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Development of chemical reaction kinetics of VOC ozonation

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Abstract

Volatile Organic Compounds (VOCs) causes many health issues related to Indoor Air Quality (IAQ). The indoor air quality improvement has been instituted by various organizations based on the concentration level of different pollutants. Though VOCs in indoor air has various adverse health effects and are primary reason for sick building syndrome, there are only few abatement technologies currently available. Ozonation of VOCs is one of the techniques to improve indoor air quality. In this paper, a compact yet comprehensive reaction kinetics of VOC ozonation have been developed for understanding the underlying chemistry behind the process. The new mechanism was developed by combining detailed reaction kinetics of Toluene, Benzene, Isobutylene and Formaldehyde oxidation reactions containing 329 species and 1888 reversible reactions and detailed Ozone decomposition reaction mechanism containing 6 species and 17 reversible reactions. Then the detailed mechanism has been reduced using DRGEPSSA (Directed relation graph with error propagation and sensitivity analysis) and unimportant reaction elimination technique to 36 species and 123 reversible reactions for practical use in Computational Fluid Dynamics (CFD) simulations. The reduction was done for low temperature conditions. Then the sensitivity analysis was done to identify the most sensitive reactions. It was found that Isobutylene, Toluene and Formaldehyde readily react with nascent oxygen and undergoes oxidation reaction to give intermediate small species. Then its applicability was tested in Ansys Fluent CFD package and found it could be used to predict the VOCs ozonation and its intermediate reactions.

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1. Introduction

Volatile organic compounds (VOCs) cause many health issues related to indoor air quality (IAQ) [1–3] and improvement of IAQ has been instituted by local, state and federal agencies around the globe based on the concentration of different indicator pollutants [4–6]. Treatment of indoor air not only helps improve the living

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standards of people but also is a benefit in terms of energy savings by reducing the amount of outdoor air intake [7,8]. Though VOCs in indoor air may exhibit a variety of adverse health effects and are often the primary reason for so-called sick building syndrome, there are only few abatement technologies currently available. VOC abatement technologies can be broadly classified as a) Destruction of VOCs which includes techniques like oxidation and bio-filtration, and b) Recovery of VOCs which includes processes such as absorption, adsorption, condensation and membrane separations [9]. Each of the methods has its own advantages and limitations. Thermal oxidation is the most commonly used method; however, it suffers from producing potentially harmful combustion products which require further treatment. Methods based on adsorption to a substrate (e.g., activated carbon) tend to require high capital and operating costs to separate the VOCs from adsorbent material. Absorption techniques require a knowledge database regarding vapor-liquid equilibria of different VOCs in order to design thermodynamically efficient equipment for processing. Though condensation processes are quite simple in concept, they also can involve high operating costs due to the elevated boiling points of some VOCs. Bio-filtration techniques are attractive from an energetic standpoint, but may suffer from selective VOC destruction, i.e., they typically require selective microorganisms to degrade specific VOCs. Moreover, bio-filtration systems may lose efficiency during periods of nutrient starvation when they are not exposed to VOCs [10].

One of the prominent techniques in abatement of VOCs is by gas-phase ozonation reactions [11, 12]. Ozone is a strong oxidizing agent and capable of reacting with numerous gas and aqueous-phase organics, including a wide spectrum of VOCs. Ozone, by itself (or in combination with porous and/or catalytic adsorbents) has been extensively employed for the destructive decomposition of naturally-occurring and anthropogenic pollutants in air and water [4, 13–15]. Whereas studies have demonstrated that ozone is able to transform a wide variety of gas and aqueous phase volatile organic compounds (VOCs), most investigations were experimental [16, 17] and no computational effort were observed in the literature. As a first step to increase attention to computational studies to save time and cost, a proper chemical reaction mechanism of VOC ozonation should be made available. This work aims at providing a very compact yet comprehensive chemical reaction mechanism involving ozonation of Benzene, Toluene, Isobutylene and Formaldehyde for practical use in commercial computational Fluid Dynamics (CFD) software.

2. Methodology

The new compact VOC ozonation reaction mechanism was developed from detailed Toluene, Benzene, Isobutylene and Formaldehyde oxidation reactions containing 329 species and 1888 reversible reactions [18] and detailed Ozone decomposition reaction mechanism containing 6 species and 17 reversible reactions [19] in CHEMKIN format. Many mechanism reduction methods have been successfully developed and demonstrated in the literature. Manual removal approach such as peak concentration analysis [20], systematic reduction models such as Directed Relations Graph (DRG) [21–24], Directed Relation Graph with Error Propagation (DRGEP) [25], Directed Relation Graph Aided Sensitivity Analysis (DRGASA) [24] and Directed Relation Graph with Error Propagation and Sensitivity Analysis (DRGEP-SA) [26] are often used to identify and eliminate unimportant species. An isomer lumping approach [24] was also developed to group isomers with the same molecular weight and similar thermal and transport properties, and being represented by a common species. Unimportant reaction elimination is often carried out using reaction flux analysis [20] or computational singular perturbation (CSP) [24]. In the present study, the reduction was done using DRGEP-SA technique and unimportant reaction elimination using CSP technique. The reduction process is shown in Figure 1. Initially, the detailed chemical reaction mechanism in CHEMKIN format is given as input to the DRGEP-SA program along with initial conditions of pressure and temperature and error tolerance. DRGEP first produces a preliminary skeletal mechanism. The species in the preliminary skeletal mechanism are classified into two categories: 1) Limbo species that are analysed and 2) Retained species that are retained without any analysis. Then the sensitivity analysis is performed by removing each species in the limbo category one at a time and calculating the induced error. Species are arranged in order based on the differences between induced errors and the error of the DRGEP skeletal mechanism. The final skeletal mechanism is generated by removing species one at a time in order until the resulting error reaches the required tolerance level.

3. Results and Discussion

The detailed chemical reaction mechanism is not convenient to use with any commercially available CFD packages, the skeletal mechanism was developed using DRGEP/SA chemical reaction reduction technique. The species in the final skeletal mechanism is provided in Table 1.

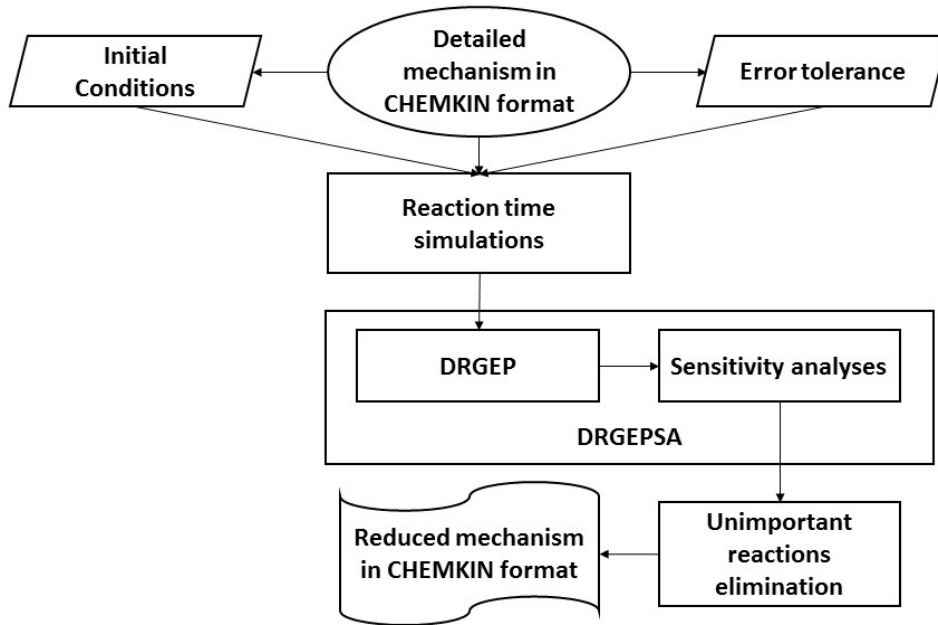


Fig. 1. Steps involved in chemical reaction mechanism reduction.

Table 1. An example of a table.

List of species					
O3	C6H5	HOC6H4CH3	O2	CO	HCCO
O2SI	C6H5OO	OC6H4CH3	OH	CO2	CH3COCH3
OSI	BZCOOH	C6H5CHOH	H2O	CH2O	IC3H7
C6H5CH3	C6H5CHO	H	N2	HCO	C3H5-A
C6H5CH2	C6H5CO	H2	HO2	CH3	C3H3
C6H6	C6H5O	O	H2O2	CH2O	IC4H8

3.1. Validation

The validation of the final skeletal mechanism was done by comparing the reaction time calculated from both detailed reaction mechanism and final skeletal mechanism. The reaction time were calculated for different temperature ranges (295-325K), typical room temperature conditions. The reaction time between the detailed reaction mechanism, intermediate reaction mechanism after DRGEP and final skeletal reaction mechanism were compared in Figure 2. The intermediate reaction mechanism obtained after DRGEP reduction contained 46 species

and 205 reactions which is still big for CFD simulations. Therefore, the mechanism was further reduced by eliminating unimportant species and reactions. It was found that the error between the reaction time calculated from detailed reaction mechanism and final skeletal reaction mechanism is around 7% maximum over the calculated temperature range.

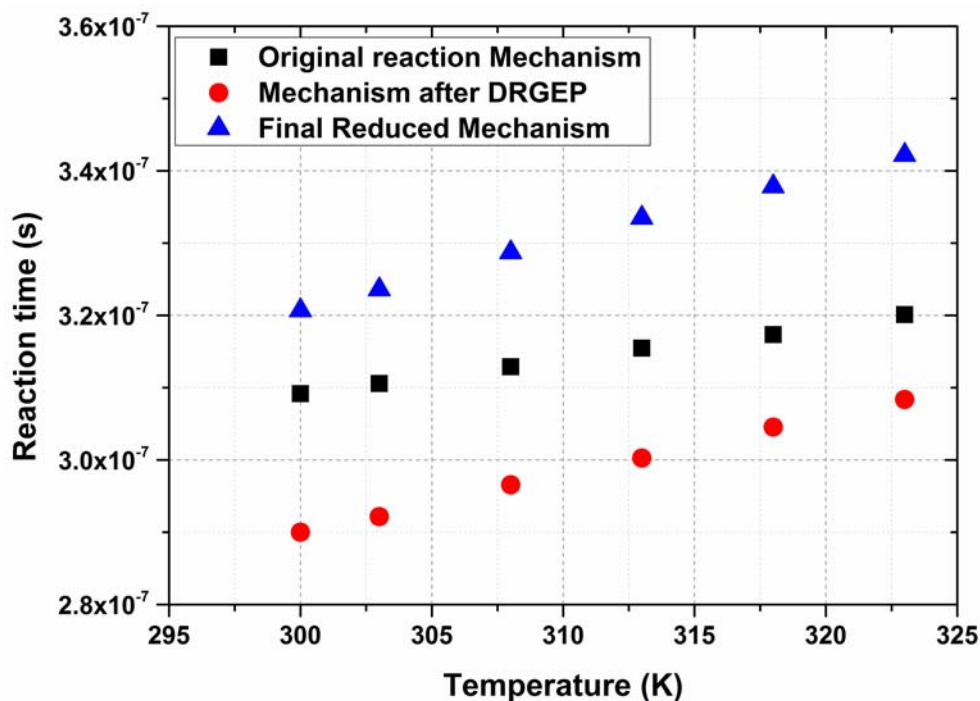


Fig. 2. Comparison of reaction time between detailed reaction mechanism, mechanism obtained after DRGEP and final skeletal reaction mechanism.

3.2. Sensitivity Analysis

A sensitivity analysis was done to identify the most important reactions. The most important chemical reactions are shown in Figure 3. From Figure 3, it can be found that the HCO oxidation is the most likely reaction to take place, followed by oxidation of Isobutylene with nascent Oxygen. Following Isobutylene, Formaldehyde and Toluene also readily reacts with the nascent Oxygen to form intermediate compounds. It should also be noted that the intermediate compounds like IC₃H₇, C₆H₅CH₂ and HCO also further undergoes oxidation with nascent Oxygen to form smaller and less detrimental compounds. Interestingly, it was found from the sensitivity analysis, the Benzene does not undergo any oxidation with Ozone. However, through our other study using molecular dynamics simulation to understand Benzene and Ozone reaction we found that about 96.2% of the 1198 bimolecular collisions analysed resulted in single or double hydrogen abstraction from the benzene ring (Figure 4). A significant proportion of hydrogen abstractions were coupled with oxygen additions (56.3%) and oxygen substitutions (11.5%). Approximately 15.5% of collisions resulted in open-ring (i.e., linear chain) products. It was also found that no Formaldehyde or Formaldehyde-like precursor compounds were formed. Therefore, further investigations are required to understand the phenomenon why Benzene and Ozone reaction is not identified as a significant reaction.

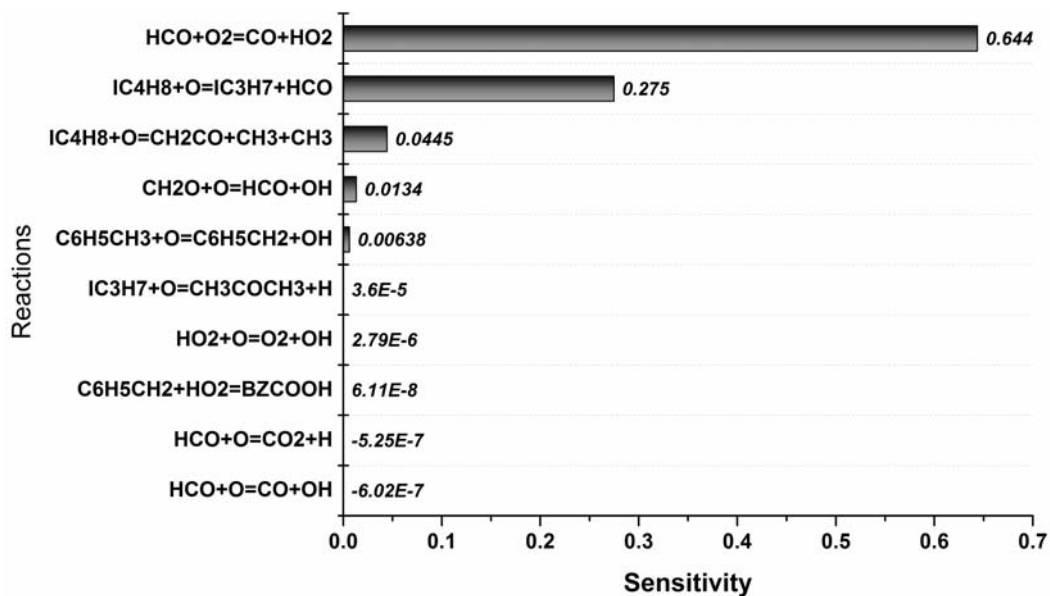


Fig. 3. Most important reactions identified through sensitivity analysis.

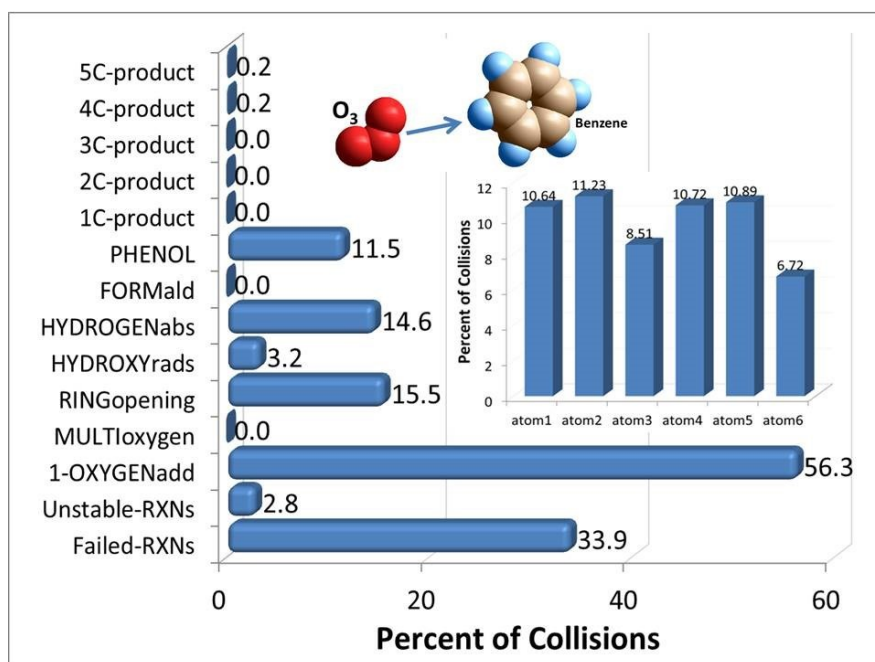


Fig. 4. Product distributions and atom centre locations of electrophilic (oxygen radical) attack on the benzene ring in the SFMD simulation of the reaction of ozone with benzene. A total of 1198 collisions were analysed. Note the low probability of ring fragmentation. No strong preference was observed for localization of electrophilic addition/substitutions (inset graph), which is consistent with benzene isotropic symmetry.

3.3. Application in CFD

The newly developed skeletal reaction mechanism was tested for its applicability in Ansys Fluent CFD package. A 2D simulation was performed to check the developed reaction mechanism. A fine structured mesh of size 100*100 of a chamber of size 1m*1m was created in Gambit as shown in Figure 5a. The simulation was considered to be quasisteady state simulation. For the simulations, the air inside the chamber was assumed to be premixed with Benzene, Toluene, and Formaldehyde of 50ppm each. Then through an opening at 200mm from bottom ozone is injected along with air at 1liter/min. The Ozone concentration in air was maintained at 75ppb which is slightly higher than the specified limit of 50ppb by National Environmental Agency (NEA), Singapore. It was found that the Ozone reacts with VOCs and forms CO and CO₂ as shown in Figure 5b-g. The initial concentration of CO was set to zero, and after simulation it was found that a significant amount of CO was formed which can occur only when there is oxidation of VOCs with Ozone. This result shows that the developed reaction mechanism is good at predicting the VOC ozonation reactions. Interestingly it was also found that the temperature inside the chamber is slightly reduced as shown in blue colour in the temperature contour in Figure 5h. This shows that the VOC ozonation reaction is endothermic in nature. This may be the result of energy absorbed from the surroundings by the Ozone to decompose to Oxygen and nascent Oxygen.

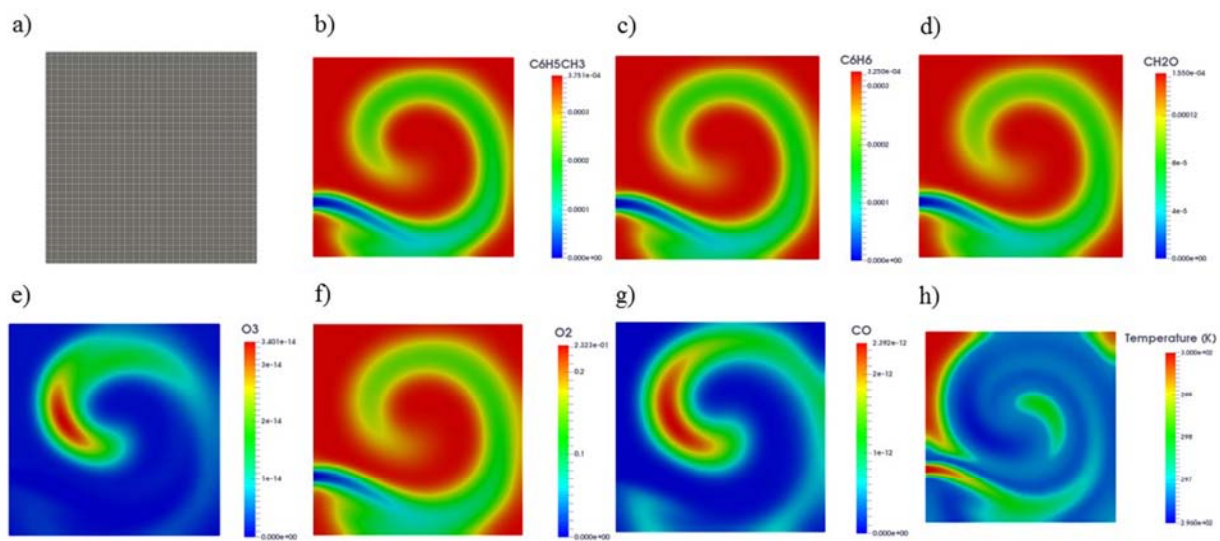


Fig. 5. CFD simulation results a) mesh used for simulation, b) Toluene concentration contour, c) Benzene concentration contour, d) Formaldehyde concentration contour, e) Ozone concentration contour, f) Oxygen concentration contour, g) CO concentration contour and h) temperature contour.

4. Conclusions

In this study, a new skeletal reaction mechanism for VOCs ozonation reaction was developed. Four major VOCs, namely, Benzene, Toluene, Isobutylene, and Formaldehyde were considered in the reaction mechanism. The skeletal reaction mechanism was validated with the detailed reaction mechanism in terms of reaction time calculated from both mechanisms. Then a sensitivity analysis was performed to identify the most important reactions when VOCs were treated with Ozone. It was found that the reactions with nascent Oxygen is more pertinent in nature. Then finally, the developed skeletal mechanism was tested for its suitability in commercial CFD package and found it can be very well used to predict the VOC ozonation reactions.

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