Chemosphere 171 (2017) 49–56

Contents lists available at ScienceDirect

Chemosphere

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

Understanding the insight into the mechanisms and dynamics of the Cl-initiated oxidation of $(CH_3)_3CC(O)X$ and the subsequent reactions in the presence of NO and O_2 ($X = F$, Cl, and Br)

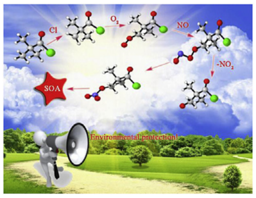
Feng-Yang Bai, Shuang Lv, Yuan Ma, Chun-Yu Liu, Chun-Fang He, Xiu-Mei Pan*

Institute of Functional Material Chemistry, National & Local United Engineering Lab for Power Battery, Faculty of Chemistry, Northeast Normal University, 130024, Changchun, People's Republic of China

HIGHLIGHTS

- We studied mechanism of Cl-initiated oxidation of $(CH_3)_3CC(O)X$ ($X = F$, Cl, and Br).
- The total rate constants are computed for $(CH_3)_3CC(O)X$ ($X = F$, Cl, and Br) at 298 K.
- Atmospheric lifetimes and GWPs for $(CH_3)_3CC(O)X$ ($X = F$, Cl, and Br) are estimated.
- The subsequent reactions may produce organic aerosol in the presence of O_2/NO.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 October 2016
Received in revised form
7 December 2016
Accepted 8 December 2016
Available online 10 December 2016

Handling Editor: I. Cousins

Keywords:
Halogenated organic volatile compounds (HVOCs)
Chlorine atom
Reaction mechanism
Atmospheric lifetime
Rate constant

ABSTRACT

In this work, the density functional and high-level *ab initio* theories are adopted to investigate the mechanisms and kinetics of reaction of $(CH_3)_3CC(O)X$ ($X = F$, Cl, and Br) with atomic chlorine. Rate coefficients for the reactions of chlorine atom with $(CH_3)_3CC(O)F$ (k_1), $(CH_3)_3CC(O)Cl$ (k_2), and $(CH_3)_3CC(O)Br$ (k_3) are calculated using canonical variational transition state theory coupled with small curvature tunneling method over a wide range of temperatures from 250 to 1000 K. The dynamic calculations are performed by the variational transition state theory with the interpolated single-point energies method at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-311++G(d,p) level of theory. Computed rate constant is in good line with the available experimental value. The rate constants for the title reactions are in this order: $k_1<k_2<k_3$, suggesting that the effect of halogen substitution on the mechanisms and dynamics is different. The subsequent and secondary reactions for the hydrogen abstraction intermediates are studied involving NO and O_2 molecules in the atmosphere. The atmospheric lifetime and global warming potential (GWP) of $(CH_3)_3CC(O)X$ ($X = F$, Cl, and Br) are estimated, and it shows that $(CH_3)_3CC(O)F$ have larger GWP value than that of $(CH_3)_3CC(O)Cl$ and $(CH_3)_3CC(O)Br$. Due to the presence of Cl and Br atoms, the environmental impact of $(CH_3)_3CC(O)Cl$ and $(CH_3)_3CC(O)Br$ may be given more concerns.

1. Introduction

The impact of halogenated compounds still prompts significant interest in the lifetime of halogenated organic volatile compounds

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* Corresponding author.
E-mail address: panxm460@nenu.edu.cn (X.-M. Pan).

http://dx.doi.org/10.1016/j.chemosphere.2016.12.037
0045-6535/

(VOCs) in their atmospheric degradation products (Vereecken and Francisco, 2012). The oxygenated or halogenated VOCs in the atmosphere will have an impact on air quality, climate, and the ozone layer (Good and Francisco, 2003; Mellouki et al., 2015). The trimethylacetyl chloride $(CH_3)_3CC(O)Cl$ is a the typical halogenated VOCs (boiling point (bp): 375–377 K) and may be released into the atmosphere. It can decompose in the gas phase at 626–699 K into isobutylene, carbon monoxide, and hydrogen chloride with the rate constant by $k = 2.52 \times 10^{14} \exp(-55150/RT)\ s^{-1}$ (Lennon and Stimson, 1969). Trimethylacetyl chloride can be come from the secondary reaction of pivalaldehyde $(CH_3)_3CC(O)H$ with atomic chlorine. Crane et al. (2004) and Rayez et al. (2011) have reported the rate coefficient of $(CH_3)_3CC(O)H$ with Cl atom in experiment $(1.15 \pm 0.30) \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$ and theory $(1.44 \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1})$ at 298 ± 2 K, respectively. The results indicate that the H-abstraction reaction from −C(O)H site is the most favorable pathway and thus $(CH_3)_3CC(O)Cl$ may be formed by $(CH_3)_3CC(O\bullet)$ with Cl atom in this style. Chlorine atoms are known to contribute high reactivity and high concentration in the marine boundary layer (Oum et al., 1998; Spicer et al., 1998). Therefore, the oxidations by Cl atoms play a vital role in determining the lifetime of $(CH_3)_3CC(O)Cl$ and cannot be ruled out in the atmosphere. Crane et al. (2004) have investigated on the kinetics for reaction of $(CH_3)_3CC(O)Cl + Cl$ by the relative rate technique and the experimental rate constant was found to be $(6.86 \pm 1.50) \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$ at 296 K. The $(CH_3)_3CC(O)F$ (bp: 340.5–341 K) and $(CH_3)_3CC(O)Br$ (bp: 397–399 K) are also the important acyl halides, it is significative to establish the order of reactivity of these three trimethylacetyacetyl halides reaction with Cl atom. And also the difference and similarity in mechanisms and kinetics of the three acyl halides reactions with Cl atom are very desirable. Nevertheless, there is no experimental research on the Cl-initiated oxidation of $(CH_3)_3CC(O)F$ and $(CH_3)_3CC(O)Br$. It is necessary to systematic formulate or explain the sets of scattered experimental data. Herein, we firstly examine the reaction mechanism and kinetics of $(CH_3)_3CC(O)X + Cl$ (X = F, Cl, and Br) reactions using DFT and dual-level direct dynamic methods.

$(CH_3)_3CC(O)F + Cl \rightarrow \bullet CH_2(CH_3)_2CC(O)F + HCl$ (R1a–R1e)

$(CH_3)_3CC(O)Cl + Cl \rightarrow \bullet CH_2(CH_3)_2CC(O)Cl + HCl$ (R2a–R2e)

$(CH_3)_3CC(O)Br + Cl \rightarrow \bullet CH_2(CH_3)_2CC(O)Br + HCl$ (R3a–R3e)

The objective of the present work is to make a kinetic and mechanistic study of the reactions of Cl atoms with $(CH_3)_3CC(O)X$ (X = F, Cl, and Br) and consequently to evaluate their subsequent behaviors in the presence of NO/O_2 and atmospheric implications. The atmospheric lifetime and global warming potential (GWP) of $(CH_3)_3CC(O)X$ (X = F, Cl, and Br) are also computed. The computational research on the fate and decomposition pathways of $\bullet OCH_2(CH_3)_2CC(O)X$ radicals (X = F, Cl, and Br) via four various pathways involving oxidation, bond dissociation, and water participation processes are reported as well (see Fig. 1). The rate constants of $Cl + (CH_3)_3CC(O)X$ (X = F, Cl, and Br) are obtained and compared each other to give some meaningful evidence for the effects of halogen substitution on the dynamics of these kinds reactions.

2. Computational methods

The electronic structure calculations are carried out with the GAUSSIAN 09 program (Frisch et al., 2009). Optimized geometries and corresponding energies for reactants, products, complexes, and transition states are determined using the B3LYP/6-311++G(d,p) method (Becke, 1993; Stephens et al., 1994), which has been proved to be an economical and accurate computational model for obtaining reliable results and has been employed widely (Bai et al. 2015, 2016a; Canneaux et al., 2012; Gao et al., 2015; Ng et al., 2013; Wang et al., 2015; Weber et al., 2014). The spin contamination for all species shows insignificant. The harmonic frequencies of all species are computed at the same level of theory in order to confirm the nature of the stationary points and to determine zero-point energies. The calculated harmonic vibrational frequencies were multiplied by an appropriate scaling factor (0.9688). Intrinsic reaction coordinate (IRC) analysis is performed to verify that each transition states uniquely connected the corresponding reactants with the products (Gonzalez and Bernhard Schlegel, 1989). The energy profiles of the title reactions are refined at the high-accuracy method of CCSD(T) (Purvis and Bartlett, 1982; Scuseria et al., 1988) in conjunction with the aug-cc-pVDZ basis set (Dunning, 1989; Kendall et al., 1992) to confirm the reliability based on the geometries mentioned above. Enthalpies of formation for the reactants (R1, R2, and R3) and product radicals (P1a, P1b, P1c, P2a, P2b, P2c, P3a, P3b, and P3c) at 298 K are estimated by the isodesmic reactions 1a-6c in the supporting information.

The paths for reactions of $(CH_3)_3CC(O)X$ (X = F, Cl, and Br) with Cl atom are computed via direct dynamics and all dynamic computations are executed with POLYRATE program (Corchado et al., 2007). Theoretical rate constants for each reaction channel over the temperature range of 250–1000 K are calculated by canonical variational transition state theory (CVT) (Garrett and Truhlar, 1979; Garrett et al., 1980). The tunneling transmission probability is calculated by the small-curvature tunneling approximation (Liu et al., 1993; Lu et al., 1992). The CVT thermal rate constant is computed by Eqs. (1) and (2):

$$k_s^{CVT}(T) = min\ k^{GT}(T, s) \quad (1)$$

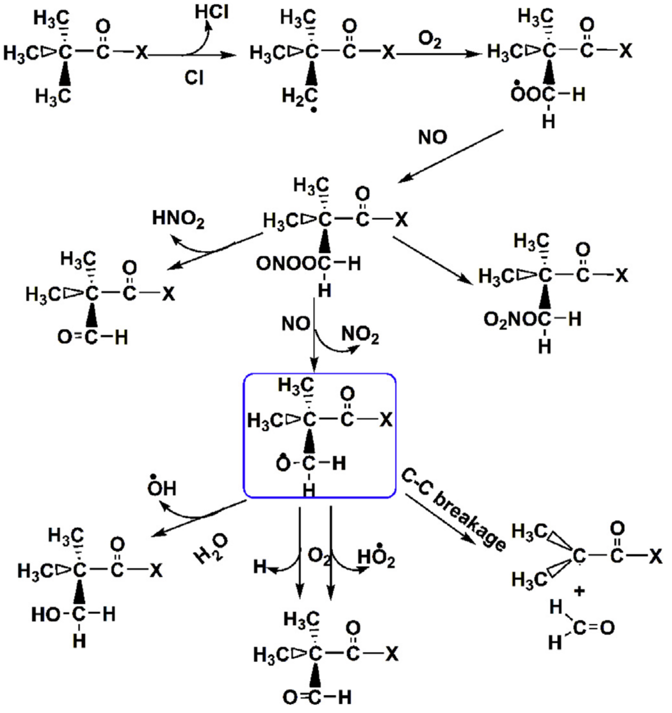

Fig. 1. Atmospheric degradation of $(CH_3)_3CC(O)X$ (X = F, Cl, and Br) by Cl atom in the presence of NO and O_2.