Theoretical studies on the kinetics and mechanism of multi-channel gas-phase unimolecular reaction of ethyl acetate

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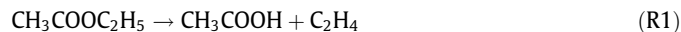
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ABSTRACT

The potential energy surface of the gas-phase unimolecular decomposition of ethyl acetate is investigated by using various quantum chemical methods including CCSD(T), GBS-QB3, BB1K, M06-2X, MP2 and B3LYP. Modified strong collision/RRKM theory was used to calculate the unimolecular rate constants of different reaction channels as a function of pressure and temperature. It is found that the major reaction pathway is the channel producing ethylene and acetic acid. Some reaction channels could contribute to the overall rate constant at high temperatures. The computed rate constants are compared with the available experimental data.

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1. Introduction

The unimolecular decomposition reaction of esters is of great importance from theoretical and practical stand points. As typical biodiesel fuels, numerous engine combustion studies have been performed using methyl- and ethyl-ester compounds along with their constituents [1]. Due to the high molecular weights of biodiesel fuels, simpler esters like methyl butanoate and ethyl propanoate are used in chemical kinetics modeling of combustion of these fuels [2,3]. Smaller esters have the essential chemical structural features of biodiesel fuels and can be used to simulate the chemical reactions of biodiesel. As a consequence, the unimolecular decomposition reaction of ethyl acetate has also been the subject of extensive experimental studies [4–20]. On the basis of the results from experimental investigations reported in the literature and the present theoretical study, many reaction channels for unimolecular reaction of ethyl acetate might be written as follows:

$$CH_3COOC_2H_5 \rightarrow CH_3COOH + C_2H_4 \quad (R1)$$
$$\rightarrow 2CH_3COH \quad (R2)$$
$$\rightarrow CH_3CH_2OH + CH_2CO \quad (R3)$$
$$\rightarrow CH_3COO^{\cdot} + {}^{\cdot}C_2H_5 \quad (R4)$$
$$\rightarrow CH_3^{\cdot} + {}^{\cdot}COOC_2H_5 \quad (R5)$$
$$\rightarrow CH_3COOCH_2^{\cdot} + {}^{\cdot}CH_3 \quad (R6)$$

$$\rightarrow CH_3CO^{\cdot} + {}^{\cdot}OC_2H_5 \quad (R7)$$
$$\rightarrow CH_3COOCH^{\cdot}CH_3 + {}^{\cdot}H \quad (R8)$$
$$\rightarrow H^{\cdot} + {}^{\cdot}CH_2COOC_2H_5 \quad (R9)$$
$$\rightarrow CH_3COOC_2H_4^{\cdot} + {}^{\cdot}H \quad (R10)$$

Although all reaction channels could have contributions to the overall reaction [2,3], several experimental studies have focused at the reaction R1 which is shown to be the major channel. In pioneering studies, Blades and Gilderson [4,5] have investigated the pyrolysis of ethyl acetate in a flow system with toluene as a carrier gas and reported the Arrhenius equation $k_1 = 3.06 \times 10^{12} \times \exp(-199.78 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ for the reaction R1 over the temperature range of 782–884 K. The rate constant expression $k_1 = 4.94 \times 10^{11} \times (T/298) \times \exp(-194.55 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ has been reported by Scheer et al. [6] for the reaction R1 over the temperature range 725–810 K. Kwart et al. [8] have investigated the reaction R1 by gas chromatography techniques and obtained the rate expression $k_1 = 1.87 \times 10^{12} \times \exp(-195.39 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ in the temperature range from 745 to 834 K.

In 1972, Beadle et al. [9] have studied the reaction channel R1 at very low pressures (about 0.1 Torr) using Mass spectrometry technique. They reported a first-order kinetics with the Arrhenius expression $k_1 = 3.98 \times 10^{12} \times \exp(-200.83 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$. In order to understand the substituent effect on the nature of the transition state in ester pyrolysis, Taylor et al. [10–13] have studied extensively the thermal decomposition of several esters including ethyl acetate. The rate constant expression for k_1 was found as $k_1 = 3.13 \times 10^{12} \times \exp(-202.92 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$. By using a laser induced fluorescence analytical technique [abstract], Zitter et al. [15] found the Arrhenius expression for the reaction R1 as

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$k_1 = 1.35 \times 10^{13} \times \exp(-202.00 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ over the temperature range of 813–952 K at the pressure 50 Torr. An infrared laser was used as a "thermal switch" to study pyrolysis reactions under effectively wall-less conditions by McMillen et al. [17] and the rate constant expression $k_1 = 6.31 \times 10^{12} \times \exp(-205.01 \text{ kJ mol}^{-1}/RT)$ s^{-1} was obtained in the temperature range from 950 to 1000 K at the pressure 100 Torr. In the most recent study which covers the wide and high temperature range of 1300–1800 K, Swihart et al. [20] have performed pulsed laser powered homogeneous pyrolysis along with gas chromatography analytical technique to measure rate parameters for unimolecular decomposition of ethyl acetate and reported the rate constant expression as $k_1 = 2.57 \times 10^{17} \times \exp(-274.04 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$.

To the best of our knowledge, no ab initio study is performed on the kinetics and mechanism of the unimolecular decomposition of ethyl acetate. In the present study, the potential energy surface of ethyl acetate has been investigated in order to locate the stationary points, i.e., minimum energy structures and saddle points. Several dissociation channels of these compounds have been examined using different quantum chemical calculations. RRKM and transition state theories are employed to calculate the unimolecular rate constants as a function of pressure and temperature. The computed molecular parameters and rate constants are compared with the available experimental data.

2. Computational details

All of the quantum chemical calculations were performed with the Gaussian 09 package of programs [21]. Second-order Møller–Plesset perturbation (MP2) theory [22] in combination with the standard 6-311+G(2d,2p) basis set were employed to optimize the geometries of all stationary points, i.e., reactants, saddle points and products. Restricted wave functions for closed-shell system and unrestricted wave functions for open-shell system were used. Vibrational frequencies of all species were obtained at the same levels of theory. The vibrational frequencies of transition states were examined using molecular visualization to verify that the imaginary frequency corresponds to the reaction coordinate. Energies at all of the stationary points were then recalculated with the coupled cluster method with single, double, and noniterative triple excitations uCCSD(T) [23] along with the 6-311+G(2df,2p) basis set. In addition, the energies of all stationary points were also calculated by the complete basis set CBS-QB3 [24] method. This method is a combination of many single point energy calculations on the geometries optimized by B3LYP/CBSB7 method and designed for accurate enthalpies of formation, ionization potentials, electron affinities, proton affinities and reaction energies.

The hybrid meta density functional methods (HMDFT), BB1K [25] and M06-2X [26] methods along with the 6-31+G(d,p) and MG3S basis sets [27] were also used for the purpose of comparison. These methods are optimized against a representative database of very high level calculations of saddle point geometries and energies. These two methods mix a pure DFT functional with some non-local exchange with kinetic energy density which depends on density as well as the gradient of density and give remarkably accurate barrier heights with slight deterioration of reaction energetics.

Electronic structure calculations at the BB1K/6-311+G(d,p) level of theory were performed to explore the minimum energy path (MEP) from transition states to the corresponding minima. Intrinsic reaction coordinate (IRC) [28] method in the mass-weighted Cartesian coordinates with a step size of 0.1 $(\text{amu})^{1/2}$ bohr was used in order to compute the minimum energy path. In addition, the geometry optimizations and the frequency calculations were performed at the B3LYP level with the correlation-consistent polarized triple-ζ basis set cc-pVTZ [29].

In this research, RRKM theory was used to compute the rate constants for decomposition of ethyl acetate, as a function of temperature and pressure [30,31]. According to the RRKM theory, the energy-specific rate constant for unimolecular reaction is given by equation:

$$k(E) = L^{\ddagger} \frac{Q_1^+}{Q_1} \frac{G(E_{vr}^+)}{h\rho(E)} \tag{1}$$

where $L^{\ddagger}$ is the statistical factor, $G(E_{vr}^+)$ is the sum of active vibrational and rotational states for the transition state, $\rho(E)$ is the density of active quantum states for reactant, Q_1^+ and Q_1 are the partition functions for the adiabatic rotations in the transition state and reactant. In the Whitten–Rabinovitch approximation [32], the following expression is used for the vibrational sum of state.

$$G(E^+) = \frac{(E^+ + aE_z)}{s!\prod_{i=1}^{s} h v_i} \tag{2}$$

Here E is the vibrational internal energy, E_z is the zero-point energy, s is the number of the vibrational degrees of freedom, and v_i is the frequency of the ith vibrational mode. The parameter a is calculated via the equations

$$\alpha = 1 - \beta w(\varepsilon) \tag{3}$$

with β being the modified dispersion frequency parameters

$$\beta = \frac{s-1}{s} \frac{\langle v^2 \rangle}{\langle v \rangle^2} \tag{4}$$

By comparing with the state sums for various organic and inorganic molecules calculated by direct count, Whitten and Rabinovitch obtained the following expression for w.

$$w = (5.00\varepsilon + 2.73\varepsilon^{0.5} + 3.51)^{-1} \quad 0.1 < \varepsilon < 1.0 \tag{5a}$$

$$w = \exp(-2.4191\varepsilon^{0.25}) \quad 1.0 < \varepsilon < 8.0 \tag{5b}$$

Here, ε is the internal energy scaled with the zero-point energy.

$$\varepsilon = E/E_z \tag{6}$$

The expression for the density of state is obtained from the derivative of Eq. (2) as follows.

$$\rho(E) = \frac{(E + aE_Z)^{s-1}}{(s-1)! \prod h v_i} \left[1 - \beta \left(\frac{dw}{d\varepsilon} \right) \right] \tag{7}$$

The first-order rate constants were calculated by the following expression.

$$k_{uni} = \frac{L^{\ddagger} Q_1^+ \exp(-E_0/RT)}{hQ_1Q_2} \int_{E^+=0}^{\infty} \frac{\{W_{vr}^+\} \exp(-E^+/RT) \, dE^+}{1 + k_a(E^*)/\beta_C Z[M]} \tag{8}$$

Here, Q_1 and Q_2 represent the rotational and vibrational partition functions for reactant, Q_1^+ is the rotational partition functions of transition state, E_0 is the barrier height corrected for zero-point energy, E^+ is the total non-fixed energy of a given transition state, dE^+ is the energy increment. $W(E_{vr}^+)$ is the sum of active vibrational–rotational states of the transition state, $k_a(E^*)$ is the rate constant for conversion of energized molecule to products, β_c is the collisional deactivation efficiency, Z is the collision number, and $[M]$ is the concentration.

To compute the integral in Eq. (7), a step size $\Delta E^+ = 0.4 \text{ kJ mol}^{-1}$ up to 400 kJ mol^{-1} was used. ω is the rate constant for de-energization of the activated adducts which is given by

$$\omega = \beta_c Z \tag{9}$$

where Z is the collision frequency and β_c is the collision efficiency. Here, the data for the viscosity of gaseous molecules are used to