

EXECUTIVE SUMMARY

UGC-MAJOR RESEARCH PROJECT

Quantum Mechanical and Molecular Mechanical studies on the reactions of pollutants in atmosphere and in water

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The aim of the project is to study the possible reaction pathways for the gas phase reaction of volatile organic compounds (VOC) with OH, NO₃, and O₃ in the atmosphere and calculating the kinetics of the minimum energy paths to determine the lifetime of the VOC in the atmosphere. In this project work we have studied the oxidation of dimethyl phenol, bromoxynil, perfluoropolymethylisopropylether (PFPMIE), nitrosamines and dimethyl ether (DEE) by OH radical. Also we have studied the depletion of ozone by nitrogen dioxide, and studied the oxidation of tyrosine by ozone and nitrogen dioxide. The executive summary of the findings are given below.

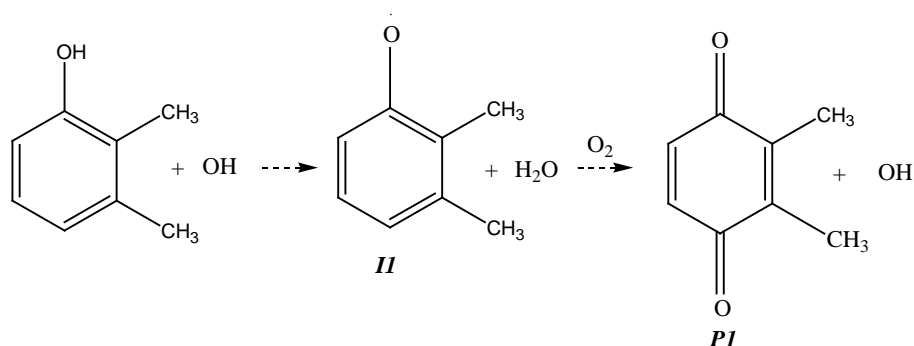
Mechanism and kinetics of the oxidative degradation of dimethylphenol isomers by OH radical

In the atmosphere, the reaction between dimethylphenol isomers and OH radical proceed through different ways, by H-atom abstraction from phenol group or from methyl group or electrophilic addition of OH radical to the aromatic ring or H-atom abstraction by OH radical from the aromatic ring. The H-atom abstraction from phenol group of dimethylphenol results in the formation of dimethyl-benzoquinones and epoxides on subsequent O₂ additions. The H-atom abstraction reactions from methyl group and from the aromatic ring of dimethylphenol are subsequently followed by O₂ addition reactions which lead to a peroxy radical intermediate. This intermediate has excess energy to further react with HO₂ and NO to produce hydroperoxide adducts and alkoxy radicals. The electrophilic addition reaction results in the formation of a cyclohexadienyl radical, which on further reaction with O₂ results in the formation of phenolic compounds and peroxy radical. The peroxy radical further isomerizes and cyclizes to yield epoxy and bicyclic radicals. This bicyclic radical is responsible for the major pathway leading to ring-cleavage products.

The number and position of the OH or CH₃ substituent have a greater influence on the reactivity of dimethylphenols. Depending upon the position of the substituent, the reaction mechanisms and the degradation products differ. This is because the positions activated by OH group are considerably more reactive than those activated by CH₃ group. In spite of the activation of OH group, the presence of methyl groups in these positions provides steric hindrance to electrophilic addition and therefore this leads to reduction in reactivity. The crowded arrangement of two methyl groups on the dimethylphenol isomers is likely to be attacked by the OH radical to abstract H-atom from methyl group. The presence of phenol

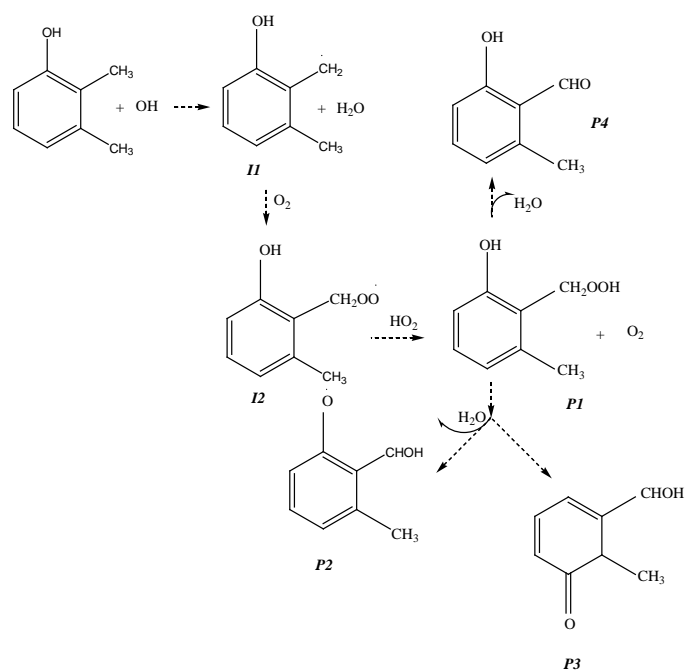
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group between two methyl groups will influence the incoming OH radical to attack at phenol site due to the high resonance potential of the phenol group. Also, the ortho-para directing property of OH and CH₃ substituents has a profound influence on the initial reactions. The H-atom abstraction from phenol group is found to occur dominantly in 2,3-dimethylphenol and the reaction pathway involves barrierless formation of reactant and product complexes through a transition state lying 0.85 kcal/mol above the reactants. This initial step subsequently react with O₂ to form 2,3-dimethylphenol-benzoquinone. The methyl H-atom abstraction by OH radical is found to dominate in 2,3-dimethylphenol leading to an alkyl radical which further reacts with O₂ and subsequently favorably with HO₂ to form hydroperoxide and O₂. This abstraction reaction is observed in all isomers except 2,6-dimethylphenol. This is because of the high resonance potential of the phenol group between the methyl groups which enhances the attack of OH radical towards the OH group of 2,6-dimethylphenol. The H-atom abstraction from the aromatic ring by OH radical is found to occur likely in 3,5- and 2,5-dimethylphenol isomers due to the ortho-para directive influence of the methyl group. The reaction scheme for the four different initial reactions is shown below:

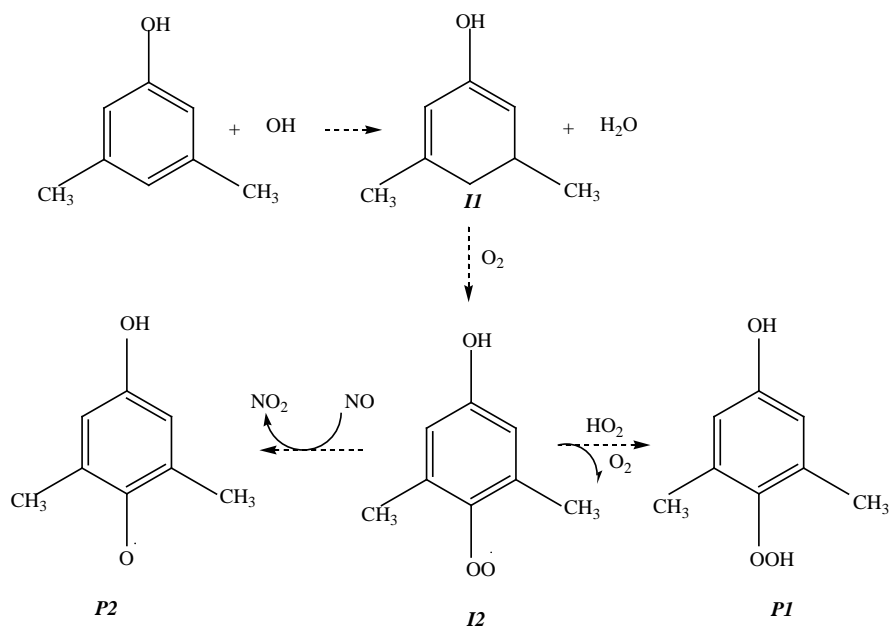


Scheme 1: The proposed reaction scheme corresponding to H-atom abstraction from phenol group of 2,3-dimethylphenol

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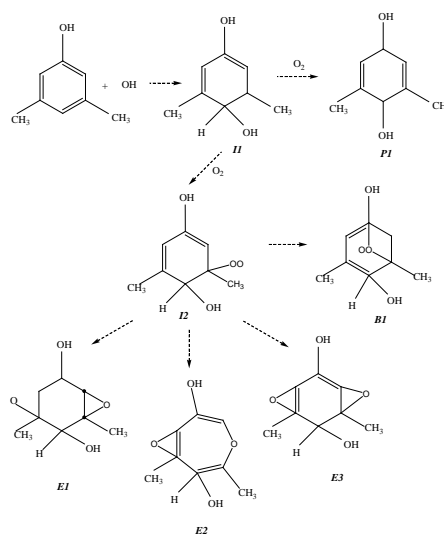


Scheme 2: The proposed reaction scheme corresponding to H-atom abstraction from methyl group of 2,3-dimethylphenol



Scheme 3: The proposed reaction scheme corresponding to H-atom abstraction from aromatic ring of 3,5-dimethylphenol

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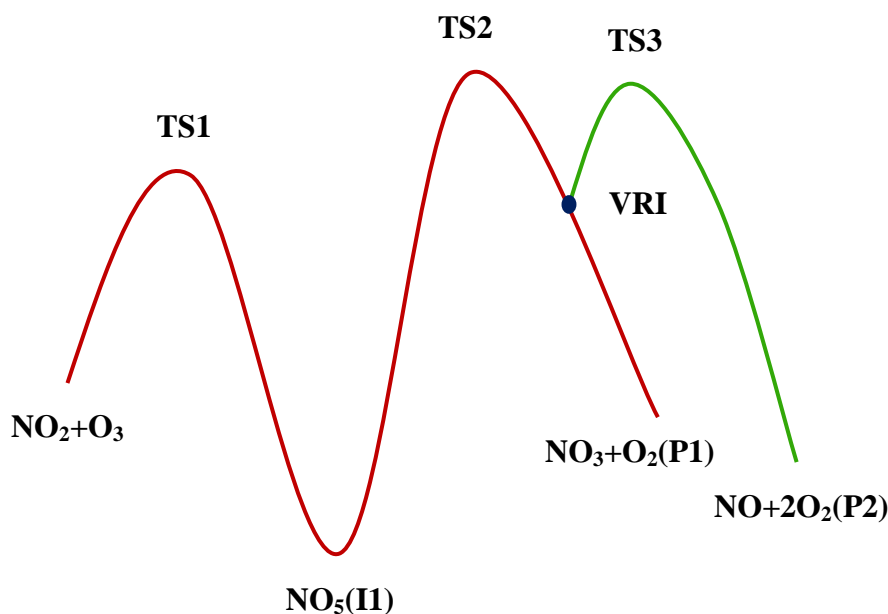
Scheme 4: The proposed reaction scheme corresponding to electrophilic addition of OH radical to 3,5-dimethylphenol.

The O₂ addition to the initial step results in a peroxy radical which exits via its reaction with NO to form alkoxy radical and NO₂ through a transition state with a small barrier of 2.57 kcal/mol, leading to the lowest energy pathway. The electrophilic addition of OH radical to the aromatic ring is found to occur favorably in 3,5-dimethylphenol resulting in the formation of a cyclohexadienyl radical which subsequently react with O₂ to form phenolic compounds and peroxy radical. The peroxy radical further isomerizes to form epoxide radicals and cyclizes affording a bicyclic radical. The epoxy radical E3 is found to be more stable than the bicyclic radical B1 and its peroxy radical precursor. The epoxy radical E1 and the bicyclic radical B1 are found to form equivalently with a barrier of 2.8 kcal/mol. These radicals propagate the oxidation of 3,5-dimethylphenol to the formation of various ring cleavage products. Thus the position of the OH and CH₃ substituent on the aromatic ring influences the reactivity of the methyl substituted phenolic compounds and depending upon the principal oxidation steps, the subsequent reaction mechanisms and the reaction products differ.

Depletion of atmospheric ozone by NO₂:

Theoretical investigation on the reaction of NO₂ with O₃ in the context of ozone depletion is performed. The progress of this reaction in single or concrete steps is an open and highly challenging question for both experimentalists and theoreticians. The reaction is studied through DFT methods, M06-2X, BHHLYP and MPW1K with 6-311++G(2df,2p) basis set and also at UCCSD and CASPT2 methods with 6-31G(d,p) basis set. The single

point energies of the reactive species are calculated at CASSCF, UCCSD(T), UQCISD(T) and MRCI methods with 6-311++G(2df,2p) basis set. The reaction scheme for the studied reaction is shown in Figure below.



Schematic representation of the bifurcation of the reaction path on the PES NO₂ + O₃ reaction system.

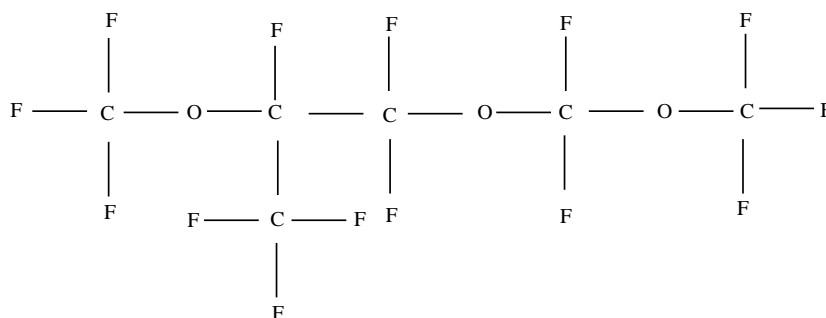
The reaction proceeds along an intermediate through a rate-limiting first transition state. This intermediate is followed by a second transition state and the intrinsic reaction coordinate (IRC) calculations from this transition state show that the reaction path follows a product channel and another transition state. Two sequential transition states are calculated and the potential energy surface bifurcation is observed through a valley-ridge inflection (VRI) point. The IRC calculations from third transition state lead to second product channel in which NO and O₂ are formed. The energy barrier calculated for the formation of NO₃ and O₂ in the first product channel is 33.96 kcal/mol and an energy barrier of 34.07 kcal/mol is calculated for the formation of NO+2O₂ product channel.

The rate constant calculated at 298 K for the two product channels is $2.31 \times 10^{-7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These results show that the formation of the two product channels is equally probable. The photodissociation wavelength of the reactive species involved in the reaction system is calculated using equation of motion coupled cluster (EOMCC) method. The calculated photodissociation wavelength shows that a significant amount of NO₂

photofragment enters into the stratosphere and potentially involves in the depletion of ozone. The photodissociation wavelength of the reactive species calculated using EOMCC method is in good agreement with the available experimental data.

Mechanism and kinetics of the atmospheric degradation of perfluoropolymethylisopropyl ether by OH radical

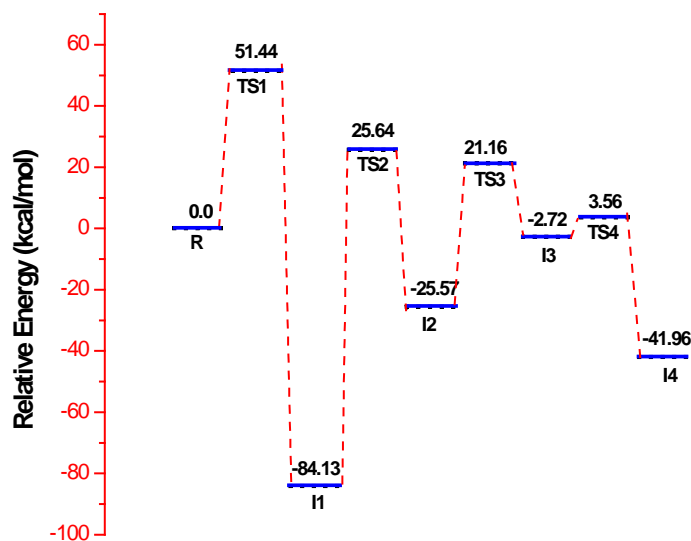
The reaction between Perfluoropolyethers and OH radical is studied in detail. Perfluoropolyethers (PFPEs) are a family of perfluorinated fluids used mainly in industrial applications. Perfluoropolyethers, along with hydrofluoroethers (HFEs), are used as replacements for CFCs. PFPEs and HFCs do not contain Cl and do not deplete the ozone layer. However, PFPEs and HFEs may be associated with other environmental risks. The reactions of PFPE with OH radicals lead to decomposition of PFPE. The structure of perfluoropolymethylisopropylether (PFPMIE), which is one of the perfluoropolyethers is shown in following Figure.



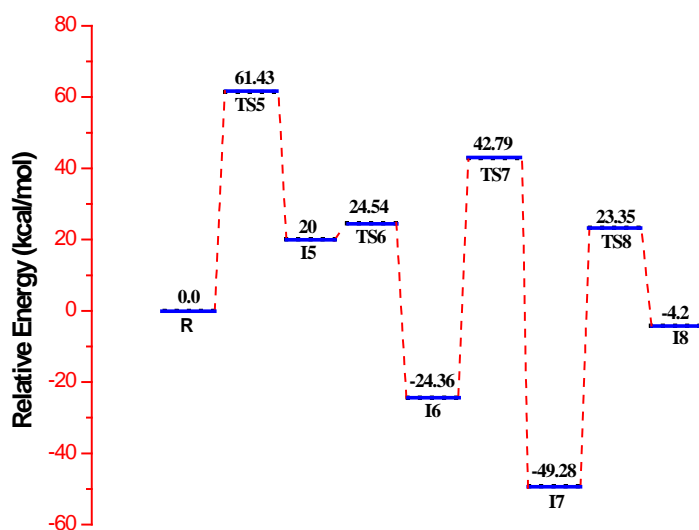
The chemical structure of PFPMIE

The geometry of the reactants, intermediates, transition states and products were optimized at DFT-M06-2X/6-31G(d,p) level of theory. The atmospheric oxidation of perfluoropolymethylisopropyl ether (PFPMIE) occurs exclusively by reaction with OH radical. The OH initiated reaction of PFPMIE takes place via an unzipping reaction mechanism which proceeds either by the breaking of C-C bonds or breaking of C-O bonds of PFPMIE by OH radical. The C-C bond breaking reaction mechanism results in the formation of two COF₂ molecules, while the C-O bond breaking reaction mechanism leads to the formation of four COF₂ molecules.

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The energy profile for the C-C bond breaking reaction of PFPMIE by OH radical



The energy profile for the C-O bond breaking reaction of PFPMIE by OH radical

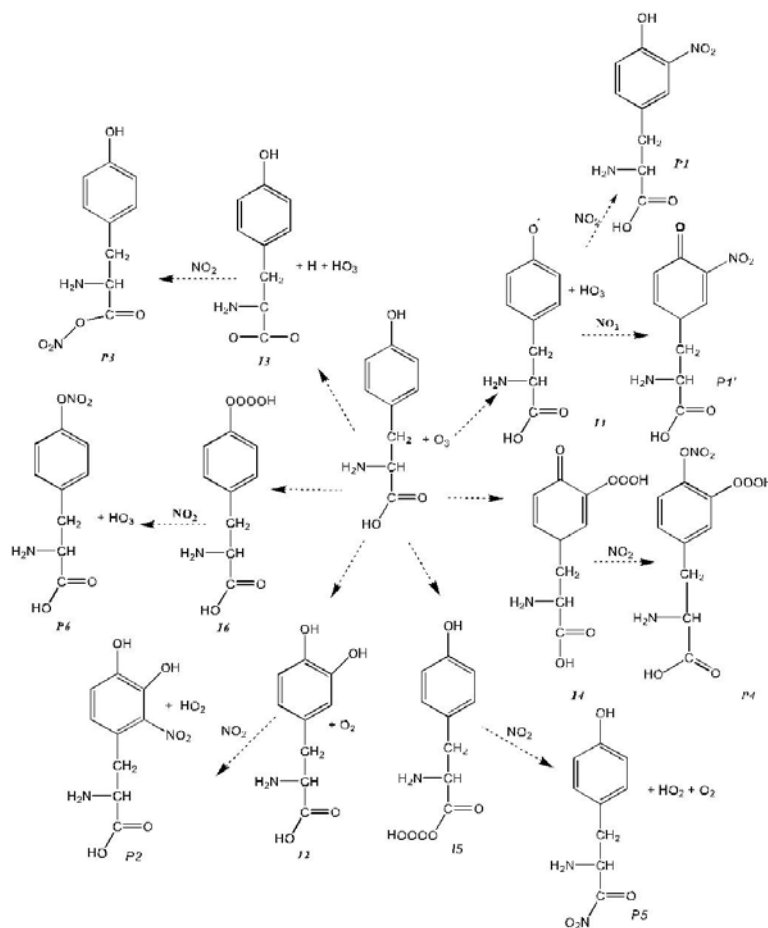
The lifetime of PFPMIE is 519 years, which show that PFPMIE degrade faster in the atmosphere. The short lifetime of PFPMIE suggest a large global warming potential. For a 20 years time horizon, the global warming potential of PFPMIE is 1.02, relative to CFC₁₁, which is in agreement with the experimental results for similar compounds. The results obtained

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from this study reveal that the reaction of PFPMIE with OH radical is the dominant degradation process for PFPMIE. Further, when compared with CFCs, PFPMIE has large global warming potential and it can be used as a better alternative.

Reaction between tyrosine and O₃ and NO₂:

The nitration of tyrosine by O₃ and NO₂ is studied using density functional theory methods M06-2X and B97-D with 6-311+G(d,p) basis set. The nitration of tyrosine is a two-step process; the first step is the oxidation of tyrosine by O₃ followed by nitration by NO₂ in the second step. We found six intermediates for the initial oxidation and subsequent nitration reactions were studied. The reaction scheme is shown in following Figure:



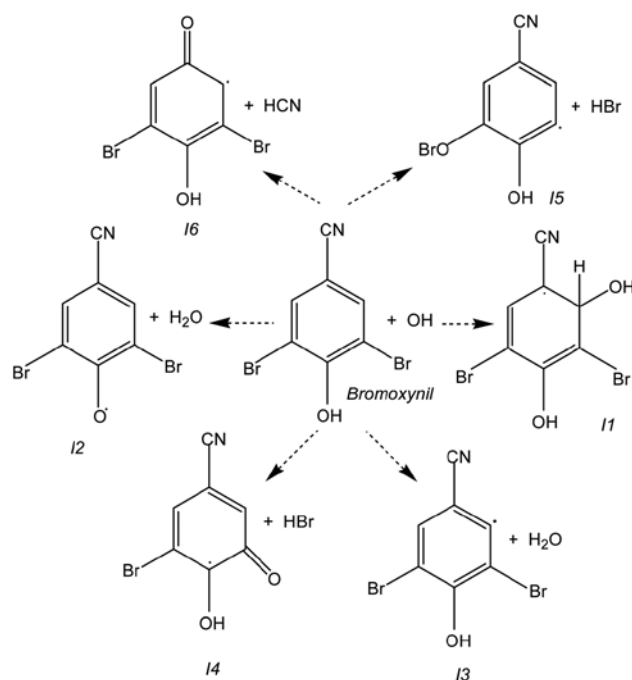
The reaction scheme for the initial oxidation and subsequent nitration reactions of tyrosine

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In order to incorporate the environmental effect on nitration, the reactions are studied in gas, water and lipid phases. The solvent effect is incorporated in the reaction using SMD model. The activation energy of the reactive species is also calculated at CCSD(T)/6-31+G(d,p)//M06-2X/6-311+G(d,p) level of theory. The reaction between tyrosine and O_3 proceeds by H-atom abstraction and addition reactions leading to the formation of six intermediates. Of all the intermediates studied, the intermediate I3 in which a tyrosine radical is formed is found to be the most favorable with a small energy barrier in all the three phases studied. The tyrosyl radical I1 observed in the earlier experimental studies is found to be the rate determining intermediate in the initial oxidation reaction in gas and lipid media. In aqueous media, the formation of the tyrosyl radical (I1) occurs with a small energy barrier of 3.88 kcal/mol. The tyrosyl radical is stabilized through self-reaction resulting in the formation of tyrosine dimer. This dimerization reaction occurs favorably in gas and aqueous media with energy barrier of 35.56 and 21.23 kcal/mol, respectively, whereas the reaction is less feasible in the lipid medium. This dimer alters the protein assembly and assists protein degradation. The subsequent nitration reaction is studied for all the intermediates in the three media. The results show that the nitration affects both the side chain as well as the aromatic ring of tyrosine. The formation of nitrotyrosine, P1, occurs more feasibly in the aqueous media, and the nitrated form of tyrosine, P3, resulting from the nitration of tyrosine radical, I3, occurs more favorably in the gas phase. The fate of the tyrosine radical, I3, is determined by its reaction with an antioxidant glutathione. The reaction regenerated the tyrosine in a barrierless reaction, along with a glutathione thiyl radical. The conversion of glutathione into glutathione biradical causes inability of the living organisms to resist stress. The tyrosine radical is formed more favorably than the tyrosyl radical and possesses significant biological implications as the tyrosyl radical. Hence, it is very important to analyze through experimental studies whether the formation of P3 product channel is a general feature observed in a wide range of inflammatory immune responses, which is responsible for oxidative stress. The results of this study clearly demonstrate that tyrosine is efficiently nitrated by O_3 and NO_2 present in polluted air. The study provides a molecular rationale for understanding the atmospheric chemistry behind the nitration process in the context of supporting the hypothesis that protein nitration by polluted air may induce the allergic diseases.

Reaction between bromoxynil and OH radical:

Bromoxynil is a selective foliage herbicide used to control weeds. The degradation of bromoxynil in the atmosphere takes place dominantly via reaction with OH radical. In this work, the OH initiated reactions of bromoxynil is studied using density functional theory methods M06-2X, B3LYP and MPW1K with 6-311++G(d,p) basis set. The relative energy of the reactive species is also calculated at CCSD(T)/6-311+G(d,p) level of theory. The OH initiated reaction of bromoxynil is found to proceed through H-atom abstraction and OH addition reactions leading to the formation of six intermediates. In bromoxynil, the phenol group donates the electrons into the ring by resonance and favors the OH radical attack at para position of bromoxynil. The OH radical addition reaction leads to the formation of 3,5-dibromo-2,4-dihydroxy benzonitrile (I1). The OH radical abstracts the H-atom from the phenol group or from the aromatic ring of bromoxynil, leading to the formation of 2,6-dibromo-4-cyanophenoxy radical (I2) or 2,6-dibromo-4-cyano-1-hydroxy benzene radical (I3). The OH radical undergoes radical termination reaction in which the Br-atom attached to the bromoxynil is abstracted by the H-atom of OH radical resulting in the formation of hydrogen bromide and the O-atom of OH radical binds with C-radical site in bromoxynil resulting in the formation of 5-bromo-4-hydroxy-3-oxocyclohexa-1,5-diene carbonitrile (I4). In one of the reactions, the O-atom of OH radical binds with the Br-atom of bromoxynil and thus 3-bromosyl-5-cyano-2-hydroxybenzene radical (I5) is formed. Also, in the radical termination reaction, the H-atom abstracts the cyano group of bromoxynil leading to the formation of hydrogen cyanide and the O-atom of OH radical binds with the C-radical site of bromoxynil, resulting in the formation of 3,5-dibromo-4-hydroxycyclohexa-2,4-dienone (I6). Thus six different intermediates are formed and each intermediate has its own impact in the environment by undergoing subsequent reactions with other atmospheric oxidants. The corresponding reaction scheme is shown in the Figure below:



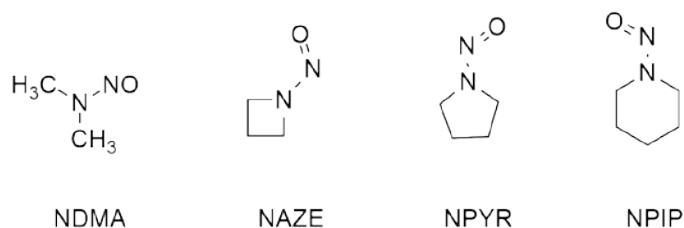
The reaction scheme for the initial reaction of bromoxynil with OH radical

The reactions subsequent to the principal oxidation steps are studied and the different reaction pathways are modeled. The radicals formed in the initial and subsequent reactions have a greater ability to undergo self-coupling reaction which yields dioxin and dioxepine products. These products are shown to be highly toxic and carcinogenic. These initially formed intermediates have sufficient energy to undergo subsequent reactions with other atmospheric oxidants. Of the six intermediates studied, the formation of 3,5-dibromo-2,4-dihydroxy benzonitrile(I1), 2,6-dibromo-4-cyanophenoxy radical (I2) and 2,6-dibromo-4-cyano-1-hydroxy benzene radical (I3) are found to be the most favorable with a small energy barrier. The initially formed radicals react with molecular oxygen resulting in the formation of peroxy, epoxy and bicyclic radicals. The peroxy radical reacts with HO₂, NO and NO₂ resulting in the formation of hydroperoxide adducts, alkoxy radical and nitroso compounds. The most favorable secondary reaction pathway from the intermediate, I1 is the formation of a seven-membered ring dihydroxy epoxide intermediate, I9. These highly soluble epoxides are responsible for the formation of organic aerosols. The intermediate, I9 further decomposes into HOBr, which is responsible for the formation of carcinogenic bromate ions in ozonized water. Tetrabromo-tetrahydrobenzo-cyclopentadioxepine- dicarbonitrile (TeBDD, P4) is formed with a small energy barrier of 11.52 kcal/mol and it is the most favourable secondary reaction pathway from intermediate, I2. The most favorable secondary

reaction pathway from intermediate, I3 is the formation of hydroperoxide adduct along with O₂ (P6). As discussed in previous sections, the initially formed radicals can undergo direct reaction with NO₂ yielding nitro brominated compounds. Also, these radicals can undergo oxidative coupling to form dibrominated compounds through a series of intermediates and transition states. The overall rate constant and the branching ratio calculated for the intermediates, I1, I2, and I3 show that the contribution of intermediate, I2 is significant in determining the environmental evolution of bromoxynil. The lifetime of bromoxynil is 14 hours, that is the reaction between bromoxynil and OH radical is the major atmospheric sink for bromoxynil. Note that the products formed from the secondary reactions are equally toxic as the parent bromoxynil, since their lifetime is expected to be more than that of parent bromoxynil. Hence, the use of bromoxynil as a herbicide should be limited.

Mechanism and Kinetics of the Reaction of Nitrosamines with OH radical:

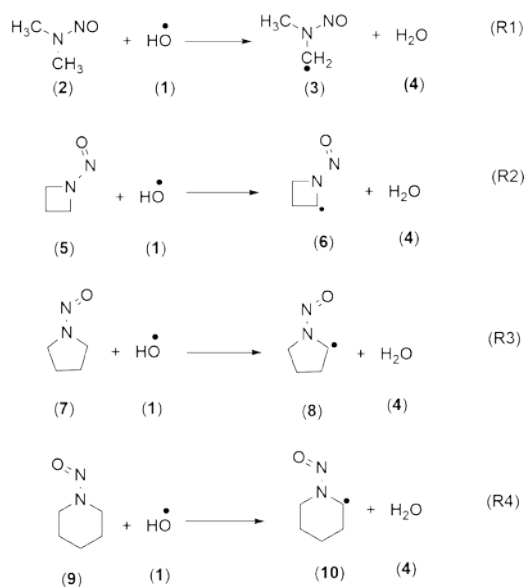
The reactions of nitrosodimethylamine (NDMA), nitrosoazetidine (NAZE), nitrosopyrrolidine (NPYR) and nitrosopiperidine (NPIP) with OH radical. The chemical structure of the studied nitrosoamines is shown in below.



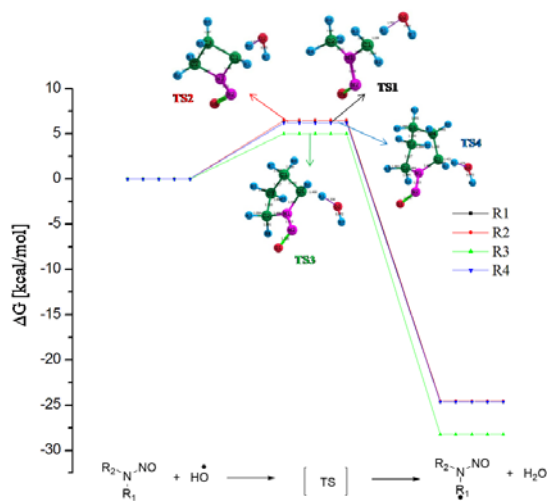
Chemical Structure of the studied nitrosamines.

The geometry optimization of the reactant, transition states, intermediates and products was performed using density functional theory methods, M06-2X, MPW1K and BHandHLYP with 6-311+G(d,p) basis set. The reaction scheme and energy profile for the initial H-abstraction reaction is shown in below:

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Reaction scheme for OH-initiated reactions of NDMA (2), NAZD (5), NPYR (7) and NPIP (9).



Free-energy profile of the OH-initiated reactions of nitrosamines

The H-atom abstraction reactions results in the formation of alkyl radicals. The Gibbs free energy barrier for initial H-atom abstraction reaction is around 6 kcal/mol and the reaction is exothermic with enthalpy of -24.62 kcal/mol. The subsequent reactions are studied for initially formed alkyl radical intermediate with O₂, HO₂ and NO radical which leads to the formation nitroso-hydroperoxide, methyl-nitrosoformamide and Nitroso-azetidin-2-one,

1-nitroso-pyrrolidin-2-one and 1-nitroso-piperidin-2-one. The calculated activation energy and reaction energy of various oxidation channels for NDMA, NAZE, NPYR and NPIP show that the increase in the number of methyl groups does not necessarily affect the reaction barrier or reaction energy. The rate constant calculated for the initial H-abstraction reaction at 298 K is (k_3) 2.89×10^{-12} , 2.5×10^{-12} , 2.34×10^{-12} $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$, $2.98 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ for NDMA, NAZE, NPYR and NPIP. The calculated rate constant increases with increasing in temperature and shows a linear Arrhenius behavior. The lifetime of NDMA, NAZE, NPYR and NPIP is around 4 to 6 days. The calculated reaction enthalpy, rate constant and lifetime for initial H-atom abstraction reaction of nitrosamines is in good agreement with the available literature data.

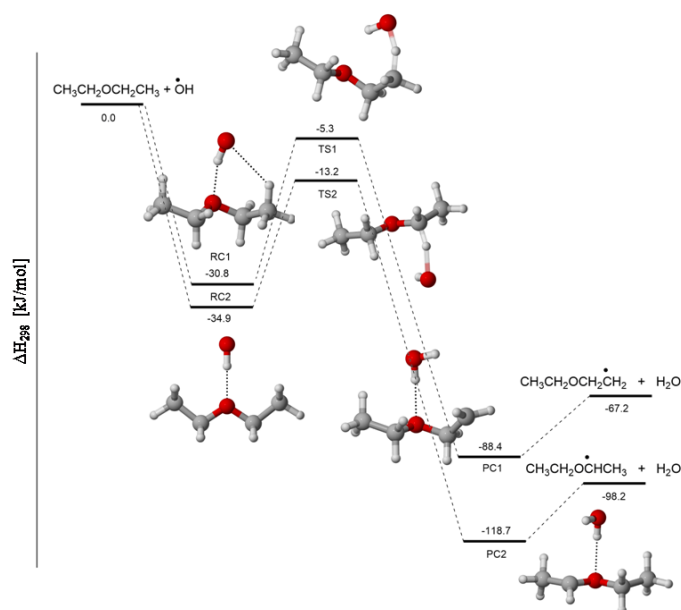
Atmospheric oxidation mechanism of OH-initiated reactions of diethyl ether

The oxidation of diethyl ether (DEE) by hydroxyl radical is studied by means of density functional theory and coupled cluster methods. The geometries of the stationary points involved in the oxidation of DEE by OH radical are optimized using M06-2X method with 6-311++G(d,p) basis set. The single point energy calculations were performed using M06-2X/aug-cc-pVTZ, UCCSD(T)/6-311++G(d,p) and UCCSD(T)/aug-cc-pVDZ levels with the geometries optimized at M06-2X/6-311++G(d,p) level. The thermochemistry of the reactions are calculated using highly accurate CBS-QB3 method. Further, the kinetics of the reactions are studied using canonical variational transition state (CVT) theory with small curvature tunnelling (SCT) corrections from the potential energy surface (PES) calculated at M06-2X/6-311++G(d,p) level of theory. The OH-initiated reactions were found to proceed by H-atom abstraction from $-\text{CH}_3$ or $-\text{CH}_2$ groups of DEE, in which the latter reaction is found to be more favourable than the former. The secondary reactions associated with peroxy radical and the following alkoxy radical chemistry of DEE is explored in detail. The 1-ethoxy ethoxy radical resulting from the peroxy radical chemistry of DEE undergoes $-\text{CH}_3$ as well as H-atom elimination reactions leading to the formation of ethyl formate and ethyl acetate in the respective reactions, where both the reactions are kinetically competitive. The next significant reaction in the 1-ethoxy ethoxy radical decomposition is its reaction with O_2 , where ethyl acetate and HO_2 are formed. The decomposition of 1-ethoxy ethoxy radical via C-O bond cleavage is less feasible when compared to the above reactions.

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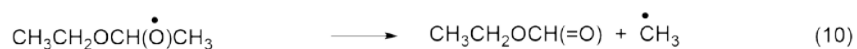
The initial H-atom abstraction and secondary propagation with O₂ resulting from the –CH₂ H-atom abstraction reactions are energetically more favourable than the corresponding –CH₃ H-atom abstraction reactions. The energy profile for the initial H-abstraction reaction of DEE by OH radical is shown in Figure.



The energy profile of the OH-initiated reactions of DEE.

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The isomerisation of the peroxy radical is thermodynamically as well as kinetically not favourable. The 1-ethoxy ethoxy radical formed in the peroxy radical oxidation and subsequent reaction with NO reacts with O₂ resulting in ethyl formate and this reaction is competitive with the unimolecular dissociation of 1-ethoxy ethoxy radical by –CH₃ group and H-atom elimination, resulting in ethyl formate and ethyl acetate as products, respectively. The dissociation of 1-ethoxy ethoxy radical via C-O bond cleavage is not as competitive as the above reactions. The reactions of 1-ethoxy ethoxy radical with nitrates resulting in ethyl acetate along with HNO and HONO products are the thermodynamically driven reactions with a larger exothermicity, but these reactions are not kinetically favourable. The calculated reaction rate constants for the plausible alkoxy radical chemistry of DEE show that the unimolecular dissociation of 1-ethoxy ethoxy radicals (reactions 10 and 11) are kinetically more favourable than the reaction of 1-ethoxy ethoxy radical with O₂. Further, both the –CH₃ and H-atom elimination reactions are equally competitive, where the latter is about 10⁴ times more rapid than the former. The plausibility of the alkoxy radical chemistry of DEE arranged in terms of kinetic favourability is as shown below:



The results show that the ethyl formate is the major oxidation product in the oxidation chemistry of DEE, followed by ethyl acetate formation in comparably less quantities to ethyl formate, but its contribution is significant as reflected from the rate constants. Our computed results are in excellent agreement with the experimental study on oxidation of DEE by Cl. From this work, we conclude that the major oxidation products resulting from the DEE oxidation by OH radicals are ethyl formate and ethyl acetate, which have more possibility to involve in photooxidation in the troposphere. The co-products such as methyl radical and H-radical have the greater chance to initiate photooxidation process.

LIST OF PUBLICATIONS OUT OF THE PROJECT

1. Mechanism and Kinetics of the Atmospheric Oxidative Degradation of Dimethylphenol isomers initiated by OH radical - published in **Journal of Physical Chemistry A (J. Phys. Chem. A 2013, 117, 4611–4626)**.
2. Depletion of atmospheric ozone by nitrogen dioxide – A bifurcated reaction pathway - in **Theoretical Chemistry Accounts (Theor. Chem. Acc 2013, 132, 382)**
3. Reaction mechanism and kinetics of the degradation of bromoxynil initiated by OH radical - in **RSC Advances (RSC Adv., 2014, 4, 7749-7759)**.
4. Oxidation and Nitration of Tyrosine by Ozone and Nitrogen Dioxide: Reaction mechanisms and Biological and Atmospheric Implications - in **Journal of Physical Chemistry B (J. Phys. Chem. B 2014, 118, 3479-3490)**
5. Theoretical Studies on the mechanism and kinetics of the degradation of perfluoropolymethylisopropyl ether by OH radical - in **Structural Chemistry (Struct. Chem. 25 (2014) 1773)**.
6. Atmospheric oxidation mechanism of OH-initiated reactions of diethyl ether –The fate of 1-ethoxy ethoxy radical is submitted to **Journal of Physical Chemistry A**.
7. Mechanism and kinetics of the reaction of Nitrosamines with OH radical- A Theoretical Study is submitted to **Journal of Physical Chemistry A**.