Computational and Theoretical Chemistry 971 (2011) 51–57

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Theoretical study of mechanism and kinetics for OH-initiated oxidation of o-cresol in the troposphere

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ARTICLE INFO

Article history:
Received 14 April 2011
Received in revised form 2 June 2011
Accepted 2 June 2011
Available online 12 June 2011

Keywords:
O-cresol
Hydroxyl radical
Reaction mechanism
B3LYP
CCSD(T)
Transition state study

ABSTRACT

Reaction mechanisms for the OH-initiated oxidation of o-cresol in the troposphere were investigated using B3LYP hybrid density functional method with the 6-311++G(2df,2pd) basis set. Single-point energy calculations with the same basis set were performed using the coupled cluster method with single, double, and perturbative triple configurations, CCSD(T). The equilibrium geometries, energies, and thermodynamics properties of all the stationary points along the addition reaction pathway and hydrogen abstraction reaction pathway were calculated. The rate constants and the branching ratios of each pathway were evaluated using classical transition state theory (TST) in the temperature range of 200–360 K, to simulated temperatures in all parts of the troposphere. The ortho (at position ortho- to the hydroxyl group) addition pathway was found dominant, accounting for 95.3–75.0% of the overall products from 200 to 360 K. The calculated rate constants are in good agreement with available experimental values. The addition reaction and hydrogen abstraction reaction are both thermodynamically irreversible.

1. Introduction

Aromatic compounds are precursors of photo-oxidants and secondary organic aerosols (SOA). The contribution of aromatic compounds to urban air pollution is widely recognized today [1,2]. The major sources of aromatic compounds in the atmosphere, including benzene, toluene, xylenes, and trimethylbenzenes, are emissions from vehicle exhaust and solvent use. Toluene is the most abundant aromatic compound in the urban air. The dominant products from the OH-initiated oxidation of toluene are cresols, and o-cresol accounts for about 80% of the cresol isomers [3]. However, the products of further reactions, particularly the OH-initiated oxidation of o-cresol, are still unclear. In the presence of NO_x ($NO + NO_2$), the gas-phase oxidation products include nitrocresols, pyruvic acid, acetyl peroxynitrate (PAN) and various particulate nitro-aromatic compounds [3–7]. Albarran and Robert [6] reported five initial products, including dihydroxytoluene and 2-hydroxybenzyl alcohol. These products are expected from the addition of OH at the ring or from the hydroxylation of the methyl group of o-cresol. Romeo et al. [7] also studied the ring-retaining products using FT-IR spectroscopy in the presence of NO_x. They didn't found the hydroxybenzaldehyde isomers from the hydroxylation of the methyl group of o-cresol, but found the 6-methyl-2-nitrophenol from the hydrogen abstraction by the hydroxyl group of o-cresol and the further reaction of the phenoxy radicals formed with NO_2.

The kinetics of the reaction of o-cresol with OH were studied [8–12]. Semadeni et al. [11] obtained the rate constant Arrhenius expression $k(T) = 2.1 \times 10^{-12}\exp[(881 \pm 356)/T]$ for the temperature range from 299 K to 373 K. The rate constants were negatively dependent on temperature.

It was shown in a recent study that the OH-initiated oxidation of o-cresol might closely be involved in the SOA formation in urban atmospheres [14]. However, very little is known about the detailed mechanism for the OH-initiated oxidation of o-cresol. At tropospheric temperatures, the OH-initiated oxidation of o-cresol proceeds either by the addition of OH to the aromatic ring to yield adducts, or by the abstraction of H atom from the methyl or hydroxyl group. To our best knowledge, no theoretical study has been reported on the mechanisms and kinetics of the o-cresol + OH reaction. The branching ratios of the several possible pathways have not been obtained. In this work, we attempt to carry out a systematic study of the reaction. We have determined the reaction pathways and rate constants for the addition and abstraction reactions, respectively. The equilibrium geometries, energies, and thermodynamics properties of all the stationary points are calculated using the B3LYP/6-311++G(2df,2pd) method, along with single-point energy calculations using the CCSD(T)/6-311++G(2df,2pd)//B3LYP/6-311++G(2df,2pd) method. Classical transition state theory (TST) is used to determine reaction rate constants in the range of temperatures from 200 K to 360 K. The branching ratios will be obtained from the calculated rate constants.

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doi:10.1016/j.comptc.2011.06.001

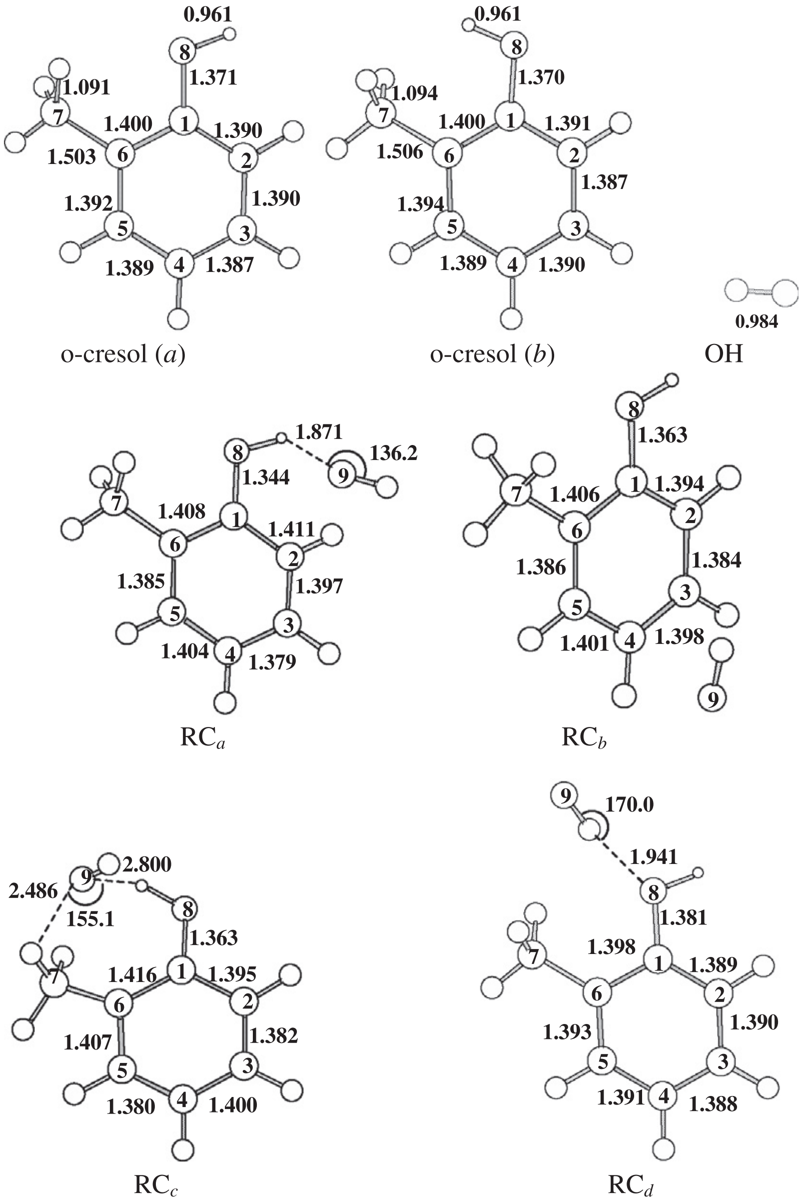
2. Computational methods

Density functional theory (DFT) with B3LYP hybrid functional [15–18] and the 6-311++G(2df,2pd) basis set has been used to obtain equilibrium geometries for the reactant complexes, transition state and product complexes. The stationary points were confirmed by analyzing the calculated harmonic frequencies: each potential minimum was confirmed by all positive frequencies while each transition state was confirmed by a single imaginary frequency. It is verified that the motion along the reaction coordinate corresponds to the expected transition vector. Single-point energy calculations were performed on the B3LYP/6-311++G(2df,2pd) geometries using the coupled cluster method with single, double, and perturbative triple configurations, CCSD(T), with the same basis set. All quantum chemical calculations were performed using the GAUSSIAN 03 [19] program package. The restricted (R) methods are used for singlet closed-shell species, and unrestricted (U) methods for doublet open-shell species.

The rate constants were calculated for the range of temperatures from 200 K to 360 K, matching possible temperatures in the troposphere. The calculations were carried out using the Computational Science and Engineering Online (CSEO) program package provided by Truong Research Group at University of Utah [20]. Classical transition state theory (TST) [21–23] with Eckart tunneling correction was used, and no tunneling corrections were made for reactions with negative activation energies [24–26]. According to classical TST, the rate constant, k, is calculated as

$$k = \Gamma \frac{k_B T}{h} \frac{Q^{TS}}{Q^{R}} e^{\left(-\frac{E^{TS}-E^{R}}{k_B T}\right)}$$

where Γ is the tunneling factor, k_B is Boltzmann's constant, h is Planck's constant, E^X and Q^X are total molecular energies (at 0 K) and standard molar partition functions (divided by Avogadro's number) of the TS and the reactant (marked as R), respectively. The partition functions were approximated as products of electronic, vibrational, internal–rotational (where applicable), rotational and translational partition functions. Standard molar partition functions were calculated for the ideal gas at the standard pressure, 1 atm. The contribution of the imaginary frequency of the



o-cresol (a) o-cresol (b) OH

RC$_a$ RC$_b$

RC$_c$ RC$_d$

Fig. 1. Optimized geometries of the reactants and the reactant complexes (RC) with selected bond distances (in Å) and bond angles (in °).