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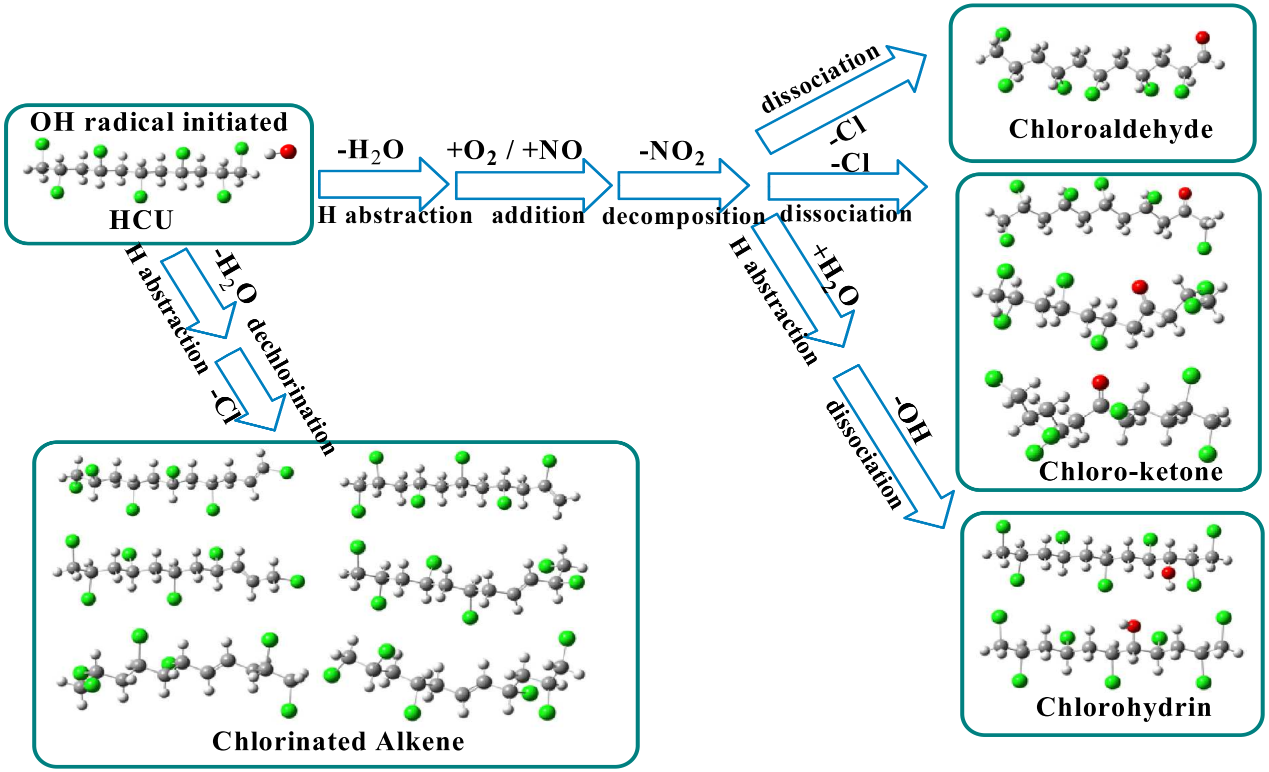

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ARTICLE TYPE

# The OH-initiated Chemical Transformation of 1,2,4,6,8,10,11-heptachloroundecane in the Atmosphere

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**Abstract**: The short chain chlorinated paraffins (SCCPs) have recently drawn the public attention because they have properties similar to persistent organic pollutants. In this study, a model molecule called 1,2,4,6,8,10,11-heptachloroundecane (HCU) is selected to investigate the chemical transformation of SCCPs using the density functional theory (DFT) method. After hydroxyl (OH) radicals initiate the hydrogen (H) atom abstraction reactions, the produced intermediates could be further oxidized in the presence of $O_2$/NO. The main products would be chloro-aldehydes and chloro-ketones after dechlorination reactions, or chloro-hydrins after the reaction with $H_2O$. There are strong water solubility and polarity in these products. The Cl and OH radicals are also generated in the degradation process, which have strong reactivity. The rate constants are calculated using the transition state theory and the Arrhenius formulas are fitted. The total rate constant of HCU with OH radicals is about $1.67\times10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at room temperature. The atmospheric lifetime of HCU relative OH radicals is about 7.1 days.

## Introduction

Chlorinated paraffins (CPs) are complex mixtures of polychlorinated *n*-alkanes, which include many congeners and isomers.[1] Generally, CPs can be classified into short chain CPs (SCCPs, $C_{10}$-$C_{13}$), medium chain CPs (MCCPs, $C_{14}$-$C_{17}$) and long chain CPs (LCCP, $C_{18}$-$C_{30}$) according to their carbon chain length (molecular formula: $C_xH_{(2x-y+2)}Cl_y$). [2]

Since the 1930s, hundreds of CPs had been used as additives in sealant, paint, rubber, metal working fluid, flame retardant and plasticizer. [3] Recently, more and more attention has been paid to their harmful properties, especially to SCCPs.

As by-products in the production of MCCPs and LCCPs, there are such properties in SCCPs as potential toxicity, persistence, bioaccumulation and long-range transport, which are similar to persistent organic pollutants (POPs). [4,5] At the Conference of the Stockholm Convention (SC) for persistent organic pollutants, SCCPs have been reviewed five times from 2007 to 2012 (except in 2011) for their draft risk profile. But the review is postponed since studies are insufficient. [6,7] However, several countries including the United States and Canada and the European Union have still restricted the use of SCCPs. [8] It can be expected that once SCCPs are listed into SC, the manufacturing activities of CPs and the relevant economy will be deeply influenced. [7]

SCCPs are ubiquitous in both natural and human living environment, such as air, water, sediment, aquatic organism, terrestrial wildlife and so on. [9-15] The partition coefficients for *n*-octanol-water vary from 5.06 to 8.12, [3,16] while the coefficients for *n*-octanol-air are about 8.2-9.8, indicating bioaccumulation and biomagnification through the food chain. [17] The exposure experiments prove that SCCPs are carcinogenic to rats and can also cause the chronic toxicosis of aquatic organisms. [18] Besides, a series of reports about their toxicological effects indicate that there is potential harmful impact on human health. [19,20]

Usually SCCPs can be discharged from or deposited into the municipal wastewater network, and finally be accumulated in the wastewater treatment plants (WWTPs). [21] From 14 WWTPs in UK, Steven *et al.* observed that the concentration of SCCPs in sludge varied from 7 to 200 mg/kg dry weight. [22] A nationwide survey of sewage sludge samples from 52 WWTPs was carried out in China. It was found that concentrations of SCCPs ranged between 0.80 and 52.7 mg/kg dry weight and most of the samples shared the similar congener distribution patterns. [23] It could be speculated that the improper application of sludge may cause secondary pollution due to the stability of SCCPs.

Owing to the increased public awareness, advanced equipments and improved evaluation methods, SCCPs have been studied for many years and frontier scientific data have been achieved. [7] Recently, Jiang's group studied the concentration and distribution of SCCPs in farm soils, [10] the distribution patterns in 52 WWTPs nationwide, [23] the environmental fate, behavior and possible removal in sewage treatment plants, [24] the migration behaviors in the coastal East China Sea, [25] and the spatial and temporal trends in Bohai and Yellow Sea. [26] In China, Wang also investigated the air, soil and atmospheric deposition process of SCCPs in the Pearl River Delta. [27] However, SCCPs are very complex mixtures and are difficult to separate in current experimental conditions. In addition, there are little standard analytical methods. [7] Moreover, the reported results are different from different laboratories,

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sometimes even with 300% deviations.[28] Therefore, most of the studies are still at the monitoring stage, and a few reports on experiments about dechlorination or degradation of SCCPs could be found. Zhang synthesized nanoscale zero-valent iron particles to test the reductive dehalogenation of SCCPs.[29] In Lu's experiment, the degradation efficacy was tested by a bacterial strain in pure culture in which SCCPs was utilized to supplement carbon and energy.[22]

Recent studies showed that the density functional theory (DFT) could offer accurate prediction of kinetics, pathways and products by calculating the reaction mechanism in many fields.[30-32] To our knowledge, quantum chemical study on SCCPs is very scarce. In order to make up for the inadequacy of degradation experiment,[7] a specific model molecule is selected to explore theoretical possibilities and completed mechanisms of the dechlorination or degradation of SCCPs for the first time in a computational approach of quantum chemistry. Some useful data for related experiments will be provided.

In atmospheric chemistry, the reactions initiated by OH radicals are of paramount importance. They could be produced and recycled by solar ultraviolet radiation spontaneously.[33] Thus, we assume that the reactions of SCCPs with OH radicals may be the dominant removal process. In this study, the OH-initiated degradation reactions of the model molecule, in the presence of $O_2$, NO and $H_2O$, are selected to be calculated with density functional theory (DFT). The rate constants are also computed by transition state theory (TST).

## Computational methods

### Quantum chemistry calculation

To select a proper model molecule, the optimization is calculated at the b3lyp/6-31+g(d) level. In reaction processes, the optimization of reactants, transition states, intermediates and products are calculated at the M062x/6-31+g(d,p) level. Based on previous reports the M062x function performs well consistently for computing energies and enthalpies of small and large organic molecules with lower computational costs.[34-38] It takes weak interactions into account well and appears to provide comparable energy prediction performance and reliable and reasonable descriptions to the best performing function available currently.[39] The vibrational frequencies are also calculated at the same level to confirm the nature of stationary points.

### Kinetic calculation

Transition state theory (TST) is used to determine rate constants with a statistical representation. The model is based on the potential interaction between reactants and products.[40] Taking a bimolecular reaction as example:

$$A + BC \rightarrow AB + C \qquad (1)$$

The rate constant is calculated by applying the following formula.

$$K_{TST} = \frac{k_B T}{h}\frac{Q_x}{Q_A Q_{BC}}\exp\left(-\frac{V_a}{RT}\right)\frac{RT}{P^{\theta}}\frac{10^6}{N_A} \qquad (2)$$

For unimolecular reactions,

$$K_{TST} = \frac{k_B T}{h}\frac{Q_x}{Q_A}\exp\left(-\frac{V_a}{RT}\right) \qquad (3)$$

Where $k_B$ is the Boltzmann constant, $T$ is the temperature, $h$ is the Planck constant, $R$ is universal gas constant, $Va$ is the barrier, $P^{\theta}$ is standard pressure and $N_A$ is Avogadro constant. $Q_x$ is the partition function of the transition state, while $Q_A$, $Q_{BC}$ are those of the reactants. The reaction rates were calculated with temperature ranging from 200K to 400K in 10 K steps.

## Results and discussion

### Selection of target molecule

Since the quantum chemical calculation is based on the analysis of specific molecules, the concrete structure must be known. As we know, SCCPs are complex mixtures with thousands of unseparated homologs and isomers[1] and there is no particular representative in published reports. Based on our experiences, we'd like to select one molecule derived from SCCPs but with relatively stronger abundance and lower energy. Firstly, the general formula ($C_xH_{(2x-y+2)}Cl_y$, x=10~13, y=1~13) is confirmed. From various published reports, we found that many SCCPs samples in different environment media displayed very similar congener distribution patterns and relative abundance,[10,23,25-27] with $C_x$ (x=10,11) and $Cl_y$ (y=6,7,8) as the dominant congener group. After comparison on relative abundance preliminarily, $C_{11}H_{17}Cl_7$ was chosen as the target formula.

Secondly, we fixed the structure with lower energy, which is stable and abundant among the isomers. One hundred structures were drawn randomly, in which chlorine atoms are substituted for different numbers of hydrogen atoms on one carbon atom. Then their energies were compared. Results showed that those with only one chlorine atom on one carbon got lower energy. So the scope is narrowed down naturally.

According to permutation and combination theory, for mono-substituted $C_{11}H_{17}Cl_7$ on each carbon atom, there are 170 isomers altogether in this category. All of them were drawn and optimized. The structure with the lowest energy was chosen as the model molecule to be analyzed afterwards. It is 1,2,4,6,8,10,11- heptachloroundecane (HCU) which is symmetrical (**Fig. 1**).

**Fig. 1** The atom numbers on the structure of 1,2,4,6,8,10,11-heptachloroundecane (HCU)

### OH-initiated abstraction reactions

As shown in **Fig. 1**, there are 9 different hydrogen atoms in HCU structure and they can be initiated by OH radical respectively for atmospheric oxidation. Hydrogen atoms are labeled from No.1 to No.9 for convenience. Under the atmospheric conditions, OH radical can easily initiate chemical reactions by attacking hydrogen atoms since it is strongly nucleophilic. So H atom abstraction from HCU should be the first step. It's obvious that the 9 hydrogen atoms can be divided into 4 kinds according to the relative location: H1(H2), H3, H4(H5,H7,H8) and H6(H9), which will be discussed separately.

The H1 and H2 can be abstracted by the OH radicals respectively. The transition states (TSa1 and TSa2) can be found in this process, in which the transition vectors display the motion of H1(H2) atom between the C10 atom and the O atom in the OH

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radical. The abstraction pathways can generate $H_2O$ and IMa1 via a potential barrier of 4.12 kcal/mol and IMa2 with the barrier of 1.60 kcal/mol, releasing the energy with 16.49 and 16.10 kcal/mol. The reaction mechanisms of Route 3 to 9 are similar to those in Route 1 and 2, and the potential energy profiles are shown in **Scheme. 1**. Generally, the potential barriers of TSa3 to TSa9 are 0.044~5.24 kcal/mol, and all the other abstraction reactions are strongly exothermic, giving out energy with 17.78~20.60 kcal/mol (**Scheme. 1)**. The $\triangle E_b$ is the potential barrier and the $\triangle E_r$ is the reaction heat in the elementary reaction.

**Scheme. 1** Schematic diagram of the reaction pathways in the H abstraction and dechlorination reaction mechanisms of HCUwith the barriers $\Delta E_b$ (kal/mol) and reaction heats $\Delta E_r$ (kcal/mol).

The data indicate that all kinds of H abstraction reactions have low barriers and give out much energy. The above reactions are expected to occur easily and may play an important role in the degradation of HCU in the atmosphere. Since the intermediates are still active, they will be further oxidized by $O_2$/NO.

It should be noted that H1 and H2 are connected with the same C atom. After abstraction and geometrical optimization, IMa1 and IMa2 are identical, and so are IMa4 and IMa5, IMa7 and IMa8. Therefore only IMa1, IMa3, IMa5, IMa6, IMa7, IMa9 are selected for further discussion.

**Fig. 2** Profile of the potential energy surface for the oxidation and further dechlorination of IMa1

**Fig. 3** Profile of the potential energy surface for the oxidation and further dechlorination of IMa3

**Fig. 4** Profile of the potential energy surface for the oxidation and further dechlorination of IMa5

### Subsequent reactions

The intermediates from IMa1 to IMa9 are rich in energy, and they may carry out further reactions through two pathways: dechlorination and oxidation by $O_2$/NO.

### Dechlorination to alkene

As shown in **Fig. 1**, the numbers of carbon atoms from 10 to 15 and chlorine atoms from 16 to 19 are also labeled. After abstraction reactions the bond length between intermediate atoms changes a lot, which may naturally lead to further dechlorination. For IMa1, the bond length of C10-Cl16 and C10-C11 becomes shorter, varying from 1.80 Å to 1.72 Å and from 1.52 Å to 1.49 Å, respectively. And in the meantime C10 atom becomes unsaturated. It is assumed that the structure tends to eliminate Cl17 to form a double bond between C10 and C11. As for IMa5, the distance between C12 and C11 or C12 and C13 becomes shorter too (from 1.50Å to 1.47Å). Meanwhile the neighboring C-Cl bond gets elongated (from 1.80Å to 1.84Å). Hence the structure could be transformed into two kinds of alkenes (Pa4 and Pa5) by dechlorination on either side. As well, the dechlorination of IMa3 is similar to that of IMa1 while IMa7 is similar to IMa5. For IMa6 or IMa9, there is no chlorine atom connected with the C atom next to C13 or C15. As a result, the intermediates could not generate alkenes after dechlorination (**Scheme. 1)**. However, no transition state could be found in this process and the reactions are all endothermic, with the energy of 21.13~22.55 kcal/mol. Therefore the pathways of dechlorination need to absorb heat from the environment.

### Reactions in the presence of $O_2$/NO

IMa1 is taken as an example for the second pathway. It could be further oxidized by ubiquitous $O_2$ in atmosphere, which is a barrierless process. The oxidation reaction is strongly exothermic, and up to 69.57 kcal/mol of energy is released. The generated IMb1 will react with NO immediately to form IMc1 and the reaction releases the energy with 24.63 kcal/mol as a barrierless process. Promptly IMc1 reacts in a directly unimolecular decomposition via cleavage of the O-O bond to produce IMd1 and $NO_2$. The elimination has to cross a transition state with an energy barrier of 47.53 kcal/mol and absorbs a little energy of 12.21 kcal/mol. However, the energy in need is far lower than the released from the previous reactions (IMa1→IMb1→IMc1). So this whole process could occur easily. The mechanisms in those processes from IMa1 to IMa9 are similar, with slight differences in their energy. The profiles of potential energy surfaces of IMa1, IMa3, IMa5 are drawn in **Fig. 2, 3 and 4** as representatives, while IMa6, IMa7 and IMa9 are shown as follows.

| | |
|---|---|
| $IMa6 + O_2 \rightarrow IMb6$ | $\Delta E_r = -66.51$ kcal/mol |
| $IMb6 + NO \rightarrow IMc6$ | $\Delta E_r = -23.80$ kcal/mol |
| $IMc6 \rightarrow TSb6 \rightarrow IMd6 + NO_2$ | $\Delta E_b = 48.53$ kcal/mol, |
| | $\Delta E_r = 10.06$ kcal/mol |
| $IMa7 + O_2 \rightarrow IMb7$ | $\Delta E_r = -70.00$ kcal/mol |
| $IMb7 + NO \rightarrow IMc7$ | $\Delta E_r = -22.62$ kcal/mol |
| $IMc7 \rightarrow TSb7 \rightarrow IMd7 + NO_2$ | $\Delta E_b = 52.73$ kcal/mol, |
| | $\Delta E_r = 13.05$ kcal/mol |
| $IMa9 + O_2 \rightarrow IMb9$ | $\Delta E_r = -65.58$ kcal/mol |
| $IMb9 + NO \rightarrow IMc9$ | $\Delta E_r = -21.67$ kcal/mol |
| $IMc9 \rightarrow TSb9 \rightarrow IMd9 + NO_2$ | $\Delta E_b = 45.06$ kcal/mol, |
| | $\Delta E_r = 7.08$ kcal/mol |

### Formation of products

After the $NO_2$ elimination reaction, intermediates from IMd1 to IMd9 are active which could further undergo decomposition or addition reactions to form alcohol, aldehyde or ketone in different routes. For IMd1, IMd3, IMd6 and IMd9, the fracture of the C-Cl bond and the formation of the carbon-oxygen double bonds may occur to generate the products (Pb1, Pb3, Pb6 and Pb9). The Cl atoms are also separated in the processes through transition states. Pb1 is chloro-aldehyde but Pb3, Pb6 and Pb9 are chloro-ketones.

| | |
|---|---|
| $IMd1 \rightarrow TSc1 \rightarrow Pb1 + Cl$ | $\Delta E_b = 11.34$ kcal/mol, |
| | $\Delta E_r = 3.81$ kcal/mol |
| $IMd3 \rightarrow TSc3 \rightarrow Pb3 + Cl$ | $\Delta E_b = 9.09$ kcal/mol, |
| | $\Delta E_r = 2.36$ kcal/mol |
| $IMd6 \rightarrow TSc6 \rightarrow Pb6 + Cl$ | $\Delta E_b = 7.76$ kcal/mol, |
| | $\Delta E_r = -0.95$ kcal/mol |
| $IMd9 \rightarrow TSc9 \rightarrow Pb9 + Cl$ | $\Delta E_b = 8.84$ kcal/mol, |

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$\Delta E_r$ = 1.50 kcal/mol

For IMd5 and IMd7, no Cl atoms are attached to the reactive C atoms and carbon-oxygen double bonds are not generated. However, the reaction between unsaturated O atom and $H_2O$ should not be ignored.

$$\text{IMd5} + H_2O \rightarrow \text{TSc5} \rightarrow \text{Pb5} + \text{OH} \qquad \Delta E_b = 11.59 \text{ kcal/mol},$$

$$\Delta E_r = 9.15 \text{ kcal/mol}$$

$$\text{IMd7} + H_2O \rightarrow \text{TSc7} \rightarrow \text{Pb7} + \text{OH} \qquad \Delta E_b = 13.28 \text{ kcal/mol},$$

$$\Delta E_r = 11.98 \text{ kcal/mol}$$

It is known that $H_2O$ is the third most prevalent component in the atmosphere, which accounts for about 1.5% as vapor by mass and about 2% if clouds and ice crystals are included.[41] The active IMd5 and IMd7 could seize the H atom from $H_2O$ to form chlorohydrins (Pb5 and Pb7), with OH radicals regenerated simultaneously. It's well recognized that OH radicals contribute a lot in atmospheric chemistry as the dominant reactive species, which can initiate a new round of reactions of HCU, or to degrade other organic compounds in the troposphere.[42] So far, the whole mechanism of general degradation is discussed in detail. The above degradation mechanism is similar to that of other SCCPs compounds.

**Table 1**. Arrhenius formulas of rate constants k for elementary reactions at 200-400K ($^a$ $cm^3$ $molecule^{-1}$ $s^{-1}$, $^b$ $s^{-1}$)

### Kinetics property

The kinetic calculations are carried out with the TST method as well. The barrierless $O_2$/NO oxidation reactions are not included. A suitable range of 200 - 400K is chosen to calculate rate constants, and they are fitted in the Arrhenius formula $k = A\exp(-Ea/RT)$. The reaction rates at the temperature of 298 K and the formula are shown in **Table1**. They can provide helpful information for the fate assessment of pollutants and the atmospheric model study.[43] In the multichannel reaction of HCU with OH radical, the total constant is about $1.67\times10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298K. Recently Li has calculated the OH radical reaction rate constant with different SCCPs, with the results that $k_{OH}$ of $C_{11}H_{16}Cl_8$ and $C_{10}H_{15}Cl_7$ are 1.6 and 2.0 $\times10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ at 298K.[43] It was reported that the average OH radical concentration is $9.7\times10^5$ molecule $cm^{-3}$ [44] and the atmospheric lifetime of HCU can be approximated by $\tau = 1/(k_{OH}[OH])$,[45-47] which is determined to be 7.1 days. OH radical seems to play an important role in the elimination process of HCU.

The experimental information for the SCCPs degradation reaction system is awfully absent. There is no comparison between experimental results and the calculated data. It is expected that the data and mechanism in this paper could provide a reference for future experiments. More studies on SCCPs are needed.

## Conclusions

Though SCCPs have the properties of long-range transport and persistence, they could be degraded in the atmosphere to some extent, especially in the presence of OH radical. Other mechanisms initiated by $NO_3$ or $O_3$ would be further studied. Based on our study, we predict that the SCCPs can be transformed to the chlorinated alcohols, aldehydes or ketones in the degradation processes, which have higher reactivity and water solubility than those of SCCPs. Then the subsequent atmospheric reactions will occur easily. Meanwhile, the Cl atom is released. As a highly active radical, Cl atom contributes to the oxidative chemistry. Compared to OH radical, Cl reacts up to 100 times faster in the analogous oxidation of organic compounds, as several experimental investigations indicated.[48-51] Besides, Cl atom intensifies the ozone depletion as well, which exerts a negative effect on the ecological and environmental conditions. Alternatively, with sufficient oxides of nitrogen Cl reacts quickly with organic molecules, leading to ozone formation in turn.[52] Obviously, the chlorinated alcohols, aldehydes, ketones and Cl atoms will produce profound impact on environmental quality and human health.

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## Notes and references

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1 F. J. Santos and J. Parera, M. T. Galceran, *Anal. Bioanal. Chem.,* 2006, **386**, 837-857.
2 G. T. Tomy, A. T. Fisk, J. B. Westmore and D. C. G. Muir, Rev. *Environ. Contamin. Toxicol.*, 1998, **158**, 53–128.
3 H. Bettina, F. Hermann, V. Wolfgang and C. Mehmet, *Environ. Sci Technol.*, 2011, **45**, 2842-2849.
4 H. J. Poremski, S. Wiandt and T. Knacker, *Organohalogen Compounds,* 2001, **52**, 397-400.
5 Q. Li, J. Li, Y. Wang, Y. Xu, X. Pan, G. Zhang, C. Luo, Y. Kobara, J. Nam and K. C. Jones, *Environ. Sci Technol.*, 2012, **46**, 11948-11954.
6 Eighth meeting of the Persistent Organic Pollutants Review Committee (POPRC.8), Geneva, Switzerland, 2012, Oct. 15-19.
7 T. Wang, Y. Wang and G. Jiang, *Environ. Sci Technol.*, 2013, **47**, 11924-11925.
8 E. Sverko, G. T. Tomy, C. H. Mä rvin, D. C. G. Muir, *Environ. Sci. Technol.*, 2012, **46**, 4697−4698.
9 M. Houde, D. C. G. Muir, G. T. Tomy, D. M. Whittle, C. Teixeira and S. Moore, *Environ. Sci Technol.*, 2008, **42**, 3893-3899.
10 L. Zeng, T. Wang, W. Han, B. Yuan, Q. Liu, Y. Wang and G. Jiang, *Environ. Sci. Technol.*, 2011, **45**, 2100-2106.
11 P. Castells, J. Parera, F. J. Santos and M. T. Galceran, *Chemosphere*, 2008, **70**, 1552-1562.

RSC Advances Accepted Manuscript

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12 M. Chen, X. Luo, X. Zhang, M. He, S. Chen and B. Mai, *Environ. Sci. Technol.*, 2011, **45**, 9936-9943.

13 I. O. Koh, W. Rotard, W. H. P. Thiemann, *Chemosphere*, 2002, **47**, 219-227.

14 U. E. Fridén , M. S. McLachlan and U. Berger, *Environ. Int*., 2011, **37**, 1169-1174.

15 K. H. Harada, T. Takasuga, T. Hitomi, P. Wang, H. Matsukami and A. Koizumi, *Environ. Sci. Technol.*, 2011, **45**, 7019-7027.

16 D. T. H. M .Sijm and T. L. Sinnige, Chemosphere, 1995, 31, 4427-4435.

17 B. C. Kelly, M. G. Ikonomou, J. D. Blair, A. E. Morin and F. A. P. C. Gobas, *Science*, 2007, **317**, 236-239.

18 H. M. Cooley, A. T. Fisk, S. C. Wiens, G. T. Tomy, R. E. Evans and D. C. G. Muir, *Aquat. Toxicol.*, 2001, **54**, 81-99.

19 A. T. Fisk, Tomy G T, Cymbalisty C D and D. C. G. Muir, *Environ. Toxicol. Chem.*, 2000, **19**, 1508-1516.

20 B. Burýšková, L. Bláha, D. Vršková, K. Šimková and B. Maršálek, *Act. Vet. Brno*., 2006, **75**, 115-122.

21 M. Lu, *J. Chem. Technol. Biot.*, 2014, **89**, 1118-1118.

22 J. L. Stevens, G. L. Northcott, G. A. Stern, G. T. Tomy and K. C. Jones, *Environl. Sci. Technol.*, 2003, **37**, 462-467.

23 L. Zeng, T. Wang, T. Ruan, Q. Liu, Y. Wang and G. Jiang, *Environ. Pollut.*, 2012, **160**, 88-94.

24 L. Zeng, H. Li, T. Wang, Y. Gao, K. Xiao, Y. Du, Y. Wang and G. Jiang, *Environ. Sci. Technol*., 2013, **47**, 732-740.

25 Z. Zhao, H. Li, Y. Wang, G. Li, Y. Cao, L. Zeng, J. Lan, T. Wang and G. Jiang, *Environ. Sci. Technol*., 2013, **47**, 5013-5022.

26 L. Zeng, R. Chen, Z. Zhao, T. Wang, Y. Gao, A. Li, Y. Wang, G. Jiang and L. Sun, *Environ. Sci Technol.*, 2013, **47**, 11449-11456.

27 Y. Wang, J. Li, Z. Cheng, Q. Li, X. Pan, R. Zhang, D. Liu, C. Luo, X. Liu and A. Katsoyiannis, G. Zhang, *Environ. Sci. Technol*., 2013, **47**, 2679-2687.

28 F. Pellizzato, M. Ricci, A. Held, H. Emons, W. Bohmer, S. Geiss, S. Iozza, S. Mais, M. Petersen and P. Lepom, Trends. *Anal. Chem*., 2009, **28**, 1029−1035.

29 Z. Zhang, M. Lu, Z. Zhang, M. Xiao and M. Zhang, *J. Hazard. Mater.*, 2012, **243**, 105-111.

30 M. Altarawneh, B. Z. Dlugogorski, E. M. Kennedy and J. C. Mackie, *J. Phys. Chem. A,* 2006, **110**, 13560-13567.

31 Q. Zhang, X. Qu and W. Wang, *Environ. Sci. Technol*., 2007, **41**, 6109-6116.

32 J. Zhou, J. Chen, C. Liang, Q. Xie, Y. Wang, S. Zhang, X. Qiao, X. Li, *Environ. Sci. Technol.*, 2011, **45**, 4839-4845.

33 C. Zhang, T. Sun and X. Sun, *Environ. Sci. Technol*., 2011, **45**, 4756-4762.

34 Y. Zhao and D. G. Truhlar, *Org. Lett*., 2006, **8**, 5753-5755.

35 S. E. Wheeler and K. N., *J. Chem. Theory. Comput.*, 2010, **6**, 395-404.

36 S. Rayne and K. Forest, *J. Mol. Struc-THEOCHEM*., 2010, **948**, 102-107.

37 S. Rayne and K. Forest, *Nat. Preced.*, 2010, Sep. 7.

38 S. Rayne and K. Forest, *Nat. Preced.*, 2010, Nov. 6.

39 B. Boekfa, S. Choomwattana, P. Khongpracha, J. Limtrakul, *Langmuir*, 2009, **25**, 12990-12999.

40 P. R. P. Barreto, A. F. A. Vilela, R. Gargano, *J. Mol. Struc-THEOCHEM*., 2003, **639**, 167-176.

41 X. Sun, C. Zhang, Y. Zhao, J. Bai, Q. Zhang and W. Wang, *Environ. Sci. Technol.*, 2012, **46**, 8148-8155.

42 R. Atkinson, *Chem. Rev.*, 1986, **86**, 69-201.

43 C. Li, H. Xie, J. Chen, X. Yang, Y. Zhang, X. Qiao, *Environ. Sci. Technol.*, 2014, **48**, 13808-13816.

44 R. G. Prinn, R. F. Weiss, B. R. Miller, J. Huang, F. N. Alyea, D. M. Cunnold, P. J. Fraser, D. E. Hartley and P. G. Simmonds, *Science*, 1995, **269**, 187-192.

45 G, P, Brasseur, J. J. Orlando and G. S. Tyndall, in Atmospheric Chemistry and Global Change, Oxford University Press, USA, 1999.

46 X. Tang, Y. Zhang and M. Shao, in Atmospheric Environmental Chemistry, Higher Education Press, Beijing, China, 2006.

47 B. J. Finlayson-Pitts and J. N. Pitts Jr, in Upper and Lower Atmosphere, Academic press, New York, 1999.

48 H.B. Singh, J.F. Kasting, *J. Atmos. Chem.*, 1988, **7**, 261-285.

49 B.J. Finlayson-Pitts, *Res, Chem. Interm.*, 1993, **19**, 235-249.

50 C.W. Spicer, E.G. Chapman, B.J. Finlayson-Pitts, R.A. Plastridge, J.M. Hubbe, J.D. Fast, C.M. Berkowitz, *Nature.*, 1998, **394**, 353-356.

51 K.W. Oum, M.J. Lakin, D.O. DeHaan, T. Brauers, B.J. FinlaysonPitts, *Science.*, 1998, **279**, 74-76.

52 B. J. Finlayson-Pitts and J. N. Pitts Jr, Atmospheric Chemistry: Fundamentals and Experimental Techniques (Wiley, New York, 1986).

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Table 1. Arrhenius formulas of rate constants k for elementary reactions at 200-400K ($^a$ $cm^3$ $molecule^{-1}$ $s^{-1}$, $^b$ $s^{-1}$)

| Reactions | $k_{298K}$ | Arrhenius formulas | | $R^2$ |
|---|---|---|---|---|
| $HCU + OH \rightarrow TSa1 \rightarrow IMa1 + H_2O$ | $7.28 \times 10^{-15}$ | $k(T)=2.00\times10^{-11}\exp(-2353.2/T)$ | a | 0.9999 |
| $HCU + OH \rightarrow TSa2 \rightarrow IMa2 + H_2O$ | $3.29 \times 10^{-13}$ | $k(T)=1.28\times10^{-11}\exp(-1083.4/T)$ | a | 0.9994 |
| $HCU + OH \rightarrow TSa3 \rightarrow IMa3 + H_2O$ | $1.44 \times 10^{-13}$ | $k(T)=2.05\times10^{-11}\exp(-1471.5/T)$ | a | 0.9997 |
| $HCU + OH \rightarrow TSa4 \rightarrow IMa4 + H_2O$ | $1.21 \times 10^{-13}$ | $k(T)=1.20\times10^{-11}\exp(-1364.9/T)$ | a | 0.9996 |
| $HCU + OH \rightarrow TSa5 \rightarrow IMa5 + H_2O$ | $5.72 \times 10^{-14}$ | $k(T)=2.96\times10^{-12}\exp(-1169.5/T)$ | a | 0.9995 |
| $HCU + OH \rightarrow TSa6 \rightarrow IMa6 + H_2O$ | $8.20 \times 10^{-16}$ | $k(T)=1.46\times10^{-12}\exp(-2222.9/T)$ | a | 0.9998 |
| $HCU + OH \rightarrow TSa7 \rightarrow IMa7 + H_2O$ | $6.75 \times 10^{-13}$ | $k(T)=1.89\times10^{-12}\exp(-300.29/T)$ | a | 0.9918 |
| $HCU + OH \rightarrow TSa8 \rightarrow IMa8 + H_2O$ | $3.39 \times 10^{-13}$ | $k(T)=8.59\times10^{-11}\exp(-1642.5/T)$ | a | 0.9997 |
| $HCU + OH \rightarrow TSa9 \rightarrow IMa9 + H_2O$ | $1.94 \times 10^{-15}$ | $k(T)=3.51\times10^{-11}\exp(-2915.4/T)$ | a | 0.9999 |
| $IMc1 \rightarrow TSb1 \rightarrow IMd1 + NO_2$ | $1.00 \times 10^{-19}$ | $k(T)=1.98\times10^{16}\exp(-24213/T)$ | b | 0.9999 |
| $IMc3 \rightarrow TSb3 \rightarrow IMd3 + NO_2$ | $9.76 \times 10^{-21}$ | $k(T)=5.18\times10^{12}\exp(-22448/T)$ | b | 0.9999 |
| $IMc5 \rightarrow TSb5 \rightarrow IMd5 + NO_2$ | $1.64 \times 10^{-24}$ | $k(T)=1.57\times10^{15}\exp(-26741/T)$ | b | 0.9999 |
| $IMc6 \rightarrow TSb6 \rightarrow IMd6 + NO_2$ | $7.88 \times 10^{-22}$ | $k(T)=8.41\times10^{14}\exp(-24715/T)$ | b | 0.9999 |
| $IMc7 \rightarrow TSb7 \rightarrow IMd7 + NO_2$ | $2.28 \times 10^{-24}$ | $k(T)=2.93\times10^{15}\exp(-26829/T)$ | b | 0.9999 |
| $IMc9 \rightarrow TSb9 \rightarrow IMd9 + NO_2$ | $4.41 \times 10^{-20}$ | $k(T)=1.33\times10^{14}\exp(-22967/T)$ | b | 0.9999 |
| $IMd1 \rightarrow TSc1 \rightarrow Pb1 + Cl$ | $7.37 \times 10^{5}$ | $k(T)=4.02\times10^{14}\exp(-5988.5/T)$ | b | 0.9999 |
| $IMd3 \rightarrow TSc3 \rightarrow Pb3 + Cl$ | $2.29 \times 10^{5}$ | $k(T)=2.76\times10^{12}\exp(-4853.0/T)$ | b | 0.9999 |
| $IMd5 + H_2O \rightarrow TSc5 \rightarrow Pb5 + OH$ | $8.58 \times 10^{-23}$ | $k(T)=7.11\times10^{-14}\exp(-6113.1/T)$ | a | 0.9999 |
| $IMd6 \rightarrow TSc6 \rightarrow Pb6 + Cl$ | $1.26 \times 10^{9}$ | $k(T)=1.62\times10^{15}\exp(-4184.0/T)$ | b | 0.9999 |
| $IMd7 + H_2O \rightarrow TSc7 \rightarrow Pb7 + OH$ | $8.24 \times 10^{-23}$ | $k(T)=1.19\times10^{-13}\exp(-6964.9/T)$ | a | 0.9999 |
| $IMd9 \rightarrow TSc9 \rightarrow Pb9 + Cl$ | $4.23 \times 10^{7}$ | $k(T)=3.36\times10^{14}\exp(-4728.5/T)$ | b | 0.9999 |

# Figure Captions

**Figure 1.** The atom numbers on the structure of 1,2,4,6,8,10,11-heptachloroundecane (HCU)

**Scheme 1.** Schematic diagram of the reaction pathways in the H abstraction and dechlorination reaction mechanisms of HCU with the barriers $\Delta E_b$ (kal/mol) and reaction heats $\Delta E_r$ (kcal/mol).

**Figure 2.** Profile of the potential energy surface for the oxidation and further dechlorination of IMa1

**Figure 3.** Profile of the potential energy surface for the oxidation and further dechlorination of IMa3

**Figure 4.** Profile of the potential energy surface for the oxidation and further dechlorination of IMa5

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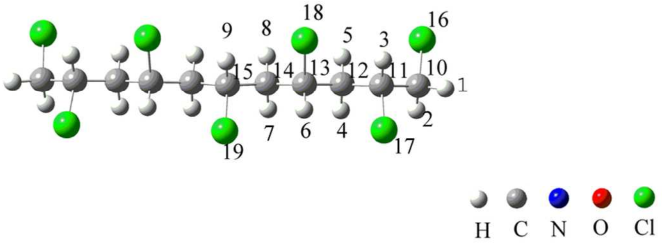

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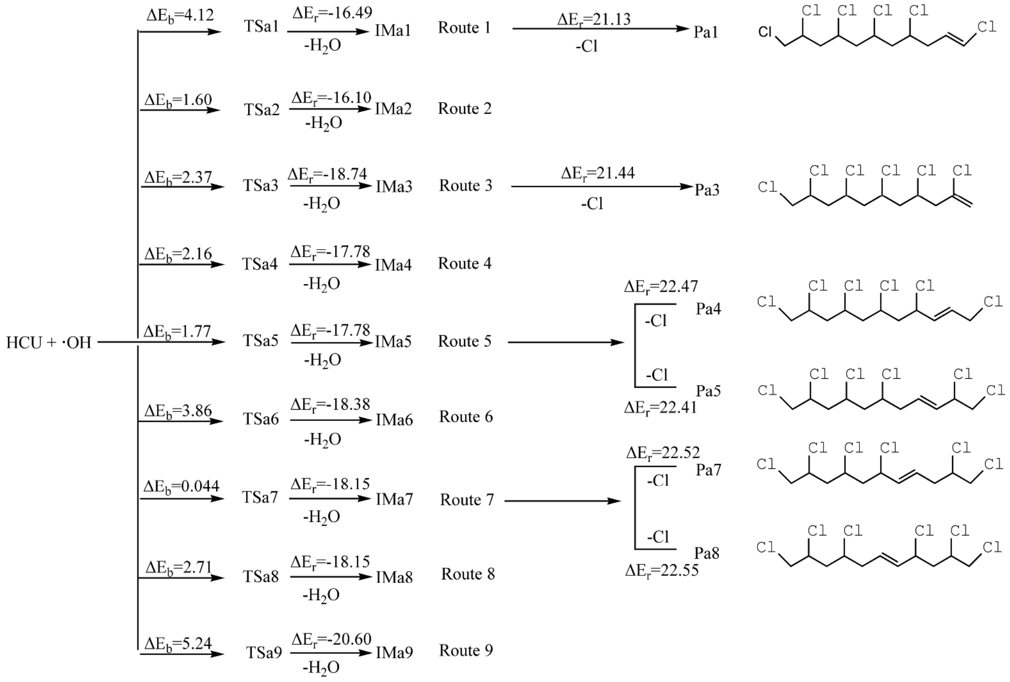

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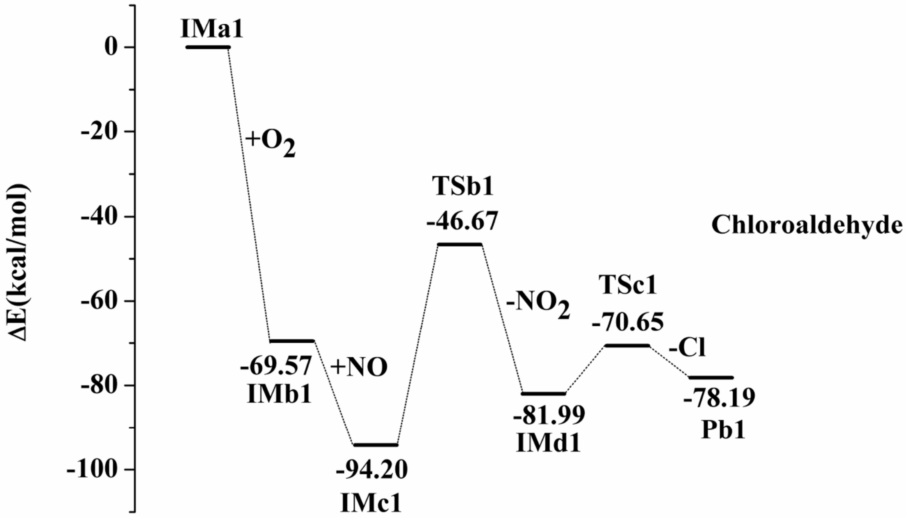

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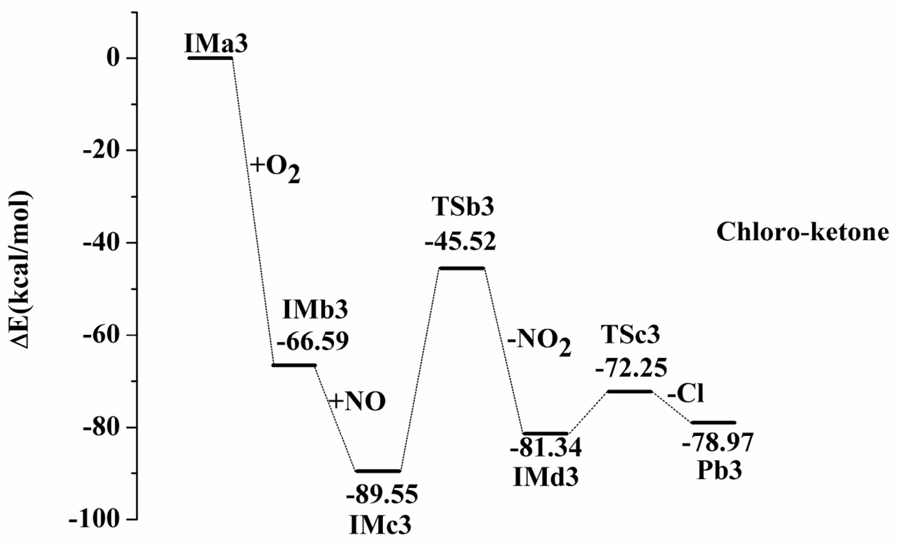

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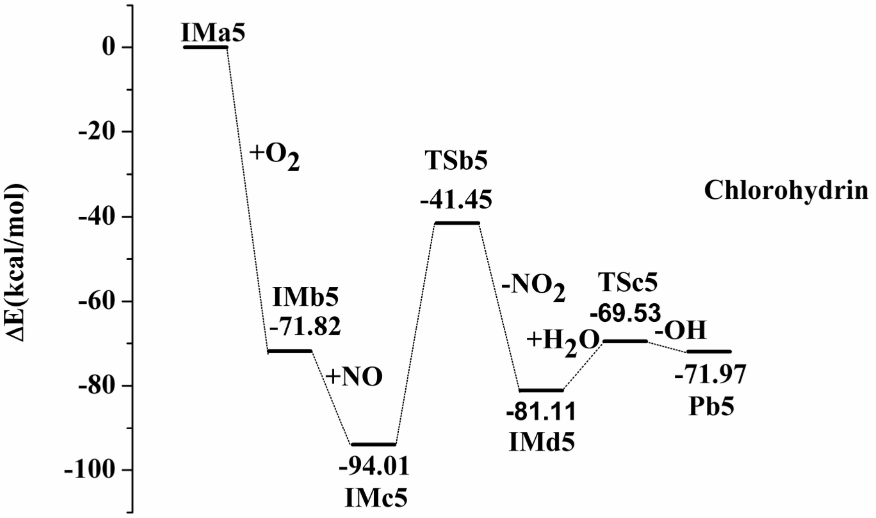

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