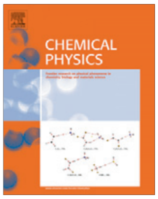
Chemical Physics 415 (2013) 161–167

Contents lists available at SciVerse ScienceDirect

Chemical Physics

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



Cycloaddition of ozone to allyl alcohol, acrylic acid and allyl aldehyde: A comparative DFT study

Jing Yang [a,*], Jiankui Miao [a], Xuejiao Li [a], Wenguo Xu [b,*]

[a] *Department of Chemistry, Tangshan Normal College, Tangshan 063000, PR China*
[b] *The Key Laboratory of Cluster Science, Ministry of Education of China, School of Science, Beijing Institute of Technology, Beijing 10008, PR China*

ARTICLE INFO

Article history:
Received 9 May 2012
In final form 8 January 2013
Available online 17 January 2013

Keywords:
Cycloaddition
Ozone
Allyl alcohol
Acrylic acid
Allyl aldehyde
Rate constant

ABSTRACT

Density functional theory and ab initio methods have been used to calculate the structures and energies of minima and transition sates for the cycloadditions of ozone to allyl alcohol, acrylic acid and allyl aldehyde. The results show that the reactivity of the compounds with respect to addition of ozone to the double bond is a function of the nature of the oxygenated substituents. The acrylic acid is more reactive toward ozone than the corresponding allyl aldehyde, consistent with the relative magnitude of the electron-withdrawing influence of the substituent oxygenated groups. In comparison with acrylic acid and allyl aldehyde, the cycloaddition of ozone to allyl alcohol should be the most favored thermodynamically. Moreover, the calculated rate constants of the three cycloaddition reactions at the BH&HLYP/6-31 + G(d, p) level of theory are in good agreement with experimental data.

1. Introduction

Volatile organic compounds, or VOCs, are an important class of air pollutants, commonly found in the atmosphere at ground level in all urban and industrial centres [1–7]. Field measurements indicate that oxygenated VOCs form a major component of the trace gasses found in the troposphere [8], and hence play an important role in determining the oxidizing capacity of the troposphere both on a regional and a global scale [9]. Oxidation of unsaturated oxygenated compounds in the atmosphere can be initiated by the reaction with ozone [10–13], nitrate and hydroxyl radicals. The reduction of VOCs can be estimated by air quality simulation models such as the regional atmospheric chemistry mechanism (RACM) or the master chemical mechanism (MCM) [14]. In these models, the initial reaction step with ozone involves some unsaturated oxygenated compounds, since they contain unsaturated carbon bonds that are the preferred sites for ozone addition. Unsaturated oxygenated compounds, such as alcohols, aldehydes, and acids et al. are of major importance in the atmosphere, which are present as a result of direct anthropogenic and biogenic emissions [15]. In comparison to the extensive kinetic and mechanistic database available on the gas-phase ozonolysis reactions of alkenes, however, the information on the gas-phase ozonolysis reactions of unsaturated oxygenated compounds is currently limited [16–21]. The reaction mechanisms and reaction rate constants should, as is the case for alkenes [22], vary as a function of the nature of substituents. Therefore, in this paper, allyl alcohol, acrylic acid, and allyl aldehyde are considered as model VOCs to evaluate the effect of different functional groups in the ozonolysis reactions. In this context, thermodynamics and kinetics studies of relevant gas-phase reactions of ozone with these important compounds would assist in understanding their fates in the atmosphere and industry.

The mechanisms of ozonolysis of the alkenes introduced by Criegee [23,24], now widely accepted in literatures, have been proven in a remarkable way: the path for the ozonolysis reaction passes through an O-envelope-shaped van der Waals (VDW) complex and a transition state, and then produces a primary ozonide with a similar structure to the transition state. In this work, transition states for the relatively simple model compounds allyl alcohol, acrylic acid, and allyl aldehyde in their reaction with ozone will be determined and the heights of the reaction barriers will be calculated. A detailed analysis of the geometries of the stationary points on the potential energy surfaces is given. The results are briefly discussed with respect to substituent effects on reactivity. The thermal rate constants of the title reactions are calculated using the conventional transition state theory (TST) [25], the canonical variational transition state theory (CVT) [25–28] coupled with the small-curvature tunneling (SCT) correction (CVT/SCT) [29–31] and the microcanonical variational transition state theory (μVT) [25,32,33] based on the density functional theory calculations.

---

[*] Corresponding authors. Fax: +86 0315 3863291.
E-mail address: yjlzddove@tstc.edu.cn (J. Yang).

http://dx.doi.org/10.1016/j.chemphys.2013.01.005

2. Calculation methods

2.1. Electronic structure calculations

Earlier studies have shown that the hybrid Hartree–Fock density-functional method, abbreviated HDFT, can provide reasonably accurate prediction of the information along the reaction path. In this study, the geometries and frequencies of all stationary points (reactants, transition states and the primary ozonides) are optimized using the BH&HLYP method in conjunction with 6-31 + G(d, p) basis set that was also demonstrated to be an effective basis set in Truhlar et al.'s study [34]. Synchronously, to validate the reliability of the BH&HLYP method, the same calculations are performed by MPWB1K [35,36] and MPW1K [37–39] methods with the same basis set. The graphical representations of all stationary points for the title reactions are depicted in Figs. 1–3, respectively. Single-point energy calculations are performed at the CCSD(T)/6-31 + G (df, p) level of theory based on BH&HLYP-optimized geometries. The minimum energy paths (MEPs) from $s = -1.50$–$1.50\ \mathrm{amu}^{1/2}$ bohr are done in the mass weighted Cartesian coordinate with a step size of $0.01\ \mathrm{amu}^{1/2}$ bohr, using the intrinsic reaction coordinate (IRC) method at three DFT levels of theory. Along this energy path, the reaction coordinate s is defined as the signed distance from the saddle point, with $s > 0$ referring to the product side. At 20 selected points (selected by a focusing technique [40]) along the MEP, the force constant matrixes as well as the harmonic vibrational frequencies are calculated at the same levels of theory. Furthermore, the energies of the selected points are refined by the CCSD(T) method. In addition, the method of natural bond orbital (NBO) analysis [41] has been used to study the orbital interactions as well as the electronic structure of these compounds at the BH&HLYP/6-31 + G(d, p) level. The calculated absolute energies, harmonic frequencies, and zero-point energies of the molecules considered in this work are given in the Supporting Information (Tables 1S and 2S). All the above calculations are performed using the Gaussian 03 [42] program.

2.2. Rate constant calculations

The conventional transition state theory, the canonical variational transition state theory, and the microcanonical variational transition state theory are employed to calculate the rate constants for the two bimolecular reactions. There exists the considerable literatures on the TST, CVT and μVT formalisms. Below, we give only a brief description of them, which has been implemented in the Vklab 1.0 [43] programs.

Within the transition-state theory (TST) [25] framework, thermal rate constants of a reaction can be expressed as

$$K(T) = \kappa(T)\sigma\frac{k_B T}{h}\frac{Q^{\neq}(T)}{\Phi^R(T)}e^{\{-\Delta V^{\neq}/k_B T\}}$$

where κ is the transmission coefficient accounting for the quantum mechanical tunneling effects; σ is the reaction symmetry number; $Q^{\neq}$ and Φ^R are the total partition functions (per unit volume) of the transition state and reactants, respectively; $\Delta V^{\neq}$ is the classical barrier height; T is the temperature; k_B and h are the Boltzmann and Plank constants, respectively.

The variational transition state rate constant for a gas-phase bimolecular reaction is determined by varying the location of the dividing surface along a reference path to minimize the rate constant at a given temperature. In other words, CVT minimizes the recrossing effects by effectively moving the dividing surface along the minimum energy path (MEP) so as to minimize the rate constant. In the present study, the MEP is defined as the steepest descent path from the saddle point to both the reactant and product sides in the mass-weighted Cartesian coordinate system. The reaction coordinate, s, is defined as the distance along the MEP with the origin located at the saddle point and is positive on the product side and negative on the reactant side. For a canonical ensemble at a given temperature T, the canonical variational transition state theory (CVT) [26–28] thermal rate constant $k^{\mathrm{CVT}}(T)$ is given by

$$k^{\mathrm{CVT}}(T) = \min_s k^{GT}(T, s)$$

where

$$k^{GT}(T, s) = \left\{\sigma\frac{k_B T}{h}\frac{Q^{GT}(T, s)}{\Phi^R(T)}e^{-V_{\mathrm{MEP}}(s)/k_B T}\right\}$$

where $k^{GT}(T,s)$ is the generalized transition state theory rate constant at the dividing surface which intersects the MEP at s and is orthogonal to the MEP. Here, σ is the symmetry factor accounting for the possibility of more than one symmetry-related reaction path, k_B is Boltzman's constant and h is Plank's constant. Q^{GT} is the internal partition function of the generalized transition state with the local zero of energy at $V_{\mathrm{MEP}}(s)$. Φ^R is the reactant partition

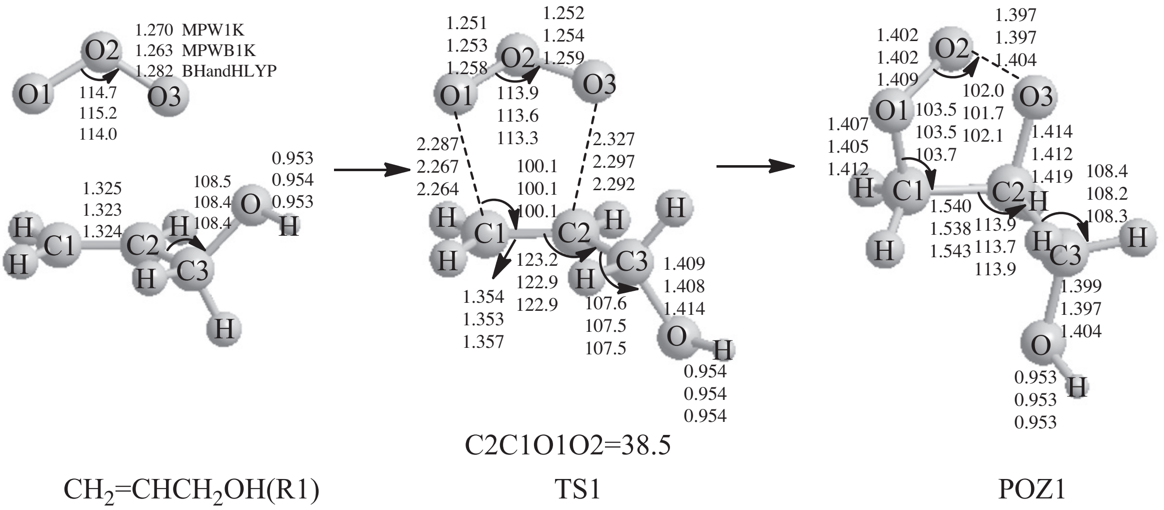


Fig. 1. Cycloaddition of ozone on allyl alcohol: Optimized BH&HLYP, MPWB1K and MPW1K geometries of the stationary points. Angles are given in degree, and bond distances are given in angstroms.