

The Removal of Volatile Organic Compounds by $\cdot\text{OH}$ Radicals: Application for Benzene

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Abstract: Volatile Organic Compounds such as C_6H_6 play a crucial role in the atmosphere. In combustion processes, the reactions of hydroxyl radicals with C_6H_6 are important in the overall fuel oxidation system. In the current study, mechanism and rate constants of $\cdot\text{OH}$ radicals with benzene ($\text{C}_6\text{H}_6 + \cdot\text{OH} \rightarrow \cdot\text{C}_6\text{H}_5 + \text{H}_2\text{O}$ and $\text{C}_6\text{H}_6 + \cdot\text{OH} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{H}$) were calculated using the CCSD(T)//B3LYP/M06-2X methods and the TST/RRKM/ME models. Calculated results reveal that $\cdot\text{C}_6\text{H}_5 + \text{H}_2\text{O}$ is the main product of the reaction between benzene and $\cdot\text{OH}$ radicals. Also, rate constants are in good agreement with the experimental data in the moderate and high temperature range (908 – 1136 K).

Keywords: Benzene; Phenol; DFT; hydroxyl radicals; RRKM/ME

1. INTRODUCTION

Volatile Organic Compounds (VOCs) are a broad class of organic chemicals defined by their high vapor pressure at ordinary room temperature, leading to significant volatilization and presence in the atmosphere. These compounds include a diverse range of chemicals, such as hydrocarbons, halocarbons, oxygenates, and others, that are both anthropogenic and biogenic in origin. The study of VOCs is critical in multiple disciplines including atmospheric science, environmental chemistry, and public health due to their significant role in environmental pollution and human health risks.¹⁻³

VOCs are emitted from numerous sources. Anthropogenic sources include industrial activities, vehicle exhaust, fuel combustion, and the use of solvents and paints. Industrial emissions can release substantial quantities of VOCs during processes such as petroleum refining, chemical manufacturing, and waste treatment. Additionally, everyday products like adhesives, cleaning agents, and personal care products contribute to indoor VOC concentrations. Biogenic sources, primarily vegetation, also emit VOCs; isoprene and monoterpenes are among the most common biogenic VOCs. These natural emissions are influenced by factors such as temperature, light, and plant species.⁴⁻⁶

The environmental impact of VOCs is profound, particularly in their role in atmospheric chemistry. VOCs react with nitrogen oxides (NO_x) in the presence of sunlight to form ground-level ozone, a primary constituent of photochemical smog. This process not only affects air quality but also has implications for climate change, as some VOCs can act as greenhouse gases or participate in the formation of secondary organic aerosols, which influence cloud formation and radiative forcing. The presence of VOCs in the atmosphere can lead to respiratory problems, cardiovascular diseases, and other health issues upon prolonged exposure, emphasizing the importance of understanding and controlling VOC emissions.⁷

Monitoring and regulating VOCs present significant challenges due to their diverse sources and complex behavior in the atmosphere. Advanced analytical techniques such as

gas chromatography-mass spectrometry (GC-MS) and proton-transfer-reaction mass spectrometry (PTR-MS) are commonly used to detect and quantify VOCs in both outdoor and indoor environments. Regulatory frameworks, such as those established by the Environmental Protection Agency (EPA) in the United States and the European Union's directives, set limits on VOC emissions and guide industries in implementing control measures.⁸⁻¹⁰

Research continues to advance our understanding of VOCs, focusing on their sources, atmospheric reactions, transport mechanisms, and health impacts. Efforts to mitigate the negative effects of VOCs include developing cleaner technologies, improving emission control systems, and formulating policies aimed at reducing VOC levels in the environment. Furthermore, public awareness and behavioral changes, such as reducing the use of high-VOC products and enhancing ventilation in indoor spaces, play a vital role in minimizing VOC exposure.¹¹⁻¹³

In conclusion, Volatile Organic Compounds represent a critical area of study due to their widespread presence and significant impacts on air quality, climate, and human health. Continued research and regulatory efforts are essential to manage and mitigate the adverse effects associated with VOCs, ensuring a healthier and more sustainable environment. Understanding the complex dynamics of VOCs in the atmosphere remains a priority for scientists and policymakers aiming to address the challenges posed by these pervasive environmental pollutants. In this study, therefore, we focus on studying and reviewing the removal of benzene in the presence of $\cdot\text{OH}$ radicals. Therefore, mechanism and kinetics of the $\text{C}_6\text{H}_6 + \text{OH}$ reaction will be examined carefully and compared with numerous previous experimental and computational investigations.¹⁴⁻¹⁸

2. COMPUTATIONAL METHODS

In this study, the density functional theory (DFT) including B3LYP¹⁹ and M06-2X²⁰ in conjunction with the Pople and Dunning basis sets denoted as 6-311++G(3df,2p)²¹ and aug-cc-pVTZ,²² respectively, were used to optimize geometric structures for all species of the reaction of benzene with $\cdot\text{OH}$

radicals. Based on the DFT optimizations, various parameters such as vibrational frequencies, moments of inertia, and zero-point vibrational energies (ZPVE) were obtained. Frequencies of all intermediate states are positive, contrary to transition states with one imaginary frequency for each TS among the frequencies of its. Each transition state was checked for the right connections with the surrounding stationary points by using the intrinsic reaction coordinate (IRC) model.²³ All the species optimized at the DFT levels were then used to calculate single-point energies at the CCSD(T) high-cost level of theory.²⁴ All the processes were computed by using the software package Gaussian with version 16.²⁵

Rate constants of the C₆H₆ reaction with [•]OH radicals have been predicted using the models of transition state theory (TST)²⁶ and RRKM²⁷ based the master equation (RRKM/ME). The Eckart tunneling correction has also been accounted for the reaction channels involving in H-shift. The predictions of rate constants have been implemented by Chemrate²⁸ (for TST) and Mesmer²⁹ (for RRKM/ME).

3. RESULTS AND DISCUSSION

The reaction between benzene and [•]OH radicals can take place in two directions so-called H-abstraction and OH-addition, in which the first direction can form a direct bimolecular product denoted as PR1 (product 1), while the second one can form an adduct (IS1) at the initial step before giving to an indirect bimolecular product PR2 (product 2) as can be seen in Figure 1. These predictions agree well with several previous studies.

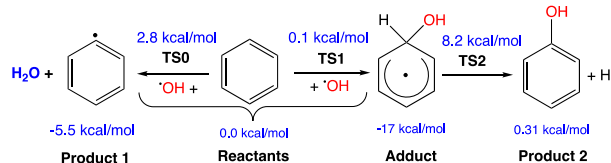


Figure 1. Diagram of the reaction between C₆H₆ and [•]OH

As shown in Figure 1, the H-abstraction channel proceeds via the TS0 transition state with barrier height of 2.8 kcal/mol, while the OH-addition channel occurs via the two transition states with barrier heights of 0.1 and 8.2 kcal/mol, respectively. Thus, it can be said that the H-abstraction process is dominant compared to the OH-addition process and these two directions can occur quickly at room temperature because the energy barriers of them are very small. It is worth noting that a pre-reaction complex occurs at the initial step of the second direction with an energy of 2.6 kcal/mol below the reactants. However, it can be ignored when calculating rate constants of the title reaction because its potential well is very shallow. The calculated energies in this work are in good agreement with those computed by Seta and co-workers.¹⁴ Geometric structures of the three transition states TS0, TS1, and TS2 shown in Figure 2 indicate that [•]OH radical attacks hydrogen atom of the benzene ring at the distance of 1.302 Å, which makes one of the C – H bonds of benzene stretched to 1.203 Å. In contrast, the attack of [•]OH radical to one of the carbon atoms of benzene (TS1) leads to the OH-addition TS with the C – OH distance of 2.011 Å and the H-abstraction bond of TS2 is recorded to be 1.205 Å.

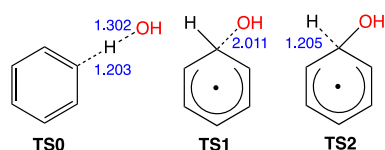


Figure 2. Geometric structures of the transition states of the reaction between C₆H₆ and [•]OH radicals.

Imaginary frequencies recorded at the structures of TS0 and TS2 are 1446i and 993i cm⁻¹, respectively, which show that the first TS vibrates stronger than the second one. However, the activation energy of TS0 is fairly lower than that of the TS2. This can be explained that the OH group pushes electrons into the benzene ring thanks to the p-π conjugation effect (electrons on the p subshell of the O atom and the π bond of the benzene ring) making the C - H bond stronger, consequently the H-abstraction of the adduct consumes more energy than that of benzene.

The product of the H-abstraction direction includes C₆H₅ and H₂O with the energy value of 5.5 kcal/mol under the reactants, while the final product of the OH-addition direction is phenol and hydrogen atom. Compared to the former direction, the latter direction is the endothermic process with 0.31 kcal/mol endothermicity.

In order to check the accuracy of our single-reference results, we performed a T1 diagnostic analysis to determine the level of multireference character in the wave function. The results for the reactants, products, and transition states involved in the reaction under study are presented in Table 1. The calculated T1 diagnostics reveal that all species show minimal multireference character, with values for singlet and doublet states below 0.015 and 0.035, respectively (noting that the threshold for T1 diagnostics is 0.02 for closed-shell species and about 0.045 for open-shell species). This indicates that single-reference methods are appropriate for our investigation. Furthermore, Table 1 shows that the spin contamination values for singlet state species are zero, while those for doublet state species are approximately 0.75, suggesting that spin contamination has a negligible impact on the calculated activation barriers and the structures of all species.

Table 1. The spin contamination $\langle S^2 \rangle$ and the T1 diagnostics at the levels of M06-2X/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ, respectively.

Species	$\langle S^2 \rangle$	T1 diagnostics
benzene (singlet)	0.0	0.014
phenol (singlet)	0.0	0.017
[•] OH (doublet)	0.75	0.023
TS0 (doublet)	0.75	0.033
TS1 (doublet)	0.76	0.031
TS2 (doublet)	0.76	0.034
Adduct (doublet)	0.75	0.032
[•] C ₆ H ₅ (doublet)	0.77	0.035
H ₂ O (singlet)	0.0	0.012

Thermochemical Properties. To verify the accuracy of the calculations, the computed thermodynamic property ($\Delta_f H_{298}^{\circ}$ K) for all species involved in the discussed reaction is presented in Table 2 and compared with literature values. As shown in the table, the calculated values align closely with the available literature data, with deviations within an acceptable range; for instance, the difference between our results and the Active Thermochemical Tables (ATcT) data is less than 1.0 kcal/mol. The strong agreement of this data with ATcT in the calculated thermodynamic parameters suggests that the methods including DFT/B3LYP/M06-2X and CCSD(T) in conjunction with basis set 6-311++G(3df,2p) and aug-cc-pVTZ employed in the current study are robust and reliable, in which the CCSD(T)/aug-cc-pVTZ will be used for kinetic calculation.

Table 2. Comparison of Enthalpy changes (in kcal/mol) of all species in this study with data derived from ATcT.³⁰

Species	$\Delta H_{298\text{ K}}$ (this work)	$\Delta H_{298\text{ K}}$ (ATcT)
Benzene	19.32	19.89 ± 0.26
Phenol	21.95	22.3 ± 0.63
C_6H_5	83.56	80.96 ± 0.63
H_2O	-57.35	-57.8 ± 0.026
OH	8.23	8.96 ± 0.026

4. KINETIC CALCULATIONS

Rate constants for the $\text{C}_6\text{H}_6 + \text{OH}$ reaction have been predicted based on the PES which energies were refined at the CCSD(T)/aug-cc-pVTZ + ZPE level of theory. Because there are no intermediate state on the H-abstraction channel, rate constants of this channel have been calculated using the CHEMRATE code based on the TST model. In contrast, the RRKM/ME model has been utilized to calculate rate constants for the OH-addition channel. The calculated results are tabulated and plotted in Table 3 and in Figure 3, respectively.

Table 3. Rate coefficients ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of the reaction paths of benzene with OH radicals in the 300 – 2000 K range, where k_1 and k_2 are rate constant of the H-abstraction and OH-addition channels, respectively.

T	k_1	k_2	T	k_1	k_2
300	5.02.E-14	2.08.E-18	1200	5.21.E-12	2.13.E-13
400	1.48.E-13	5.53.E-17	1300	6.61.E-12	3.31.E-13
500	3.23.E-13	4.66.E-16	1400	8.23.E-12	4.92.E-13
600	5.96.E-13	2.15.E-15	1500	1.01.E-11	7.03.E-13
700	9.85.E-13	6.93.E-15	1600	1.22.E-11	9.75.E-13
800	1.50.E-12	1.77.E-14	1700	1.45.E-11	1.32.E-12
900	2.17.E-12	3.83.E-14	1800	1.71.E-11	1.74.E-12
1000	3.00.E-12	7.37.E-14	1900	2.00.E-11	2.25.E-12
1100	4.01.E-12	1.30.E-13	2000	2.32.E-11	2.86.E-12

It can be seen from Table 3 and Figure 3 that both the rate constants, k_1 and k_2 increase with rising temperatures, in which the k_1 value is larger than the k_2 value in the whole temperature range of 300 – 2000 K. For example, at 300 K, k_1 is about 4 orders of magnitude bigger than k_2 ; however, at 2000 K, the difference between them is only approximately one order of magnitude. This is suitable because the energy barrier of the H-abstraction channel is much lower than that of the OH-addition channel as shown in Figure 1. The total rate constants of k_1 and k_2 are nearly equal to k_1 and these values agree well with the experimental data measured by Seta et al. in the moderate and high temperature range of 908 – 1136 K (see Figure 3).

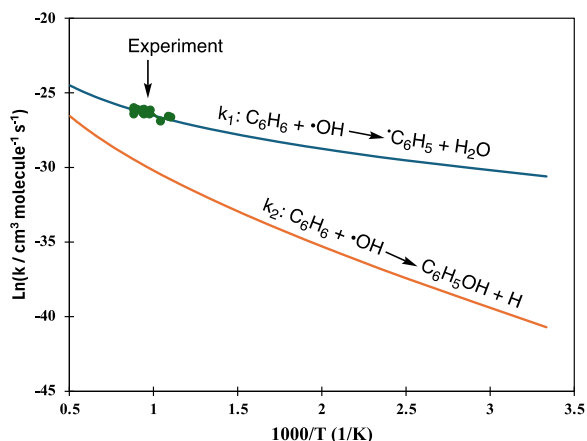


Figure 3. Rate constants of the reaction between benzene and OH radicals in the 300 – 2000 K temperature region.

It should be noted that the reaction of benzene with the OH radicals can also create some other products such as hydrogen molecule or hydrogen atom abstraction at various positions of benzene ring. However, these products are not easy to be formed because the reaction channels leading to them hold much high energy barrier. Therefore, these reaction channels have not been considered in this study. In a nutshell, it can be said that the H-abstraction path is dominant in comparison with the OH-addition channel and thus $\text{C}_6\text{H}_5 + \text{H}_2\text{O}$ is the key product of the title reaction.

5. CONCLUSION

In the present work, the $\text{C}_6\text{H}_6 + \text{OH}$ reaction was optimized at both the B3LYP/6-311++G(3df,2p) and M06-2X/aug-cc-pVTZ levels. Energies for all the species have been refined at the CCSD(T)/aug-cc-pVTZ level. All the quantum calculations were performed by using the Gaussian 16. The rate constants have been calculated over the 300 - 2000 K range. The total rate constants in this study agree well with the experimental data. The calculated results indicate that the main product of the reaction is $\text{C}_6\text{H}_5 + \text{H}_2\text{O}$.

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