

Mechanism of Polychlorinated Dibenzop-dioxins Degradation by Ozone

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Despite of its fundamental importance, the reaction mechanism of polychlorinated dibenzo-*p*-dioxins destruction by using ozone still lacks detailed investigation. As a well-established method for investigating the chemical reactions, quantum chemical calculations were employed to investigate this reaction mechanism. Theoretical results showed that polychlorinated dibenzo-*p*-dioxins were gradually destructed by ozone *via* the cleavages of the C=C bonds and aromatic rings and the calculated activation energies were about 12 kcal/mol by the UB3LYP ++/6-311G(d,p)//UB3LYP/6-31G(d) method. In order to examine the rationality of the theoretical results, the experiment of the polychlorinated dibenzo-*p*-dioxins destruction by using ozone was also performed in this work. It was found that increase in the chlorite atoms on polychlorinated dibenzo-*p*-dioxins increased the theoretical activation energies. Whereas in the experimental results the removal efficiencies were found decreased. Obviously, the increasing of activation energies leads to the descending of removal efficiencies. It is suggested that the theoretical results were backed up quite well by the experimental results.

Keywords: Polychlorinated dibenzo-*p*-dioxins, Ozone, Quantum chemistry, Reaction mechanism.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins have increasingly become a matter of worldwide concern because of their toxicological effects and associated adverse health implications^{1,2}. Polychlorinated dibenzo-*p*-dioxins are persistent organic pollutants and form almost invariably as unwanted byproducts in all thermal systems when a chlorine source is present. Since the formation of polychlorinated dibenzo-*p*-dioxins is ubiquitous to the combustion processes in municipal waste incinerators, a reliable disposal method for polychlorinated dibenzo-*p*-dioxins is urgently needed. Nowadays, many well-established methods to control the emission of polychlorinated dibenzo-*p*-dioxins have been developed including activated carbon injection, S and N-compounds addition, selective catalytic reduction and plasma technology³⁻⁷.

Ozone, as a strong oxidant, has been largely applied in medicine and water treatment. Ozone can be used to sterilize, deodorize and decompose organism efficiently. When ozone generator discharges in local air or oxygen, it has the virtue of uniform discharging, high efficiency and low electric waste. Ozone injection has been considered to be a new choice for degrading polychlorinated dibenzo-*p*-dioxins. Previous investigations indicated that volatile organic compounds and polycyclic aromatic hydrocarbons could be efficiently destructed

by using ozone especially in combination with other methods such as ultra-violet rays, catalytic metal supporting, thermal and catalytic incineration⁸⁻¹³. As volatile organic compounds and polycyclic aromatic hydrocarbons were succeeded to degrade, dioxins supposingly could be destructed efficiently by ozone. Wang *et. al.*^{14,15} indicated that polychlorinated dibenzo-*p*-dioxins could be efficiently destructed *via* ozone injection. However, to our best of knowledge, less study on the destruction mechanism of polychlorinated dibenzo-*p*-dioxins by using ozone has been reported. Therefore, for the understanding of the destruction mechanism and for the further development of the destruction efficiency, investigation on the reaction mechanism of the polychlorinated dibenzo-*p*-dioxins destruction by using ozone is essential.

As a well-established method for investigating the chemical reactions, quantum chemical calculations have been employed frequently for studying the formation mechanism and damaging mechanism of dioxins^{16,17}. Thus, the reaction mechanism of the polychlorinated dibenzo-*p*-dioxins destruction by using ozone were investigated by employing quantum chemical calculation in this paper. Furthermore, in order to examine the rationality of the theoretical results, the experiment of the polychlorinated dibenzo-*p*-dioxins destruction by using ozone was also performed in this paper.

EXPERIMENTAL

Gaussian 2003 package¹⁸ was used in the present quantum chemical calculations. All the geometry optimizations of stationary points along the reactions were performed by the quantum chemistry UB3LYP method at 6-31G(d) basis function level^{19,20}. The optimized stationary points were characterized as intermediates or transition states by diagonalizing the Hessian matrix and analyzing the vibrational normal modes. By this means, the stationary points can be classified as intermediates if no imaginary frequencies are shown, or as transition states if only one imaginary frequency is obtained. Furthermore, the particular nature of the transition states was determined by the calculation of intrinsic reaction coordinate (IRC)²¹ and the vibrational analysis of imaginary frequency. After checking, no significant spin contamination was found in geometry optimizations. All the differences between the expectation value of the total spin operator S^2 and the expected value $S(S+1)/2$ (where S stands for the total spin) are within 10 %. This indicates that the geometry optimizations in this paper are reliable.

Based on geometry optimizations made by UB3LYP/6-31G(d) method, the potential energies of stationary points of reactions were calculated by UB3LYP/6-311G++(d,p) method^{22,23}. After being corrected with zero-point energies, the activation energy (ΔE) of the reaction was calculated. Meanwhile for analyzing the configuration of compounds, the Wiberg bond order calculation²⁴ was also performed using the UB3LYP/6-31G(d) method.

As shown in Fig. 1, the experimental apparatus for degradation of polychlorinated dibenzo-*p*-dioxins by using ozone including the ozone generation, polychlorinated dibenzo-*p*-dioxins generation, quartz flow reactor, polychlorinated dibenzo-*p*-dioxins collection and online gas analysis system. Ozone was generated by a dielectric barrier discharge device manufactured by Qingdao Guolin Co. with 3.7-4kV AC voltage and 5 kHz (model CF-G-3-010G). The output concentration of ozone was monitored by an ozone analyzer continuously (In2000, In USA Co.) which has a 0-10000 ppm measuring range and 1 ppm precision. The stream with polychlorinated dibenzo-*p*-dioxins was generated by heating chlorophenols in the furnace (temperature control).

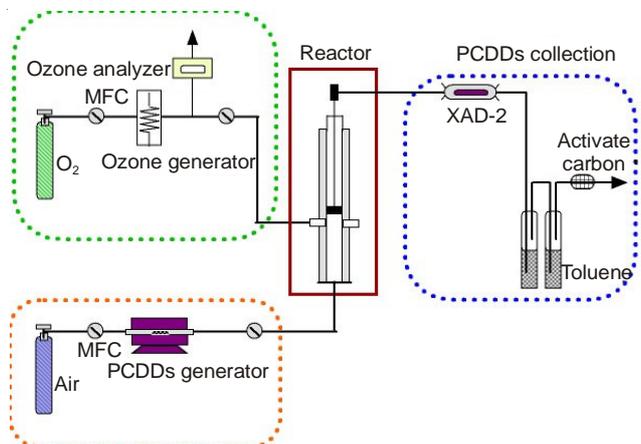


Fig. 1. Experimental setup for the degradation of polychlorinated dibenzo-*p*-dioxins by using ozone

After being reacted, the stream from the reactor was passed through ice-cooled gas traps consisting of a XAD-2 resinous column and then an impinger containing toluene. Next, acetone, methylene chloride and toluene were used for rinsing the inside of reactor, gas tubes and connectors. The rinses were included in the analysis of the gas traps. Products remaining in the solid sample residue after the experiment were also analyzed. The EPA 1613 isotope dilution method was used for determination tetra-octa polychlorinated dibenzo-*p*-dioxins. Samples were analyzed by means of high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) with a DB-5MS column. The total TEQ concentration of polychlorinated dibenzo-*p*-dioxins is calculated using international toxic equivalency factors (I-TEFs), while the TEQ of PCBs is calculated using the world health organization-TDFs²⁵.

RESULTS AND DISCUSSION

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin destruction by using ozone: Considering that dioxin congeners have similar chemical and physical properties, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), which is the most toxic congener^{26,27}, was selected as the typical object in the theoretical calculation.

According to the destruction of benzene and toluene by ozone²⁸⁻³⁰, the reaction process of 2,3,7,8-TCDD+O₃ was supposed to process *via* the addition of O₃ and the cleavages of C=C bonds. For analyzing the configuration of 2,3,7,8-TCDD, the Wiberg bond order calculation was performed using the UB3LYP/6-31G(d) method and the results were illustrated in Fig. 2. As shown in Fig. 2, there are four different types of carbon-carbon double bonds (C=C) in the symmetrical 2,3,7,8-TCDD and the sequence of their bond order is: IV-C=C(1.3165) < I-C=C(1.3591) < II-C=C(1.3768) < III-C=C(1.4035). The lower the C=C bond order, the easier the attacking of O₃ to the C=C bond. Although the bond order of IV-C=C is lowest, the attacking of O₃ to IV-C=C is believed to be very difficult because of its great stereo-hindrance effect. On the contrary, the stereo-hindrance effect for the attacking of O₃ to I-C=C is quite little. Therefore, the attacking of O₃ to I-C=C was considered to be the most possible way for the 2,3,7,8-TCDD + O₃ reaction and the other attacking ways were not considered in the present study.

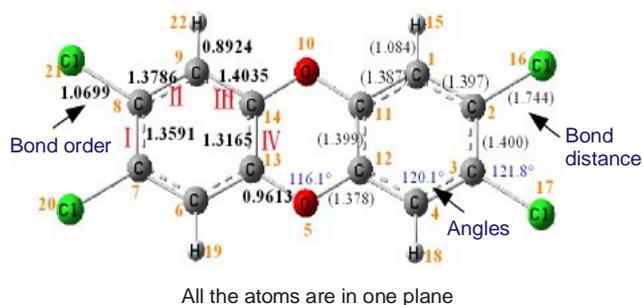


Fig. 2. Wiberg bond order analysis of 2,3,7,8-TCDD (Angles are given in degrees and bond distances are given in angstroms)

As shown in Fig. 3, two mechanistically different routes were found during the attacking of O₃ to C7=C8(I-C=C): the middle oxygen atom of ozone is either directed toward the

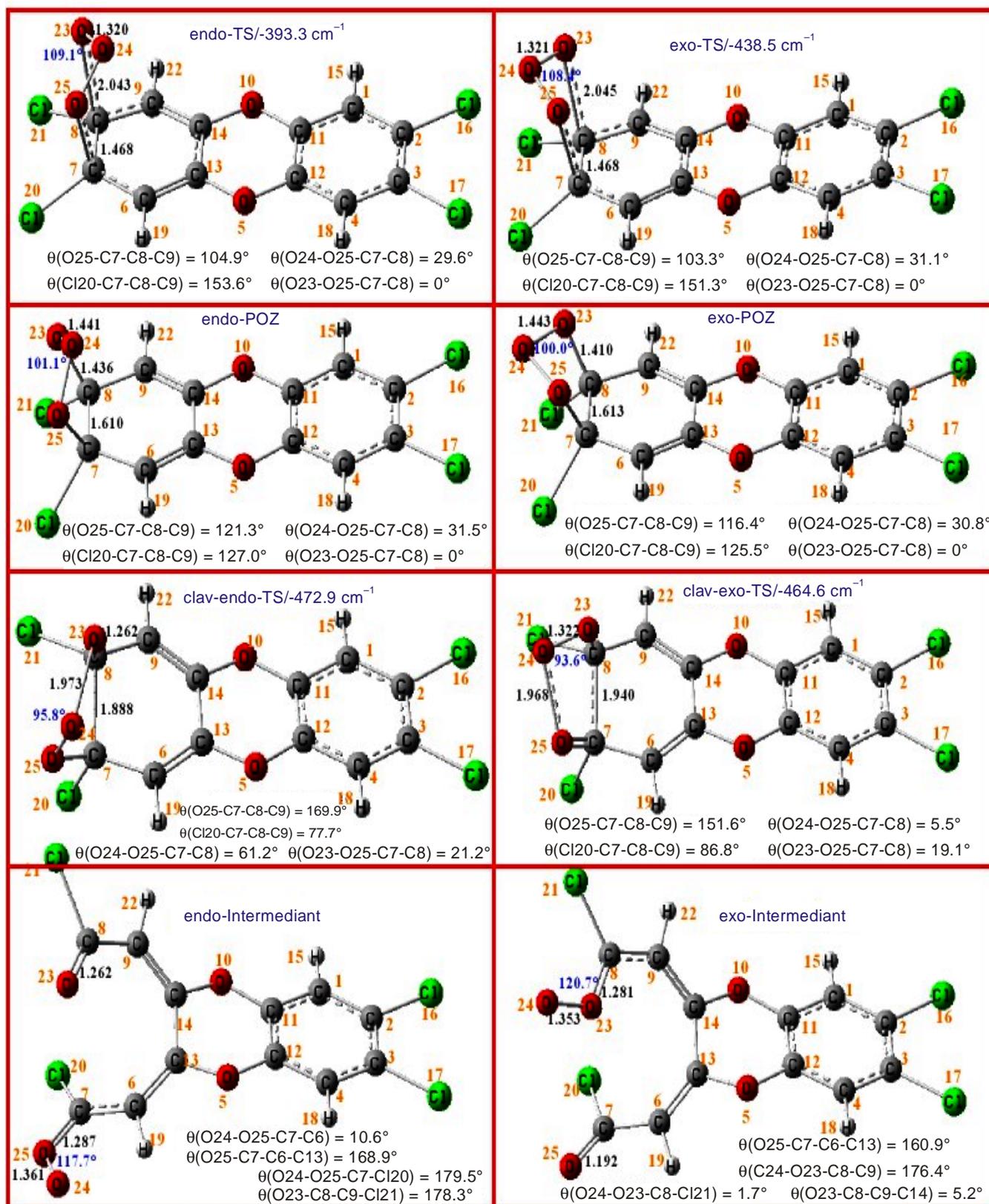


Fig. 3. Optimized geometries of the stationary points along the 2,3,7,8-TCDD+ozone reaction process. (Angles are given in degrees and bond distances are given in angstroms)

benzene ring (endo-route) or directed away from this ring structure (exo-route). For each route, the primary ozonide (endo-POZ or exo-POZ) is formed *via* a transition state (endo-TS or exo-TS); and then, the primary ozonide is cleaved to

form an intermediate (endo-intermediate or exo-intermediate) *via* another transition state (clea-endo-TS or clea-exo-TS). As shown in Fig. 3, the changes of geometric configurations about the reactants, transition states and intermediates can describe

this reaction process clearly. For example, during the process of the endo-route, the distance between two attacked carbon atoms increases gradually ($1.400\text{\AA} \rightarrow 1.468\text{\AA} \rightarrow 1.610\text{\AA} \rightarrow 1.973\text{\AA} \rightarrow \infty\text{\AA}$, ∞ denotes the distance exceeding the range of bond forming, as the same in the following text), which can describe the cleavage of C=C bond clearly. Similar changes can also be found during the process of the exo-route. The cleavage of C=C bond stands for the actual destruction of benzene ring and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin.

Based on geometry optimizations made using the UB3LYP/6-31G(d) method, all potential energies of stationary points along the reaction process of this section were calculated using the UB3LYP/6-311G++(d,p) method. After corrected with ZPE, the potential energies variation along the reaction process were illustrated in Fig. 4. Since the potential energies of endo-POZ and exo-POZ are quite lower than that of reactants, it can be concluded that both endo-POZ and exo-POZ are quite stable intermediates. Hence, the formation of endo-POZ and exo-POZ turn out to be the rate-determining steps for the whole reaction of 2,3,7,8-TCDD+O₃. Since the reaction always moves along the path with lower activation energy, the endo-route can be considered as the favorite route for the reaction process of 2,3,7,8-TCDD+O₃ and the formation of endo-POZ can be considered as the rate-determining step for the whole reaction. The obtained activation energy was 11.50 kcal/mol.

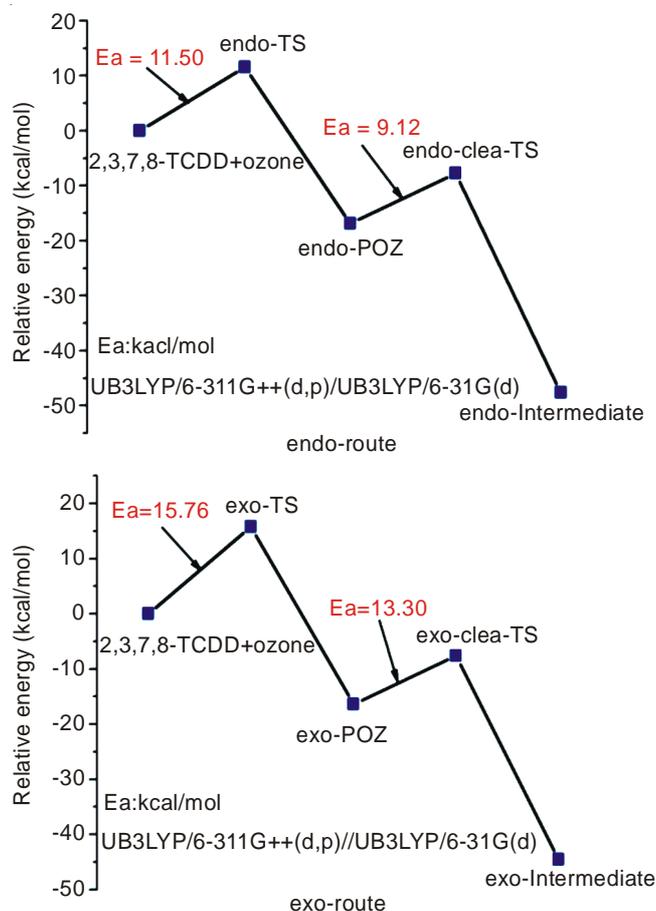


Fig. 4. Potential energies of stationary points along the reaction process of 2,3,7,8-TCDD + ozone

Based on the calculation of 2,3,7,8-TCDD, the destruction of various polychlorinated dibenzo-*p*-dioxins by using ozone was calculated in this paper. For all the polychlorinated dibenzo-*p*-dioxins, two mechanistically different routes (endo-route and exo route) were found during the attacking of ozone to C=C bond. As shown in Table-1, for all the polychlorinated dibenzo-*p*-dioxins the activation energies of the endo-route are lower than that of the exo-route. For the polychlorinated dibenzo-*p*-dioxins with asymmetry structure, taking 12378-PeCDD as an example, there are two different ways for the ozone attacking shown in Fig. 5. The activation energies for various routes of the polychlorinated dibenzo-*p*-dioxins destruction by using ozone were calculated and shown in Table-1. Since the reaction always moves along the path with lower activation energy, the lowest activation energy can be considered as the activation energy for each reaction.

TABLE-1
REACTION ROUTES AND ACTIVATION ENERGIES
FOR THE POLYCHLORINATED DIBENZO-*p*-DIOXINS
DESTRUCTION BY USING OZONE

Dioxins (polychlorinated dibenzo- <i>p</i> -dioxins)	Reaction routes	Activation energy	Reaction routes	Activation energy
2378-TCDD	endo-route	11.50	exo-route	15.76
12378-PeCDD	endo-route-1	11.85	exo-route-1	15.69
	endo-route-2	11.70	exo-route-2	15.83
123478-HxCDD	endo-route-1	12.19	exo-route-1	15.82
	endo-route-2	11.92	exo-route-2	16.08
123678-HxCDD	endo-route	12.07	exo-route	15.93
123789-HxCDD	endo-route	12.06	exo-route	15.92
1234678-HpCDD	endo-route-1	12.26	exo-route-1	16.14
	endo-route-2	12.18	exo-route-2	16.03
OCDD	endo-route	12.66	exo-route	16.28

(Activation energies: kcal/mol)

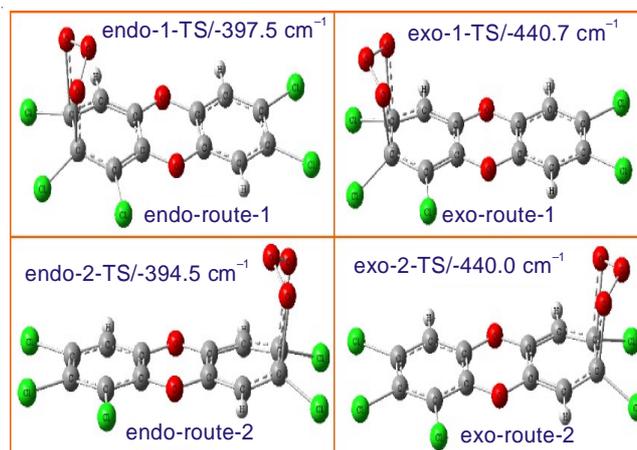


Fig. 5. Optimized TS geometries for various routes of 12378-PeCDD+ozone reaction

Therefore, it can be found that, the activation energies increases with increasing of chlorite atoms on polychlorinated dibenzo-*p*-dioxins. This may be because the H atom is reductive while the Cl atom is oxidative. Hence, the increasing of Cl atoms and the descending of H atoms on polychlorinated dibenzo-*p*-dioxins leads to the increasing of the oxidation rate and the descending of the reduction rate of polychlorinated dibenzo-*p*-dioxins. Because ozone is oxidant for the poly-

chlorinated dibenzo-*p*-dioxins destruction, the descending of the reduction rate of polychlorinated dibenzo-*p*-dioxins must lead to the increasing of the activation energies of the polychlorinated dibenzo-*p*-dioxins + ozone.

Comparison of theoretical results and experimental results: In order to examine the rationality of the above theoretical results, the experiment of the polychlorinated dibenzo-*p*-dioxins destruction by using ozone was performed in this study. Experimental results showed that the polychlorinated dibenzo-*p*-dioxins destruction by using ozone was found to be insignificant at 433 K. However, at 493 K, the polychlorinated dibenzo-*p*-dioxins destruction by using ozone was detected and their destruction efficiency were more than 90 %. This indicated that the polychlorinated dibenzo-*p*-dioxins destruction by using ozone was quite sensitive to the temperature.

Table-2 shows the comparison of theoretical results and experimental results on the polychlorinated dibenzo-*p*-dioxins destruction by using ozone. As shown in Table-2, the theoretical results were calculated and obtained by employing UB3LYP/6-311G++(d,g)//UB3LYP/6-31G(d) method. The experiment was performed under these conditions: Temperature 493 K, residence time 60 min, ozone flow 0.5 L/min, the concentration of ozone 200 ppm and the initial concentration of dioxins at approximately 200 pg/Nm³. Comparing results, it is observed that with increasing the chlorite atoms on polychlorinated dibenzo-*p*-dioxins, the activation energies increases in the theoretical results while the removal efficiencies descends in the experimental results. The increasing of activation energies leads to the descending of removal efficiencies. This implies that, the theoretical results were backed up quite well by the experimental results and indicates that studies on the mechanism of polychlorinated dibenzo-*p*-dioxins destruction reaction by using ozone by employing quantum chemical calculation in this paper was reasonable and reliable.

TABLE-2
THEORETICAL AND EXPERIMENTAL RESULTS ON
THE POLYCHLORINATED DIBENZO-*p*-DIOXINS
DESTRUCTION BY USING OZONE

Polychlorinated dibenzo- <i>p</i> -dioxins	Activation energy ^a (kcal/mol)	Removal efficiency ^b (concentration %)	Removal efficiency ^b (I-TEQ %)
2378-TCDD	11.50	100.00	100.00
12378-PeCDD	11.70	100.00	100.00
123478-HxCDD	11.92	100.00	100.00
123678-HxCDD	12.07	94.29	94.30
123789-HxCDD	12.06	90.65	90.64
1234678-HpCDD	12.18	94.07	94.05
OCDD	12.66	93.04	92.94

^aTheoretical results by UB3LYP/6-311G++(d,g)//UB3LYP/6-31G(d);

^bExperimental results at T-493 K, time 60 min, the initial dioxins concentration-200 pg/Nm³, ozone-0.5 L/min and 200 ppm

Conclusion

In conclusion, the detailed reaction mechanism of polychlorinated dibenzo-*p*-dioxins destruction by using ozone was investigated by employing quantum chemical calculation and experimental research. Theoretical results showed that polychlorinated dibenzo-*p*-dioxins were gradually destructed by ozone *via* the cleavages of the C=C bonds and aromatic rings

and the calculated activation energies were about 12 kcal/mol by the UB3LYP++/6-311G(d,p)//UB3LYP/6-31G(d) method. In order to examine the rationality of the theoretical results, the experiment of the polychlorinated dibenzo-*p*-dioxins destruction by using ozone was also performed in this paper. By comparing the experimental theoretical results, it can be found that by increasing the chlorite atoms on polychlorinated dibenzo-*p*-dioxins, the activation energies increases in the theoretical results while the removal efficiencies descends in the experimental results. The increasing of activation energies leads to the descending of removal efficiencies. Overall, the theoretical results were backed up quite well by the experimental results.

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