two higher energy conformers of dodeca-hydrate are obtained in which both the protons have been transferred to the neighboring solvent water molecules forming hydrated cluster of oxalate ion, $(COO)_{2}^{-2}$. However, they are higher in energy than the minimum energy equilibrium structure by 2.8 kcal/mol. Prediction of the minimum energy structure is done considering 23 input structures as obtained from MD simulations.

IR spectrum, bond dissociation curve and hydrogen bond energy of carboxylic acid molecules and their hydrated clusters are studied to examine the variation of these properties with the size of the hydrated clusters.⁵⁻⁸ Water clusters encapsulating carboxylic acid molecule are stable due to the formation of hydrogen bonds between the acid molecule and neighboring water molecules as well as between the water molecules. Peak positions in IR spectra due to O-H stretching modes of the acid and water molecules are



Figure 3. Simulated scaled IR spectrum of a) PhCOOH.7H₂O and b) PhCOOH.8H₂O clusters. IR stretching bands corresponding to the breaking O-H bond of the acid molecule are red shifted by 815 and 3470 cm⁻¹ with respect to free benzoic acid.

expected to shift compared with that of free acid and water, due to H-bonding interactions. Thus, simulating the IR spectra of the hydrated acid clusters can serve to keep track of the weakening of the O-H bond of the acid molecule. It can also help in determining the proton transfer from the solute acid molecule to solvent water molecules, as the presence of hydrated proton introduces new peaks in the IR spectrum. Simulated scaled IR spectra of hydrated clusters of benzoic acid molecule are given in Figure 3. The harmonic O-H stretching frequency for free benzoic acid molecule, calculated at
oB97XD/aug-cc-pVDZ level of theory, is 3838 cm⁻¹ while the same is 3567 cm⁻¹ based on experimental measurement. Due to the lack of experimental data, for higher hydrated clusters of benzoic acid, O-H stretching frequency of free benzoic acid is the taken as the basis for calculating scaling factor. Scaling factor, determined by taking the ratio of experimental to calculated O-H stretching frequency, is 0.93. It is seen that moving from the unionized heptahydrated cluster to the ionized octa-hydrated cluster of PhCOOH, there is a large red-shift of 2655 cm⁻¹. Though red-shift in C=O stretching frequency due to the weakening of carbonyl bonds is also expected, no significant red-shift is observed in the C=O peaks of hydrated benzoic acid clusters. The newly formed peaks corresponding to the hydronium ions are clearly observed in case of PhCOOH.8H,O.

A rigid potential energy scan of the acidic O-H bond can help in understanding the energy barrier for the proton transfer from the acid molecule to the neighboring water molecule in hydrated clusters of carboxylic acid molecules. The relative energy of the system, at each variation of the acidic O-H bond, with respect to the equilibrium geometry of that size cluster, is plotted against the varying O-H bond length to get the O-H bond dissociation curve. O-H bond length of ~1.0 Å implies that the proton is still with the acid molecule while O-H bond distance of 1.4 Å and beyond is a clear indication that the proton has transferred from the acid to water molecule. Depending on the position of the energy minima with respect to the O-H bond length, the process of proton transfer from the acid to water molecule can be explained. Up to penta-hydrated cluster, the energy minima of the dissociation curve is found to be around 1.0 Å. Increasing the O-H bond length further causes an increase in the energy of the system. However, in case of CF₃COOH.6H₂O, the minimum in energy for the acidic O-H bond dissociation curve is when the O-H bond length is ~1.4 Å, indicating the transfer of proton from the acid to water molecule. The destabilization of the system due to increase in O-H bond length does not seem to follow any particular order. O-H bond dissociation curves of CF₃COOH.nH₂O (n=1-6) are displayed in Figure 4.



Figure 4. Rigid potential energy scan of O-H bond of $CF_3COOH.nH_2O$, n=1-6. ΔE gives the relative energy of the system at each point of the scan of the dissociating O-H bond, with respect to the energy of the equilibrium geometry. Curves marked as t_n (n=1-6) represents potential energy surface of hydrated cluster having n solvent water molecules upon increasing bond length of dissociating O-H bond of the acid.

The dissociation of the acidic O-H bond as well as the strengthening of the H bond between the acidic H atom and the O atom of the nearest water molecule, $H.O(H_2)$, can be tracked to study the proton transfer in the hydrated carboxylic acid clusters. Hydrogen bond energy for acidic O-H and H..O(H_2) bonds shows that the former decreases and the latter increases, as the size of the cluster increases. It is seen that the hydrogen bond energy value for acidic O-H bond is higher than that of $H_{-}O(H_{2})$, when the proton resides with acid molecule while the reverse is observed when proton transfer occurs. This is expected as before ionization, the acidic O-H bond is stronger while after ionization, the $H.O(H_2)$ bond is stronger. The H..O(H_2) bond increases in strength with addition of more water molecules, and finally when the proton transfer occurs from the acid molecule to solvent water molecules, the $H.O(H_2)$ bond becomes stronger than the O-H bond of the acid. The variation of hydrogen bond energy of acidic O-H and H_{2} bonds of hydrated clusters of the carboxylic acids are given in Figure 5. The cross over in the hydrogen bond energy profiles of the two bonds can be taken as an indication for bond dissociation of the acid molecule. It is seen that cross-over occurs at

n=6, n=7 and n=8 for $CF_3COOH.nH_2O$, $(COOH)_2$. nH₂O and C₆H₅COOH.nH₂O respectively. No such cross-over is observed in case of CH₃COOH. nH₂O, implying that even eight water molecules are not sufficient to break the acidic O-H bond in acetic acid molecule.



Figure 5. Variation of hydrogen bond energy of most acidic O-H bond (E_{O-H}) and $H.O(H_2)$ bond $(E_{H.O(H2)})$ of hydrated clusters of carboxylic acids with increase in size of the hydrated cluster (n).

Microhydration studies of 2-naphthol at ground, first excited triplet and singlet states are carried out using TD-DFT. It is seen that even in the presence of four water molecules, proton transfer from naphthol to water molecules is not observed for either ground or first excited triplet state. However, proton transfer becomes a barrier-less process for first excited singlet state of tetra-hydrate of naphthol.

O-H stretching vibration frequency of 2-napthol in free and its hydrated clusters are calculated in the ground and first excited singlet state. Figure 6(a-c) presents the most stable structures of tetra hydrated cluster of 2-napthol in the ground, first excited triplet and first excited singlet states, respectively. Figure 6c clearly shows breaking of the O-H bond and transfer of the proton to solvent forming hydronium ion. This observation reveals that acidity of 2-napthol in the first excited singlet state is higher than that in the ground or first excited triplet state. Effect of successive addition of solvent water molecules



Figure 6. Lowest energy structure of tetra hydrated cluster of 2-naphthol in a) ground singlet state, S_0 ; b) first excited triplet state, T1 and c) first excited state, S1 state. Red balls represent oxygen, grey balls represent carbon and blue balls represent hydrogen atoms.

on the O-H stretching frequency of 2-napthol is clearly reflected showing large red shift in both S_0 and S_1 states. Moreover, in case of first excited triplet state, formation of hydronium ion is also manifested in the simulated IR spectrum of tetrahydrated cluster of 2-napthol. This study clearly demonstrates photo-acidity of 2-napthol with great insight.

Understanding of the effect of chemical environment on the acidity of a system and vice-versa are important in comprehending the mechanism of several processes like enzymecatalysis. The acidity of a system is defined by its pKa. Spectrophotometry, pH titrations etc. are some of the methods for determining pKa of a system experimentally. But accurate experimental pKa determination becomes complicated in many cases like very strong acids and very weak acids, due to leveling effect of the solvent etc. The experimental pKa value for H_2SO_4 ranges from -3 to -9 while that for CF_2SO_3H range from -6 to -14. Accurate pKa values for some very weak acids have been reported from kinetic measurements employing sensitive techniques such as NMR. However, accurate pKa determination from experiment remains difficult for many systems. A novel non-thermodynamic route for calculating pKa value is presented here. A linear correlation is observed between the pKa of acid and the number of water molecules (n) needed for its dissociation, in case of acids studied at present applying the same level of



Figure 7. Plot of pKa vs. number of water molecules needed for dissociation (n_m)

theory, as depicted in Figure 7. Number of solvent water molecules needed to dissociate strong acid molecule, HCl has been a point of debate. Recent computational studies explained the difference in results on the basis of temperature dependence of relative stability of the structures. Based on our own independent study, at the present level of theory, it is predicted that dissociation of HCl molecule and formation of ion-pair occurs with four water molecules. Linear fitting produces the relation: $pKa = 3.2n_w$ -18.6, with $R^2 = 0.95$. This relation can be exploited to qualitatively predict unknown pKa values based on electron structure theory, where experimental measurement is rather difficult.

Conclusion

An alternative simple route to study the geometries of large-sized hydrated clusters

ensuring that the global minimum is not missed out. Calculations of minimum energy structures are carried out first applying ADMP MD simulations for initial screening. All the equilibrium structures having relative energy greater than the minimum energy structure by 5.0 kcal/mol thus obtained are further optimized at a higher level of level of theory to identify the most stable structures of each size cluster. Certain properties like simulated IR spectra, rigid potential energy scan of breaking O-H bonds and hydrogen bond energy of hydrated clusters are presented to show characteristic features of the bond breaking event in several hydrated carboxylic acids. IR spectra for the most stable structures of each size hydrated acid clusters are simulated, and the variation in acidic O-H peak positions is in accordance with the extent of elongation of the O-H bond in the acid molecule. In the case of PhCOOH, a minimum of eight water molecules are needed for ionization, which is characterized by formation of new peaks in the octa-hydrated cluster corresponding to stretching frequencies of hydrated proton. A rigid potential energy scan, altering the dissociating hydroxyl bond, shows that there is a barrier in proton transfer from the acid to water molecules in case of mono to penta-hydrated cluster of trifluoroacetic acid. In the case of hexa-hydrated

cluster of trifluoroacetic acid, proton transfer is a barrierless process and the acid gets ionized. Calculated hydrogen bond energy profiles of the dissociating hydroxyl bond of carboxylic acid molecules show characteristic features upon dissociation of the acid molecule. Hydrogen bond between the acidic H atom of the acid molecule and the O atom of the nearest solvent water molecule also shows similar characteristic features upon dissociation of the acid molecule. Finally, an empirical linear relation is obtained for pKa vs. n_w (minimum number of water molecules needed to break the bond in acid). This relation may be used to predict pKa of an acid in a nonthermodynamic route.

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Photochemistry of free clusters in molecular beam

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Abstract

Clusters are considered as ideal and unique class of material, for understanding variation in physical and chemical properties of matter, upon its transformation from microscopic to macroscopic phase. Bridging this gap between isolated atoms/molecules and bulk matter is facilitated by unique intrinsic properties of clusters i.e. finite size, bulk like density and their isolated existence in gas-phase. When subjected to intense laser pulse, these unique properties of clusters facilitate activation of diverse photochemical processes, distinct from their analogues monomer.

Introduction

Atomic and molecular clusters, which are aggregate of atoms and molecules held together by weak forces of interaction, have been widely investigated due to their ability to exhibit diverse photochemical behaviour as a function of cluster size [1]. In addition, their properties are quite distinct from the isolated atomic and molecular species of which they are composed [2]. Though the weak interactions holding the atomic and molecular species together within the cluster are of the order $\sim 0.1 \text{ eV}$ or even less, the effect on the properties is quite significant. For example, the acetone dimer has an ionization energy of 9.26 eV, while that of the monomer is 9.69 eV [3]. Similarly, lowering in bond dissociation energies of cluster ions has been observed, as depicted in Table 1.

Table 1 Bond dissociation energies of $(CH_3I)_n^+$ cluster ions [4]

Species	Bond dissociation energy (D_0) (eV)
CH ₃ ⁺ -I	2.68
I ⁺ -CH ₃	3.42
(CH ₃ I)CH ₃ ⁺ -I	0.36
(CH ₃ I)I ⁺ -CH ₃	0.42
(CH ₃ I) ₂ I ⁺ -CH ₃	1.17

Besides, proximity of molecular species and existence of strong intramolecular bonds and weak intermolecular forces within the cluster, makes their photochemical investigation fascinating. These molecular clusters also exhibit distinct reactions i.e. concerted photochemistry and ion-molecule reactions [5]. As a result, clusters are often employed as nano-laboratories for simulating effect of solvation in bulk-phase and for detailed understanding of different chemical and physical processes, at microscopic level [6]. In addition, isolated existence of clusters in gas-phase facilitates investigation of different processes, without any perturbation from external factors. Furthermore, in a cluster all its constituents (atoms/molecules) are present on or near the cluster surface. Consequently, due to surface effect clusters exhibit distinct properties as a function of cluster size and its properties can be significantly altered by doping with different atomic and molecular species. Hence cluster exhibit size-dependent alteration in chemical, catalytic, magnetic, electrical and optical properties. Therefore, clusters have practical implications in various areas i.e. atmospheric chemistry, nanoelectronics, catalysis, biology, etc. [7]. In biology, clusters are often employed as surrogates for understanding stability and for simulating radiation damage of biomacromolecules [8]. Also, helium nanodroplets (large helium clusters) are often employed as ultra-cold bath (~ 0.4 K) for resolving complex spectra of large biomolecules [9].

In this article, representative studies carried out to investigate photochemical behaviour of molecular cluster upon irradiation with nanosecond (ns) and picosecond (ps) laser pulses over intensity range of 10^9 to 10^{13} W/cm², are presented. Over the intensity range investigated, clusters exhibit distinct photochemical behaviour as a function of cluster composition, cluster size and laser parameters (laser wavelength and intensity). Also, collective behaviour of ionized cluster under the influence of intense laser field leads to generation energetic multiply charged atomic ions, energetic electrons and high energy photons. Before discussing our results, a brief description of cluster source and experimental setup used in our investigation is presented below.

Cluster generation in molecular beam

Supersonic expansion of gases/gaseous mixture through a nozzle into vacuum, has been widely used for generation of gas-phase neutral clusters of atoms and molecules. Basic process involves adiabatic expansion of a gas/gaseous mixture held at high stagnation pressure (P_0) , though a small orifice of diameter d, into an vacuum chamber having pressure in the range of 10⁻⁶–10⁻⁵ Torr. Two-body collisions during the expansion process converts random motion of atoms/molecules into directed flow, causing lowering in translational, rotational and vibrational temperature of the molecule to few Kelvin [10]. Alongside three-body collisions, coupled with extremely low temperatures and high number density of gaseous atoms/ molecules facilitates nucleation and growth of clusters. These three-body collisions are essential during the initial phase of cluster nucleation, as the process of cluster formation is exoergic in nature and the third body is essential for removal of excess energy from the system, as kinetic energy of the carrier gas. Generally, less condensable inert gases i.e. helium and argon are used as carrier, as they efficiently remove the exothermic energy from the cluster system via collisions. With increase in cluster size, need

for third body participation is unimportant, as the excess energy can be assimilated by the cluster itself, particularly when many vibrational degrees of freedom are available to act as sink. Using this method, clusters size in the molecular beam can be varied by changing nozzle diameter (d), stagnation pressure (P_0) and initial gas temperature (T_0). The rate of three body collisions (Z_3), which determines the probability of cluster generation, is related to above parameters by the equation-

$$Z_{3} \alpha P_{0}^{2} d / T_{0}^{2}$$
 (1)

Equation 1 suggests that cluster formation is facilitated by using large diameter nozzles and higher reservoir pressure. But as the rate of three-body collision enhances with the square of the stagnation pressure and linearly with nozzle diameter, depending on the available pumping speed of the vacuum system, higher efficiency of cluster formation can also be achieved by working with small diameter nozzles and higher reservoir pressure.

Description of Experimental set-up

Two different experimental set-ups were used for studying photochemistry of clusters, upon interaction with intense laser pulses. Linear time-of-flight mass spectrometer (TOFMS) was used for characterizing different fragment ions produced upon laser-cluster interaction. Here, clusters were subjected to intense ns and ps laser pulses, in the ionization zone of linear time-offlight mass spectrometer. The TOFMS is based on Wiley-McLaren dual focussing principle and has a resolution of ~ 300. Besides, an in-house developed electron energy analyzer was also used for characterizing kinetic energy of electrons liberated upon laser-cluster interaction [11]. The electron energy analyser is based on retarding field method. Here, the electrons pass through the analyzer under the influence of kinetic energy acquired by them during the laser-cluster interaction process. By varying the retarding potential, kinetic energy of electrons liberated upon laser-cluster interaction was characterized.



Figure 1: Representative time-of-flight trace obtained from electron energy analyzer, at zero retardation potential for clusters irradiated with intense laser pulses. Inset shows actual photograph of the analyzer.

Figure 1 represents a typical signal obtained from the analyzer. As depicted in the figure, using the electron energy analyzer it was possible to differentiate between signal arising from photons (produced upon electron-ion recombination within the clusters), electrons and anions.

Some of the representative studies carried out using above setup are described below.

Photochemical behaviour of $(CS_2)_n$ clusters: Observation of diverse ionic species due to ionmolecule reactions

Clusters exhibit distinct photochemistry, as compared to their constituent monomer analogue. This is evident from figure 2a and 2b, which represent time-of-flight mass spectra obtained upon interaction of carbon disulphide (CS_2) monomer and $(CS_2)_n$ clusters with 266 nm laser pulses. In case of monomer, only ion

signal corresponding to fragment ions S⁺, CS⁺, S₂⁺ and CS₂⁺ were detected. While in case of studies carried out on $(CS_{2})_n$ cluster, additional ion signal corresponding to fragment ions i.e. $[C(CS)]^+$, $[S(CS)]^+$, $[S_2(CS)]^+$, $[C(CS_2)]^+$, $[C_2(CS_2)]^+$, $[C_3(CS_2)]^+$, $[S(CS_2)]^+$, S_3^+ and $[CS(CS_2)]^+$ were also observed. Thus, upon clusterization significant transformation in photochemical behaviour of CS₂ is observed. Generation of these fragment ions has been ascribed to rich intra-cluster ionmolecule reactions, which transpires within the cluster upon multiphoton excitation [12]. Some of the representative ion-molecule reaction, which transpire within the (CS₂)_n cluster are listed below:

$$[(CS_{2})_{x}(CS_{2})_{n\cdot x}] \xrightarrow{3 \text{ hv}} [(CS_{2})_{x}(CS_{2})_{n\cdot x}]^{*} \longrightarrow [(C)_{x}(CS_{2})_{n\cdot x}]^{*} + S_{2} (2)$$

$$\longrightarrow [(S)_{x}(CS_{2})_{n\cdot x}]^{*} + CS (3)$$

Figure 2 Time-of-flight mass spectra obtained upon irradiation of (a) CS_2 monomer and (b) $(CS_2)_n$ clusters, with 266 nm laser pulses of intensity ~ 3 x 10^{12} W/cm²

Interaction of $(TMT)_n$ clusters with 355 nm laser pulses: Generation of H_2^+ and H_3^+ ions

 H_{2}^{+} and H_{3}^{+} ions are of importance in experimental and theoretical chemical physics, as they represent a simple polyatomic molecular system. In addition, these species are considered to play a crucial role in interstellar chemistry, leading to formation of complex molecules in the rarefied environment [13]. On irradiation of several polyatomic molecules containing methyl group with femtosecond laser pulses, observation of these species has been reported. It is suggested that these species are ejected from multiply ionized molecular species, produced under the influence of ultra-short laser pulse, following molecular rearrangement i.e. hydrogen migration over femtosecond time scale within the ionized molecular ion [14]. Under our experimental conditions, generation of these species has been observed for studies carried on tetramethyltin clusters ((TMT),) subjected to 355 nm laser pulses (Figure 3). As shown in figure 3, along with ion signal corresponding to H⁺, C²⁺, C⁺, CH₃⁺ Sn²⁺ and Sn⁺, minor yield of H₂⁺ and H₃⁺ ions is also observed. Though the ion yield of H₂⁺ and H₃⁺ is significantly lower, their yield can be enhanced to a certain extent by optimizing experimental conditions. Studies carried out as a function of laser intensity suggested a strong correlation in ion yield of H⁺, H₂⁺ and H₃⁺. Based on these studies, it was concluded that intra-cluster ion chemistry initiated by H⁺ ion, leads to stepwise formation of H₂⁺ and H₃⁺ [15].

Figure 3 Time-of-flight mass spectrum recorded upon interaction of $(TMT)_n$ clusters with 355 nm laser pulses of intensity ~ 1.2 x 10¹¹ W/cm². Inset shows ion signal corresponding to H_2^+ and H_3^+ ions.

Facile generation of anionic fragment ions upon interaction of clusters with intense laser pulses.

Figure 4 Time-of- flight mass spectra of (a) $(CF_2Br_2)_n$ clusters and (b) $(CH_3I)_n$ clusters upon interaction with 532 nm laser pulses, recorded in negative ion mode.

Besides positively charged fragment ions, interaction of intense laser pulses with clusters also leads to generation of anionic fragment ions. Generation of these anionic fragment ions is facilitated by higher electron affinity of halide ions, and confinement of quasi-free electrons within the ionized cluster. In our earlier studies, carried out on monomers of halogenated organic molecules, no ion signal could be detected for studies carried out in negative ion mode, using TOFMS. Figure 4a depicts anions generated when CF₂Br₂ cluster are subjected to 532 nm laser pulses of intensity $\sim 5.6 \times 10^9 \,\text{W/cm}^2$. The most abundant species in the mass spectrum was Br- which has a high electron affinity (-3.354 eV). Moreover, other negative ions such as F⁻, Br₂-and (CF₂Br₂)Br⁻ were also observed in the time-of-flight mass spectrum [16]. No ion peak due to CF₂Br₂⁻ was observed in the mass spectrum, due to its short lifetime (~4.5 ps). Generation of these anionic species has been ascribed to dissociative electron attachment of quasi-free electrons confined within the CF₂Br₂ cluster. Here low energy electron interacts with the neutral molecule within the cluster and forming an excited state anion, which subsequently undergoes dissociation, leading to generation of these anionic species. In our study, due to higher bond dissociation energy of C-F bond (as compared to C-Br bond) no F- solvated cluster ions were observed. Ion intensity of F- and Br⁻ in the mass spectrum are also in accordance with these bond dissociation energies. On similar lines, anionic species generated upon interaction of (CH₃I)_n clusters with 532 nm laser pulses has been explained (Figure 4b) [17].

Clusters as model reactors for studying reactivity of laser-generated transition metal cations

Clusters are often employed as gas-phase reactors, for understanding chemical reactions at molecular level. Studies have been carried to investigate the feasibility of exploiting acetylene clusters as model reactors, for assessing catalytic activity of transition metal ions towards

Figure 5 Time-of-flight mass spectrum of $Fe^+(C_2H_2)_n$ clusters. Insets show ion signal corresponding to $C_6H_4^+$, $C_6H_5^+$, $C_6H_6^+$, $C_8H_6^+$, and $C_8H_7^+$ ions.

polymerization of acetylene. These studies are vital for understanding mechanisms of cycloaddition reaction of unsaturated hydrocarbons, in presence of catalyst. In these studies, neutral acetylene clusters were generated upon supersonic expansion and were subsequently interacted with transition metal ions (M^{+*}) generated by laser vaporization/ionization method. Several transition metal ions (V⁺, Fe⁺, Co⁺ and Ni⁺) were screened for their reactivity, leading to polymerization of acetylene. Figure 5 represents mass spectrum obtained upon interaction of Fe⁺ ions with acetylene clusters. Besides ionsignal corresponding to Fe-acetylene clusters (up to $Fe^+(C_2H_2)_{17}$), ion signal corresponding to fragment ions $C_6H_4^+$, $C_6H_5^+$, $C_8H_6^+$ and $C_8H_7^+$ are also observed in the mass spectrum [18]. These fragment ions have been characterized to be covalently bonded hydrocarbon ions by ion-mobility studies, which are produced via metal ion induced catalytic polymerization. Here polymerization reaction is initiated upon C-H bond activation of acetylene molecule within the cluster, followed by sequential addition of acetylene molecules to the activated acetylene monomer.

Tin-containing molecular clusters as potentials dilute debris-free tin source for extreme ultraviolet (EUV) lithography applications

As a function of laser parameters (laser wavelength and intensity), clusters exhibit distinct photochemical behaviour. For studies carried out on tetramethyl tin clusters ((TMT)) as a function of laser wavelength it was observed that at 266 and 355 nm, (TMT), clusters predominantly undergo multiphoton ionization, resulting in generation of primarily singly charged fragment ions. While for studies carried out at 532 and 1064 nm, significant yield of multiply charged tin ions was obtained, up to Sn^{6+} (I.E. ~ 94 eV) and Sn^{14+} (I.E. $\sim 282 \text{ eV}$) respectively, in addition to minor yield of singly charged fragment ions. Generation of these multiply charged atomic ions upon laser-cluster interaction under our experimental conditions can be explained based on efficient interaction of clusters, due to their solid-like density, with long wavelength laser pulses. In these studies, quasi-free electrons (ionized electrons confined within the cluster) are found to play a vital role in coupling laser energy with the cluster system. Accordingly, a three-stage cluster ionization model "multiphoton ionization ignited-inverse bremsstrahlung heating-electron impact ionization", has been proposed to explain generation of multiply charged atomic ion [19]. Based on the model, inverse bremsstrahlung heating of the cluster is facilitated by quasi-free electrons, which is found to enhance as a function of laser wavelength. Role of quasi-free electrons in generation of multiply charged atomic ions is further confirmed, based on measurement of kinetic energy of electrons liberated upon disintegration of the ionized cluster, using electron analyser set-up. As compared to 532 nm, electrons with higher kinetic energy were detected for studies carried out at 1064 nm. Figure 6a shows variation in electron signal as a function of retarding voltage, for electron kinetic energy distribution studies carried out at 1064 nm. Here reduction in electron signal as function of retarding potential is evident, which has been ascribed to exclusion of lower energy electron component from $(TMT)_n$ clusters, with increase in retarding potential. Based on these studies, it was concluded that under the influence of 1064 nm laser pulses, quasi-free electron gain kinetic energy up to ~ 300 eV [20].

In addition, multiply charged tin ions (S⁸⁺ to Sn¹³⁺) are considered as ideal emitters of extreme ultraviolet (EUV) wavelength at ~13.5 nm, which is of relevance in EUV lithography applications - for fabrication of advanced micro-electronic devices. In our studies, we have tried to optimize the ion yield of these multiply charged atomic ions by varying experimental parameters i.e. laser intensity and cluster expansion conditions. Figure 6b illustrates enhancement in ion yield of multiply charged atomic ions (Sn⁸⁺ to Sn¹³⁺) as a function of laser intensity. These studies suggest potential of tin containing clusters as a dilute debris-free tin source for EUV lithographic applications, in place of solid tin targets - having restricted commercial utilization due to debris generation.

Figure 6 (a) Time-of-flight traces obtained using electron energy analyzer for $(TMT)_n$ clusters irradiated with 1064 nm laser pulse of intensity ~7.9 × 10¹² W/cm². (b) Time-offlight mass spectra in m/z region of 7-25, depicting variation in ion yield of multiply charged tin ions (Sn⁵⁺ to Sn¹³⁺) with laser intensity (from 3.5 x 10¹² to 8 x 10¹² W/cm²) for 1064 nm laser wavelength.

Conclusions

Diverse photochemistry exhibited by clusters can be ascribed to collective behaviour of cluster constituents, under the influence of intense laser pulses. Proximity of atomic and molecular species within the cluster facilitates concerted photochemistry and ion-molecule reaction, resulting in generation of unusual fragment ions. While confinement of ionized electrons (quasi-free electrons) within the cluster enables efficient transfer of laser energy to the cluster system, enabling generation of multiply charged atomic ions and energetic electrons.

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Temperature Dependent Kinetic Studies of the Gas-Phase Reaction of Volatile Organic Compounds with the Tropospheric Oxidants and their Atmospheric Acceptability Parameters

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Abstract

Rate coefficients for the gas phase reaction of the OH radical with three Volatile Organic Compounds (VOCs) namely 1,2-propylene oxide (PPO), 1-chlorocyclopentene (CCP) and 1,3-dioxalane (DXL) have been measured using an absolute rate method employing Laser Photolysis - Laser Induced Fluorescence (LP-LIF) method over a temperature range of 262–335 K. Room temperature rate coefficients for the gas phase reaction of PPO with the OH radical and CCP with OH, Cl and O₃ have also been measured using a relative rate method employing Gas Chromatography. These rate coefficients are used to calculate the tropospheric lifetimes, which with respect to the OH radicals are found to be 12 days, 2 hours and 11 hours for PPO, CCP and DXL, respectively. Negative temperature dependence of the rate coefficients is observed for CCP reaction with the OH radical with rate coefficient expressed as $k(T) = (6.32 \pm 1.16) \times 10^{-12} exp((669 \pm 45)/T) cm^3 molecule^{-1}$ s⁻¹ and no temperature dependence is observed for the reaction of PPO and DXL with the OH radical suggesting a pre-reactive complex in the former, and a barrier-less mechanism in the latter. Theoretical calculations are done to get insight into the the potential energy surface of the reaction of the VOCs with the OH radical and their structure-activity relationship. Other atmospheric acceptability parameters such as Global Warming Potential (GWP) and Ozone Depletion Potential (ODP) are calculated.

1. Introduction

Volatile organic compounds (VOCs) are emitted into the atmosphere via a variety of natural, anthropogenic and biogenic sources¹ and can be a potential source of environmental concerns such as global warming, ozone depletion, and photochemical smog. They can enter into the atmosphere by various sources such as transport, industries, agriculture, animal waste, plants etc². Tropospheric lifetime of a VOC is an important factor to study its transport and distribution in the atmosphere. It is also related to global warming potential (GWP) for the VOC³. It is decided by the fastest of all the possible degradation processes for any VOC. One of the most important degradation processes for any VOC is reaction with tropospheric oxidative species such as Cl, OH, NO₂, NO₃ and O₃ to form secondary pollutants⁴. Some VOCs may also undergo photodissociation in the troposphere from Sun's UV light with wavelength greater than 300 nm. Water soluble VOCs can be washed out by rain. Tropospheric lifetime of majority of VOCs is determined mainly by the kinetics of their gas phase oxidation with the OH radical, which is known to be abundant and reactive oxidant in the troposphere⁵. Near marine boundary layer (MBL), Cl radicals being abundant, determine the lifetime of a VOC⁶. Ozone oxidation is important only for compounds with a double bond. The OH radical can either add to the double bonds of a VOC or abstract hydrogens leading to short-lived radicals, which decompose to smaller fragments⁷. Therefore, it is required to have a precise and accurate value of the rate coefficient for the reaction of a VOC with the OH radical in order to ascertain its environmental impact. An absolute or a relative rate method is used for studying the

kinetics of the reaction of a VOC with OH /Cl / O_{2}/NO_{2} and from the tropospheric concentration of these oxidants, tropospheric lifetime of a VOC can be calculated. In the relative rate method, the rate coefficient of the reaction of a VOC with an oxidant is obtained by measuring relative change in the concentration of the sample with that of a reference compound after reaction with the oxidant, using Gas chromatography, to determine the concentration of the VOC. Whereas, the absolute method employs Laser Photolysis -Laser Induced Fluorescence (LP-LIF) to measure changes in the absolute concentration of the oxidant as a function of time upon reaction with VOC, by monitoring the changes in fluorescence intensity of the oxidant proportional to its concentration.

Here in this work, we have measured both the absolute and relative rate coefficients of some VOCs, namely 1,2-propylene oxide (PPO), 1-chlorocyclopentene (CCP), with the OH radical and the absolute rate coefficients of 1,3-dioxalane (DXL) with the OH radical over a temperature range of 262-335 K. Apart from this, room temperature rate coefficient of the reaction of the reaction of CCP with Cl and O₃ were also determined using relative rate method. Temperature dependent studies are done to generate the Arrhenius plot and to see the changes in the lifetime of a VOC with increasing altitude. All the chosen VOCs are important from atmospheric point of view. Worldwide production of PPO, exceeds 10 million tonnes per year, most of which is used as a chemical intermediate8. PPO has a widespread usage as a pesticide in post-harvest fumigation process⁹. It is involved in the manufacture of dipropylene glycol and glycol ethers, and in the preparation of lubricants, surfactants, and oil demulsifiers¹⁰. It is also widely involved in production of polyurethane plastics and polypropylene glycols¹¹. Even traces of PPO have been found in Sagittarius B2 in Milky Way making it an interstellar compound¹². Chloro compounds like CCP are used as intermediates in synthesis of vast variety of drugs and in the preparation of synthetically important organometallic reagents like Grignard reagents¹³. Ethers like DXL are used as industrial solvents and fuel additives in the automobile industry in order to decrease the pollutants such as CO, particulates etc. in the exhaust of automobiles¹⁴.

Apart from tropospheric lifetimes, Global warming potential of PPO and CCP is calculated by measuring the IR absorption cross section of the VOC in the wavelength range emitted by the sun, i.e. 400-2500 cm⁻¹. Ozone depletion potential (ODP) is calculated only for CCP, since it has C-Cl bond and is determined by the relative amount of degradation to the ozone layer in comparison to trichlorofluoromethane (R-11 or CFC-11), whose ODP is fixed at 1.0.

2. Kinetic Studies

2.1 Absolute method

Bimolecular rate coefficient for the reaction of VOCs with the OH radical in the temperature range of 262-335 K was measured by performing kinetic measurements under pseudo first-order conditions by using Laser Photolysis - Laser Induced Fluorescence (LP-LIF) technique, under flow conditions. The experimental procedure involves the measurement of the rate of OH decay in the absence and presence of the VOC. A known pressure of VOCs in N₂ buffer gas was introduced in the premix chamber. A constant flow of N₂ gas was bubbled through approximately 50% H₂O₂ solution using a calibrated mass flow controller and then passed to the premix chamber and finally to the reaction cell. A known pressure of VOCs in N₂ buffer gas was then introduced in the premix chamber, so that VOC sample, H_2O_2 , and N₂ get mixed before entering the reaction cell. The reaction cell is made up of a double-walled jacketed glass fitted with MgF, windows kept at the Brewster angle to minimize scattering. In the blank experiment, H₂O₂ seeded in N₂, and buffer N₂ were flown through the reaction cell, without the sample, and the decay kinetics of OH were measured. Here the decay of OH concentration is due to diffusion out of the detection zone and

its reaction with H₂O₂. The OH radicals were generated by the photolysis of H₂O₂ at 248 nm (KrF excimer laser, Lambda Physik, Compex 102) operated at 20 Hz with fluence of 0.2-0.8 mJ/cm² and excited by a probe laser tuned to around 308 nm with the energy low enough (20 μ J/Pulse) to avoid the saturation of the transition. The dye laser (probe laser) is operated on DCM special dye (Lambdachrome, LC 6501, 590-640 nm), and pumped by the second harmonic of an Nd:YAG laser (Quantel, YG980). Both the pump and the probe beams were aligned to intersect in the centre of the cell at the right angle and pass through the exit windows. The $P_1(2)$ rotational line of the $A \rightarrow X$ (0-0) vibrational band of the OH radical was excited near 308 nm and the resulting fluorescence was collected using a photomultiplier tube in combination with a lens and band pass filter centred at 310 nm. Decay kinetics of OH was followed by plotting the fluorescence intensity as a function of time delay between the photolysis and the probe laser using a delay generator 10 µs to 10 ms, in steps of a few microseconds. The pressure inside the cell was measured with a capacitance manometer and was kept about 20 Torr with a total flow rate of 150 sccm. Subsequently, a known pressure of VOC in N₂ buffer gas was flown in the reactor, and the OH decay kinetics was recorded. Sufficient flow velocity of the experimental mixture was maintained (~12 cm/ sec) to allow sampling of a fresh gas mixture by each photolysis laser pulse. A pseudo first-order condition was maintained with [VOC]>>[OH], and the rate coefficient values were measured at a particular constant temperature for different number densities of VOCs. These pseudo firstorder rate coefficients were plotted against the number densities of VOCs, the slope of linear plot gave the value of the bimolecular rate coefficient at that temperature. The process was repeated at different temperatures in the range of 262 to 335 K to determine the temperature dependent rate coefficients. Temperature of the reaction cell was controlled by circulating water and ethylene glycol mixture through the outer jacket from a thermostat bath and was measured at the intersection of the pump and the probe laser beams, using a Chromel-Alumel thermocouple.

Once a sample is introduced, its reaction with the OH radical causes the OH radical to decay faster. Also, VOC was in large excess (more than two orders of magnitude) over OH concentration to maintain pseudo first-order conditions.

The overall process can be described as: $H_2O_2 + hv(248nm) \rightarrow OH + OH(1)$ $OH + VOC \xrightarrow{k_{voc}} various products(2)$ $OH + H_2O_2 \xrightarrow{k_1} HO_2 \cdot + H_2O$ (3) $OH \xrightarrow{k_d} diffusion out of detection zone(4)$

where $k_{voc'}$, $k_{1'}$, and k_{d} are the rate coefficients for the reactions of OH with VOC, OH with H₂O₂ and the diffusion process, respectively. The rate of decrease in the OH concentration is given as,

$$\frac{-d[OH]}{dt} = (k_{voc}[VOC] + k_1[H_2O_2] + k_d)[OH](5)$$

In all the experiments, the conditions, k_{voc} [VOC] >> k_1 [H₂O₂], [H₂O₂] = constant and the total pressure = constant, are maintained. Thus the above equation simplifies to

$$\frac{d[OH]}{dt} = (k_{voc}[VOC] + k_x)[OH](\mathbf{6})$$

where k_x represents $k_1[H_2O_2] + k_d$. Since [OH] << [VOC] we have $k_{voc}[VOC] + k_x = k'$ (pseudo first-order rate coefficient), and solving the differential equation leads to

$$[OH]_t = [OH]_0 e^{-k't}(7)$$

where $[OH]_0$ and $[OH]_t$ are the hydroxyl radical concentrations at t = 0 and at time t, respectively. The time t, represents the interaction time decided by time delay between the photolysis and probe laser pulses. The pseudo first-order condition was maintained throughout the experiment and confirmed by reproducibility of results on changing the

experimental conditions, which include the OH radical precursor concentration, laser intensities etc. Initially, in absence of the sample, decay kinetics of the OH radical was followed. Different concentrations of a VOC were then introduced to the reaction cell with the help of a mass flow controller (MFC). For each concentration of the VOC, at least three to four measurements were taken for a reliable result.

The pseudo first-order rate coefficient, k' is obtained from a weighted linear least-square fit of the logarithm of the ratio of signal intensity, $ln[(LIF)_t/(LIF)_0]$, with time, as shown in Fig. 1. The values of k', obtained at different concentrations of VOC at a particular temperature T, were plotted against the concentration of VOC, to obtain the required value of bimolecular rate coefficients $k_{VOC'}$ shown in Fig. 2. The slope of the linear graph gives the value of k_{VOC} for

the reaction of the OH radical with the VOC at that temperature. The values of the rate coefficients for the reaction of VOCs with the OH radical at different temperatures are provided in Table 1. The quoted errors given in Table 1 correspond to 2 σ of the linear regression, which does not include any systematic errors such as the errors in the measurements of the partial pressure of the sample and the flow rate (these errors can be approximately 5%). The Arrhenius plot is shown in Fig. 3. Negative temperature dependence of the rate coefficients is observed for the CCP reaction with the OH radical having the rate coefficient expressed as $k(T)=(6.32\pm1.16)\times10^{-12} \exp((669\pm45)/T) \text{ cm}^3$ molecules⁻¹ s⁻¹. No temperature dependence is observed for the reaction of PPO and DXL with the OH radical.

Fig. 1 The measured OH radical decay profiles at 298 K, with increasing concentration of VOC for various curves. The least-squares linear fits are shown as solid lines. The slope of the linear fit gives the value of k' at that concentration of VOC.

Temperature (K)	1000/T (K-1)	Rate coefficient (k _{PPO}) (cm ³ molecule ⁻¹ s ⁻¹)	Rate coefficient (k _{CCP}) (cm ³ molecule ⁻¹ s ⁻¹)	Rate coefficient (k _{DXL}) (cm ³ molecule ⁻¹ s ⁻¹)
261	3.83	$(4.76 \pm 0.32) \times 10^{-13}$	$(8.36 \pm 0.43) \times 10^{-11}$	$(1.27 \pm 0.12) \times 10^{-11}$
273	3.66	$(4.69 \pm 0.28) \times 10^{-13}$	$(7.38 \pm 0.43) \times 10^{-11}$	$(1.22 \pm 0.20) \times 10^{-11}$
298	3.36	$(4.65 \pm 0.24) \times 10^{-13}$	$(5.76 \pm 0.55) \times 10^{-11}$	$(1.20 \pm 0.09) \times 10^{-11}$
314	3.18	$(4.80 \pm 0.24) \times 10^{-13}$	$(5.36 \pm 0.18) \times 10^{-11}$	$(1.28 \pm 0.20) \times 10^{-11}$
335	2.98	$(4.68 \pm 0.20) \times 10^{-13}$	$(4.79 \pm 0.09) \times 10^{-11}$	$(1.39 \pm 0.22) \times 10^{-11}$

Table 1: Temperature dependent rate coefficients of the reaction of VOCs with the OH radical

Fig. 2 Variation of the k' against the concentration of VOC, with the slope corresponding to the bimolecular rate coefficient (k_{voc}) at room temperature (298 K). Value of k_{ppCY} , k_{DXL} and k_{CCP} are measured to be (4.65 ± 0.24) × 10⁻¹³, (1.20 ± 0.09) × 10⁻¹¹ and (5.76 ± 0.55) × 10⁻¹¹ cm³ molecules⁻¹ s⁻¹, respectively.

2.2 Relative rate method

A quartz reaction chamber (3 L volume), fitted with vacuum stopcocks and a sealed port for taking out samples for GC analysis, was used to carry out the reactions. The experiments were done at room temperature (298 \pm 2K). The OH radical and Cl atom were generated in situ by photolysis of H₂O₂ and oxalyl chloride (COCl)₂, respectively, by a UV lamp (Rayonett) at 254 nm. The reaction with O₃ was carried out using O_3/O_2 mixture, generated using a silent electric discharge of O2, and the mixture was added intermittently using a syringe. The reaction mixture, consisting of VOC (100-200 ppm), reference compound (50-100 ppm) and oxalyl chloride (typically~400 ppm), was prepared in the reaction chamber, using a vacuum manifold, and the total pressure was maintained at (800 \pm 3) Torr, by adding N₂/air (buffer gas). The pressure was measured, using a capacitance manometer (Pfeiffer Vacuum). Before photolysis, the prepared reaction mixture was equilibrated for 60-80 min for uniform distribution, and the same was confirmed by the reproducibility of the gas chromatogram. The mixture was photolysed for a period of 5-6 min, in steps of about 1 min, and after each photolysis step, the decrease in the VOC and the reference molecule (R) was determined, using a gas chromatograph

Fig. 3 Arrhenius plot of the average value of rate coefficient k_{VOC} (T) of the reaction of VOC with the OH radical. Reaction of CCP with OH shows negative temperature dependence of the rate coefficient while that of DXL and PPO shows no temperature dependence.

(Shimadzu GC 2014, 5% SE 30 column, flame ionization detector). The stability of the reaction mixture with respect to wall losses and dark reactions was checked for about 7 h, which is more than the total duration of a relative rate measurement. Non interference of any reaction product of VOC and that of reference with oxidant in the GC analysis was also checked independently. Using the relative rate method, assuming that both the molecules react only with oxidants, the kinetic data were obtained by plotting the fractional loss of the VOC and R, according to the relative rate equation (8),

$$\ln\left(\frac{[voc]_{t_0}}{[voc]_t}\right) = \left(\frac{k_{voc}}{k_r}\right)\ln\left(\frac{[R]_{t_0}}{[R]_t}\right)(\mathbf{8})$$

where, $[R]_{to}$ and $[VOC]_{to}$ are the concentrations of reference and VOC, respectively, at time $t_{0'}[R]_t$ and $[VOC]_t$ are the corresponding concentrations at time t, and k_{VOC} and k_r are the rate coefficients of the OH radical with VOC and reference, respectively. Thus a plot of $\ln \left(\frac{[VOC]t_0}{[VOC]t_0}\right) vs \ln \left(\frac{[R]t_0}{[R]t}\right)$ gives a straight line with zero intercept and slope of $\left(\frac{k_{VOC}}{k_r}\right)$.

The typical logarithmic plots of the relative decrease in concentration of PPO due to its reaction with the OH radical, against that of ethane and 1,2-dichloroethane as reference compounds, are shown in Fig. 4. Plots are linear with nearly zero intercepts indicating absence of any complications due to secondary reactions. Slope of the plot obtained by the method of linear least square fit, gives the ratios of the rate coefficient of reaction of PPO with the OH radical to that of the rate coefficient of reaction of reference with the OH radical. The average rate coefficient of the reaction of PPO with the OH radical (in cm³ molecule⁻¹ s⁻¹) is found to be $(4.11 \pm 0.90) \times$ 10^{-13} and $(5.96 \pm 1.38) \times 10^{-13}$ using ethane and 1,2dichloroethane, respectively, considering the the rate coefficient of ethane to be $(2.40 \pm 0.33) \times 10^{-13}$ cm³ molecule⁻¹ s^{-1 15} and that of 1,2-dichloroethane as $(2.20 \pm 0.50) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹⁶ The average rate coefficient of PPO with OH is (5.03 \pm 1.54) × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ The measured rate coefficient for the reaction of CCP with OH

Fig. 4 Fractional decrease in the concentration of PPO with respect to ethane (empty circle), and 1,2-dichloroethane (empty square) in presence of 800 Torr of N_{2} .

is $(5.77 \pm 0.77) \times 10^{-11}$ and $(6.17 \pm 0.74) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ using 1-butene and cyclopentene, respectively, with the quoted errors, including the errors in the reference. The rate coefficients for the reactions of OH at 298 K with the reference compounds, 1-butene and cyclopentene, used here are $(3.15 \pm 0.57) \times 10^{-11}$ and $(6.70 \pm 1.34) \times$ 10⁻¹¹ molecule⁻¹ cm³s⁻¹, respectively.¹⁷ The average rate coefficient of CCP with OH is (5.97 ± 1.08) \times 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. Using the calculated slope values, the rate coefficient for reaction of 1-chlorocyclopentene with Cl in N₂ is (3.92 ± 0.53) $\times 10^{-10}$, (3.36 ± 1.07) $\times 10^{-10}$ and (3.26 ± 0.42) $\times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ using 1-butene, cyclopentene and butane respectively. Thus the average rate coefficient of 1-chlorocyclopentene with Cl in N₂ atmosphere is $(3.51 \pm 1.26) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1}$ s⁻¹. The measured rate coefficient for reaction of 1-chlorocyclopentene with O_3 is $(1.5 \pm 0.19) \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹ using 1-butene as a reference molecule (depicted in Fig. 5).

3. Theoretical studies:

Reaction of CCP with the OH radical has negative temperature dependence of the rate coefficient, while that of PPO and DXL has no temperature dependence. This suggests formation of a stabilized pre-reactive complex leading to overall negative activation energy in the former, and a barrier-less mechanism in the latter. To confirm the hypothesis, we

Fig. 5 Fractional decrease in the concentration of CCP with respect to a reference molecule. For Cl reaction, reference compounds are butane (solid square), cyclopentene (solid circle) and butane (solid triangle) in 800 Torr of N_2 ; and butene (open square) and cyclopentene (open circle) in air. For OH reaction, reference compounds used are butane (solid square), cyclopentene (solid circle) in 800 Torr of N_2 .

decoded the potential energy surfaces of the reaction of VOCs with the OH radical by performing molecular orbital calculations using the Gaussian 03 program. Geometries for various stationary points, transition states, and intermediate complex were optimized at B3LYP/6-311G(d,p) level of theory followed by calculation of their single-point energy for all the species at the QCISD(T)/6-311G(d,p) level of theory. All transition state structures were found to have only one imaginary frequency and one negative eigenvalue of the force constant matrix. The relative potential energy diagram for the abstraction/addition reaction was constructed using these results.

1,2-Propylene oxide (PPO) belongs to the C1 point group and has four chemically distinct hydrogen environments. Therefore, there exist four possible H-abstraction channels for the reaction of OH with PPO (given in Fig. 6). The energies of 4.8 kcal/mol for TS_Ha, 2.0 kcal/ mol for TS_Hb, 3.3 kcal/mol for TS_Hc and 4.3 kcal/mol for TS_Hd were obtained with respect to the zero-energy of the reactant molecules, and the corresponding product molecules were stabilized by 12.5, 11.7, 10.5, 10.4 kcal/mol, respectively. Though the flanking approach of oxygen of epoxide ring with the hydrogen of the OH radical is present in TS_Ha, this is found to be the least favoured approach possibly due to the formation of a 6-membered ring in the transition state. The other possibilities of hydrogen atom abstraction involve a 5-membered transition state, which is entropically more favourable. TS_Hb is energetically privileged over TS_Hc and TS_Hd by virtue of lower O (epoxide) - H (OH radical) distance in the transition state. The lowest value of barrier energy (2.0 kcal/mol) is not much significantly higher than the thermal energy at 298 K (0.25 kcal/mol). This implies that the reaction of PPO with the OH radical is not very sensitive to temperature change. Hence, theoretical calculations support our experimental observations, suggesting a low energy barrier for the reaction.

1,3-Dioxalane (DXL) has two different types of abstractable hydrogen atoms. Therefore, there exist two possible H-abstraction channels for the reaction of OH with DXL (Fig. 6). The energies of 1.8 kcal/mol for TS_Ha, 2.0 kcal/mol for TS_Hb, were obtained with respect to the zero-energy of the reactant molecules, and the corresponding product molecules were stabilized by 17.8 and 20.3 kcal/mol, respectively. The radical centred at the C-2 is expected to be more stable than at C-4/C-5, because of enhanced stabilization by inductive effect of two oxygen atoms. TS_Ha is somewhat more favourable than TS_Hb, because here too the inductive effect of two oxygen atoms will stabilize the radical formed in the transition state. Same as PPO, the lowest value of barrier energy (1.8 kcal/mol) in DXL reaction with OH is not much significantly higher than the thermal energy suggesting a weak temperature dependence.

The reaction of OH with 1-chlorocyclopentene (CCP) may involve both abstraction of H atoms and addition to the C=C bond. There are two chemically distinct C-atoms at the two ends of the unsaturation, i.e., C1 (with a chlorine atom attached to it), and C2 (without chlorine atom). Both the addition channels may go through the formation of pre-reactive complexes between the OH radical and the π orbitals of the double bond in 1-chlorocyclopentene. It is a well-known fact that the pre-reactive complex is basically an intermediate van der Waals complex, which is formed through a barrier-less mechanism. Once formed, the complex can re-arrange to shift the OH radical to an ethylenic carbon centre. We could optimise the pre-reactive complex of the addition (shown as HB1 in Fig. 6), which is 3.1 kcal/mol more stable than the reactants. The complex undergoes rearrangement, in which the OH atom gets attached to C2, via a transition state structure, which is 4.8 kcal/mol above the complex. The radical products for addition to the C1 and C2 centres respectively are about -33.7 kcal/mol and -33.5 kcal/mol more stable than the reactants. The 1-chlorocyclopentene molecule is

Fig. 6 Optimized structures of VOCs and the pre-reactive complex of CCP and OH

also expected to undergo hydrogen abstraction in OH reactions. The molecule has four different types of H atoms (Fig. 6), implying four different mechanisms for the H atom abstraction reaction by the OH radical. Our calculations show that all these channels involve the presence of activation barriers. The presence of hydrogen bonded complexes HB1 in the reaction of CCP with the OH radical justifies the negative temperature dependence of the rate coefficient.

4. Atmospheric acceptability parameters

Three parameters, namely tropospheric lifetime, Global Warming Potential (GWP) and Ozone depletion potential (ODP), are required to assess the potential impact of a VOC on the atmosphere. Tropospheric lifetimes for majority of pollutants are decided by their reaction rates with atmospheric oxidants as well as their uptake in the cloud droplets. However, for compounds with abstractable hydrogen atoms, reaction with the OH radical happens to be a major degradation channel, thereby deciding the atmospheric lifetime. Rate coefficients of the gas-phase reaction of PPO, CCP and DXL with the OH radical have been measured. Tropospheric lifetime of PPO was calculated by using the formula,

$$\tau_{OH}^{VOC} = \frac{1}{k_{OH}^{VOC} * [OH]} (9)$$

where and represent the tropospheric lifetime and the rate coefficient of a VOC for removal by the OH radicals, respectively. The average atmospheric concentration of the OH radicals, [OH], was taken as 2.0×10^6 molecules

cm⁻³.¹⁸ The tropospheric lifetime calculated for PPO, CCP and DXL, using above equation, was found to be 12 days, 2 hours and 11 hours, respectively. This suggests that CCP will be the first to be removed in troposphere followed by DXL and then PPO.

The GWP value of any pollutant species depends upon its atmospheric lifetime and radiative forcing. The radiative forcing was estimated from the IR spectrum by measuring the IR absorption cross section of the VOC in the wavelength range 400-2500 cm⁻¹, using the method explained by Hodnebrog et al.³. The radiative forcing of PPO and CCP is calculated to be 19.8 and 22.4 mW m⁻² ppb⁻¹, respectively. This calculated value was then used to determine GWP by using formula

$$(GWP)_X(TH) = \frac{\int_0^{TH} a_x[x(t)dt]}{\int_0^{TH} a_r[r(t)dt]} (10)$$

where a_x is radiative forcing of a unit mass of x (PPO) added to the current atmosphere, x(t) is atmospheric decay function of PPO (in a time horizon TH), a_r and r(t) are the characteristic parameters for the reference molecule CO_2 . The value of $\int_0^{TH} a_r [r(t)dt]$ is taken to be 9.17 × 10⁻¹⁴ W m⁻² yr kg⁻¹ for 100 years time horizon [25]. For long lived gases, the value of $\int_0^{TH} [x(t)dt]$ can be approximated as Substituting these required values, GWP of PPO and CCP for 100 years time horizon was found to be 0.94 and 0.003, respectively, which suggests that PPO will impose almost similar radiative burden per unit weight as CO_2 on the atmosphere while CCP will impose negligible radiative burden.

Since CCP has a chlorine atom, it can possibly contribute to stratospheric ozone depletion. Similar to GWP, its ozone depletion potential (ODP) can also be estimated, using a semiempirical equation ¹⁹,

$$ODP_{CCP} = \frac{\tau_{CCP}}{\tau_{CFCL3}} \times \frac{M_{CFCL3}}{M_{CCP}} \times \frac{n}{3}(11)$$

where, τ_x and $M_{x'}$ are tropospheric lifetime and molar mass; n is the number of chlorine atoms in CCP (that is 1), and the number 3 refers to the three chlorine atoms in CFCl₃. Using the value of τ_{CFCI3} as 45 years²⁰, the ODP value of CCP is calculated to be 2.1 × 10⁻⁶. This low value of ODP suggests that CCP will have a negligible effect on the stratospheric ozone depletion.

5. Conclusion

The average rate coefficients of reactions of PPO, CCP and DXL with the OH radical were measured at room temperature (298 K) to be $(4.65 \pm 0.24) \times 10^{-13}$, $(5.76 \pm 0.55) \times 10^{-11}$, $(1.20 \pm$ $(0.09) \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, using an absolute rate method, and the corresponding tropospheric lifetimes are 12 days, 2 hours and 11 hours, respectively. The average rate coefficients of CCP and PPO with OH were also measured employing the relative rate method to be $(5.03 \pm 1.54) \times 10^{-11}$ and $(5.97 \pm 1.08) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at the room temperature. The average rate coefficients of the reaction of CCP with Cl and O₃ were $(3.51 \pm 1.26) \times 10^{-10}$ and $(1.5 \pm 0.19) \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹ respectively. Negative temperature dependence of the rate coefficients is observed for the CCP reaction with the OH radical, and the rate coefficients are expressed as $k(T) = (6.32 \pm 1.16) \times 10^{-10}$ $^{12} \exp((669 \pm 45)/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$, which suggest the formation of a stabilized pre-reactive complex. Theoretical calculations confirmed the presence of a pre-reactive addition complex lying 3.1 kcal/mol below the reactants. Weak temperature dependence is observed for the reaction of PPO and DXL with the OH radical suggesting a barrier-less mechanism which was later confirmed by theoretical calculations. Tropospheric lifetime of PPO suggests that it will have a regional impact on the atmosphere, while CCP and DXL will have a local impact. GWP (100 year time horizon) of PPO and CCP was found to be 0.9 and 0.003, which suggests that PPO will impose almost similar radiative burden per unit weight as CO_2 on the atmosphere while CCP will impose negligible radiative burden. The ODP value of CCP is calculated to be 2.1 × 10⁻⁶, which suggests that CCP will have a negligible effect on the stratospheric ozone depletion.

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