



Atmospheric oxidation mechanism of chlorobenzene



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HIGHLIGHTS

- OH addition to chlorobenzene occurs at *o*-, *m*-, and *p*-sites.
- Reaction of chlorobenzene-*o*-OH adduct with O₂ proceeds mainly by H-abstraction.
- Chlorophenol yields in chlorobenzene oxidation are high.
- Chlorophenol yields in chlorobenzene oxidation are pressure-dependent.
- Chlorinated nitrobenzenes could be formed in small yields.

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ABSTRACT

The atmospheric oxidation mechanism of chlorobenzene (CB) initiated by the OH radicals is investigated at M06-2X/6-311++G(2df, 2p) and ROCBS-QB3 levels. The oxidation is initiated by OH addition to the *ortho* (~50%), *para* (~33%) and *meta* (~17%) positions, forming CB-OH adducts as R2, R3, and R4; while the *ipso*-addition is negligible (~0.2%). The reactions of the CB-OH adducts with the atmospheric oxygen are further investigated in detail by coupling the unimolecular reaction rate theory calculations with master-equation (RRKM-ME). The CB-OH adducts react with O₂ either by irreversible H-abstraction to form chlorophenol and HO₂ or by reversible additions to form CB-OH-O₂ radicals, which subsequently cyclize to bicyclic radicals. RRKM-ME calculations show that the addition reactions of CB-OH and O₂ at the atmospheric pressure are close to but not yet reach their high-pressure-limits. The RRKM-ME simulations predict the yields of 93%, 38%, and 74% for *ortho*-, *meta*- and *para*-chlorophenols from the reactions of O₂ with R2, R3 and R4, being lower than their high-pressure-limit yields of 95%, 48%, an 80%, respectively. Overall, the yield of chlorophenols is determined as 72% at the atmospheric pressure.

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1. Introduction

Chlorobenzene (CB) is used mainly as intermediate in the synthesis of pesticides and other chemicals, and as solvent carrier for pesticides, rubber polymers and textiles dyes. CB is released into the environment upon its production and usage (EPA, 1995). With a vapor pressure of 1665 Pa at 298 K, CB exists mainly as gaseous form in the atmosphere. Concentrations of chlorobenzene in the atmosphere range typically from tens of ppt in remote areas to 1 ppb in cities, although high concentrations at tens of ppb could be detected near the sources such as the solid waste incineration sites (Chen et al., 2007; Yan et al., 2010).

Chlorobenzene is possibly removed from the atmosphere by its reactions with OH, NO₃, and O₃, photolysis and deposition. Atkinson et al. have measured the rate constants for reactions

and photolysis, and found that CB would be removed mainly by its reaction with the OH radicals, while photolysis and reactions with ozone or nitrate radicals are of negligible importance (Atkinson et al., 1985; Edney et al., 1986). Rate constant measurements (Mulder and Louw, 1987; Wallington et al., 1987; Bryukov et al., 2009) and theoretical study (Bryukov et al., 2009) found that the reaction of CB with OH would proceed via OH addition to the benzene ring at the atmospheric temperatures, while the H-abstraction and Cl-displacement become dominant only at high-temperatures. Theoretical calculations at different levels reached the same conclusion that the *ortho*- and *para*-additions would dominate over the *meta*- and *ipso*-additions, of which the barrier heights of *ipso*-addition is ~12 kJ/mol higher than others at all levels of calculations. This is different from the additions of OH to toluene (Suh et al., 2002; Wu et al., 2014), where the barrier height of *ipso*-addition is close to the others.

The atmospheric lifetime of chlorobenzene due to its reaction with the OH radicals can be estimated as ~13 days with the average OH concentration of 10⁶ molecule cm⁻³ (Atkinson et al., 1985);

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however, little information is available on the ultimate fate of CB in the atmosphere. In current study, the fate of CB in the atmosphere is investigated.

2. Theoretical methods

All the molecular structures, rotational constants and vibrational frequencies (in [Supplementary Data](#)) are calculated using density functional method of M06-2X/6-311++G(2df, 2p), which is suitable for structure optimizations and kinetic calculations (Zhao and Truhlar, 2008). The M06-2X structures are subject to electronic energy calculations by using the restricted-open-shell complete-basis-set model chemistry (ROCBS-QB3) (Wood et al., 2006) for reliable energies in kinetics calculations. High-pressure-limit rate constants for unimolecular (k_{uni} , in s^{-1}) and bimolecular (k_{b} , in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) reactions are estimated by traditional transition state theory (TST) as (Pilling and Seakins, 1999):

$$k_{\text{b}} = \sigma \cdot \kappa \cdot \frac{k_{\text{B}}T}{h} \cdot \exp\left(-\frac{\Delta_r G^\ddagger}{RT}\right) \cdot \frac{RT}{P^\circ} \cdot \frac{10^6}{N_{\text{A}}}$$

$$k_{\text{uni}} = \kappa \cdot k_{\text{B}}T/h \cdot \exp(-\Delta_r G^\ddagger/RT)$$

where k_{B} is the Boltzmann constant, $\Delta_r G^\ddagger$ the Gibbs energy barrier, σ the reaction-path symmetry number, κ the tunneling correction factor using the asymmetric Eckart model (Johnson and Heicklen, 1962). All the quantum chemistry calculations are performed using Gaussian 09 package (Frisch et al., 2009).

RRKM-ME calculations are carried out to investigate the reactions between CB-OH adducts and O_2 using the Mesmer program (Glowacki et al., 2012). The E -resolved microcanonical rate constants and collisional exponential-down model ($\langle \Delta E \rangle_{\text{d}} = 250 \text{ cm}^{-1}$) are employed to construct the master equation. The unimolecular rate constants are evaluated by the unimolecular RRKM theory (Holbrook et al., 1996):

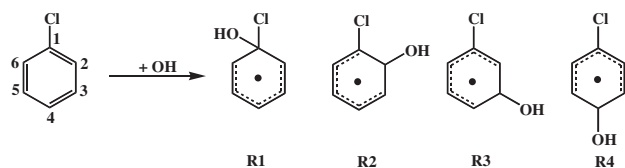
$$k(E) = \frac{\sigma m^\ddagger g_e^\ddagger}{\sigma^\ddagger m g_e} \cdot \frac{W(E - E_0)}{h\rho(E)}$$

where σ and σ^\ddagger are the external rotational symmetry numbers for the reactants and transition state, m and m^\ddagger the numbers of optical isomer, g_e and g_e^\ddagger the electronic state degeneracy, E_0 the reaction critical energy, $W(E - E_0)$ the sum of states of the transition state, and $\rho(E)$ the density of states of the reactants. The collisional parameters are estimated by the method of (Gilbert and Smith, 1990) as $\varepsilon = 720 \text{ K}$ and $\sigma = 6.7 \text{ \AA}$ for CB-OH- O_2 radicals. The RRKM-ME results at high pressures are equivalent to the results from traditional transition state theory.

3. Results and discussion

3.1. The initial OH addition

Four adducts Rn ($n = 1-4$) are possibly formed in the OH addition to chlorobenzene:



Transition states for the four additions are located at M06-2X level. Table 1 lists the calculated reaction energies and barrier heights, along with the estimated rate constants using transition state theory. The barrier heights ($\Delta E_{0\text{K}}^\ddagger$) of 11.2, -0.9, 2.3 and

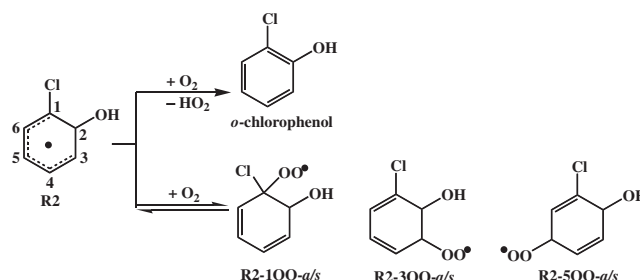
-0.7 kJ/mol at ROCBS-QB3 level are systematically lower than the M06-2X values of 23.6, 8.5, 12.8 and 8.3 kJ/mol for OH additions to C₁-C₄ positions, respectively; while the reaction energies from M06-2X and ROCBS-QB3 agree within 4 kJ/mol. Our ROCBS-QB3 barrier heights are also 2–3 kJ/mol lower than the CBS-QB3 values of 14.1, 2.6, 4.6, and 2.2 kJ/mol and 12–13 kJ/mol lower than the G3//B3LYP values of 24.0, 12.1, 14.9, and 12.4 kJ/mol by (Bryukov et al., 2009). The high barriers by G3//B3LYP are most likely due to the heavy spin contamination in the post-Hartree-Fock calculations based on the unrestricted wavefunction in G3; while CBS-QB3 contains the correction term for spin-contamination (Montgomery et al., 2000), therefore the barrier heights by CBS-QB3 are only slightly higher than those by ROCBS-QB3.

The estimated high-pressure-limit rate constant for the OH addition ($k_{\text{b},298\text{K}}$) is $5.56 \times 10^{-13} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ if using the ROCBS-QB3 barrier heights and $1.26 \times 10^{-14} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ if using the M06-2X ones. The former agrees well with the experimental values of $(8.8 \pm 1.1) \times 10^{-13} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ at atmospheric pressure (Atkinson et al., 1985), $(7.41 \pm 0.94) \times 10^{-13} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ at 50 Torr (Wallington et al., 1987), and $(6.02 \pm 0.34) \times 10^{-13} \text{ cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ at ~100 Torr (Bryukov et al., 2009). M06-2X greatly overestimates the barrier heights and therefore underestimates the rate constants. Nevertheless, ROCBS-QB3 and M06-2X predict similar branching ratios for R1–R4, e.g., 0.00, 0.50, 0.17, and 0.33 with ROCBS-QB3 versus 0.00, 0.49, 0.11, and 0.40 with M06-2X. At both levels of theory, addition to *ispo*-site is negligible, agreeing with the previous theoretical result (Bryukov et al., 2009). In the following, the fate of R2, R3, and R4 are examined on the basis of the reaction energies and barrier heights at ROCBS-QB3 level unless otherwise specified.

3.2. Fate of chlorobenzene-OH adducts

In the atmosphere, CB-OH adducts (R2, R3 and R4) can be sufficiently thermalized by collision, and are subject to reactions with O_2 , NO_x , and HO_x , etc. In analogy to the atmospheric oxidation mechanism of benzene and toluene (Suh et al., 2003; Glowacki et al., 2009; Wu et al., 2014), the reactions of CB-OH adducts with O_2 can proceed as direct H-abstraction to form (*o*-, *m*- and *p*-) chlorophenol and HO_2 irreversibly or as addition to form peroxy radicals reversibly. Besides back-decomposition to $\text{R2} + \text{O}_2$, the available unimolecular pathways for the peroxy radicals include ring-closure to bicyclic radicals, intramolecular H-shift from -OH to -OO, or concerted HO_2 elimination to chlorophenols. The peroxy radicals might also react with the atmospheric trace radicals such as NO_x , HO_2 , and RO_2 to form the alkoxy radicals and other products.

In the example of R2, its reaction with O_2 forms *o*-chlorophenol irreversibly by direct H-abstraction and R2-*iOO-a/s* ($i = 1, 3$ and 5) by reversible addition to C1, C3 and C5, where i denotes the position of O_2 addition and *a/s* (*anti/syn*) represents the O_2 approaching from the opposite or same direction of the ring with respect to the -OH group:



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