Anharmonic effect of the unimolecular dissociation of CH$_3$COOH

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RESEARCH ARTICLE

Anharmonic effect of the unimolecular dissociation of CH₃COOH

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Anharmonic and harmonic rate constants of the reactions have been calculated with the Rice–Ramsperger–Kassel–Marcus theory, and the anharmonic results are higher than the harmonic ones. The anharmonic effect and isotopic effect on the decomposition reactions have also been examined. The anharmonic effect in all the four reactions is obvious, especially at the high temperatures or energies. Relatively, the anharmonic effect on the reaction *trans*-acetic acid → TS2 radical is the least obvious among the four reactions. In the microcanonical system, the difference of the rate constants between the deuterated results and the non-deuterated results is not negligible; in other words, the isotopic effect is obvious in all the four reactions. Among these reactions, three of the deuterated results (d, d3 and d4) have a big difference.

Keywords: anharmonic effect; unimolecular reaction; rate constant; RRKM method; isotopic effect

1. Introduction

Acetic acid is a very important material of organic synthesis, which is often used for the synthesis to produce vinyl acetate and acetic anhydride. There are two reaction mechanisms for the gas-phase unimolecular decomposition of acetic acid: the dehydration process leading to water and ketene, and the decarboxylation, leading to methane and carbon dioxide,

$$CH_3COOH \rightarrow H_2O + CH_2CO, \qquad (1)$$

$$CH_3COOH \rightarrow CH_4 + CO_2. \qquad (2)$$
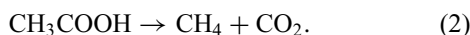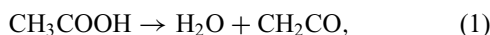
Bamford and Dewar measured the activation energies in a flow system for both the two channels at 1068–1218 K and got activation energies of 67.5 kcal mol⁻¹ for dehydration and 62.0 kcal mol⁻¹ for decarboxylation [1]. Blake and Jackson studied these reactions in both batch and flow system and concluded that the decomposition was of the first order when temperature was above 1000 K [2,3], and the activation energy was 64.9 kcal mol⁻¹ for this process. All these authors considered that a possible reason from a bimolecular mechanism might cause an artificially low activation energy in the unimolecular process and thus suggested that the 67.5 kcal mol⁻¹ activation energy measured by Bamford and Dewar should be more realistic [4]. Blake and Jackson got an activation energy of 58.5 kcal mol⁻¹ in a batch system for decarboxylation reaction and an activation energy of 69.8 kcal mol⁻¹ measured in a flow

system [2,3]. Mackie and Doolan surveyed this decomposition reaction at 1300–1950 K in a shock tube and they got the same result. This decomposition occurred via two competing unimolecular channels (reactions 1 and 2), and both of the activation energies were 72.7 kcal mol⁻¹ [5]. Thus, activation energies for reaction 1 were in the range 67.5–72.7 kcal mol⁻¹, while for reaction 2, the activation energies were in the range 64.9–72.7 kcal mol⁻¹ [4].

However, the activation energies which were given by theoretical studies were higher than experimental ones [6–9]. Decarboxylation (reaction 2) was predicted to have a higher activation energy than that for dehydration [4]. The reaction barrier of the decarboxylation process was 89.3 kcal mol⁻¹, which was proceeded with the MP4/6-31G* and HF/6-31G* methods [6]. With the MP4/6-31G* and HF/6-31G* methods, the calculations for the dehydration process obtained an activation barrier of 81.3 kcal mol⁻¹ and an activation barrier of 80.6 kcal mol⁻¹ for a two-step dehydration process: isomerisation to an enediol via hydrogen transfer as Equation (3), followed by water elimination via a four-centre transition state as Equation (4) [4,9],

$$CH_3COOH \rightarrow CH_2C(OH)_2, \qquad (3)$$

$$CH_2C(OH) \rightarrow H_2O + CH_2CO. \qquad (4)$$
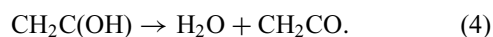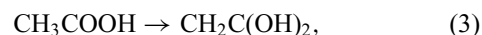
This paper mainly studies activation energies, and rate constants for the title reactions, the anharmonic effect and isotopic effect have also been discussed. Many chemists

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Table 1. The energetic parameters of the reactant and transition states, obtained from MP2/6-311 + + G (3df,2p) calculations.

		Cis-acetic acid	Enediol	*Trans*-acetic acid	TS1	TS2	TS3	TS4
Zero-point energy (MP2)	H	0.06232	0.06124	0.06209	0.05431	0.05409	0.05660	0.05583
(Hartree)	d	0.05886	0.05791	0.05865	0.05111	0.05223	0.05313	0.05369
	d3	0.05267	0.05169	0.05244	0.04610	0.04475	0.04843	0.04630
	d4	0.04920	0.04835	0.04900	0.04289	0.04288	0.04496	0.04415
Imaginary frequencies	H	–	–	–	−1811	−1980	−2113	−1629
	d				−1808	−1525	−2113	−1221
	d3				−1337	−1960	−1553	−1628
	d4				−1334	−1503	−1553	−1220
Single-point energy (CCSD(t))	H	−228.7505	−228.7057	−228.7423	−228.6228	−228.6284	−228.6290	−228.6288
(Hartree)	d							
	d3							
	d4							
Barrier (kcal mol^{-1})	H	–	–	–	75.19	66.42	72.64	44.73
	d				75.24	67.39	72.60	45.62
	d3				76.05	66.58	73.61	44.87
	d4				76.18	67.65	73.61	45.59

had observed that the anharmonic effect was considerable in molecular systems, especially in those of molecules and clusters with highly flexible transition states [10]. In 1962, Schlag and Sandsmark discovered that anharmonicity corrections might be significant in practice [11]. Then, Haarhoff considered the anharmonic corrections about the density of vibrational energy levels were for a system of simple Morse oscillators [12]. At present, many chemists have also observed that anharmonic effects are quite eventful in many dissociation of clusters and molecular systems [13–17]. It is recognised that the characteristic features of the anharmonic effect contain an increase in the bond lengths and distance of bond dissociation, and a decrease in vibrational bond-stretching frequencies [13–17]. Several authors have concentrated on the requirement for the anharmonic correction to previous reaction rate theories [18–20]. For this reason, using experimental thermodynamic data, Troe presented a simple empirical method for generating anharmonic vibrational densities of states [21]. Recently, a method proposed by Yao and Lin (YL) [22] could carry out the first principle calculations about the rate constants of molecular reactions within the framework of the transition state theory proposed. With this method, the anharmonic effect that was on the dissociation of molecular reaction had been examined. The results suggested that the YL method was appropriate to calculate rate constants of the unimolecular reaction and investigating the anharmonic effect of rate constant.

To our knowledge, although many efforts have been made to research the unimolecular dissociation of CX3COOX (X = H, D), the study of the rate constant and the anharmonic effect on the reaction is still very rare. The purpose of this paper is to calculate the harmonic and

anharmonic rate constants of the unimolecular dissociation of CX3COOX (X = H, D) and investigate the anharmonic effect on the reactions using YL method. In addition, in this paper, isotopic effect is also given which is divided into three aspects, deuterated out on the methyl hydrogens (d3), on the carboxyl hydrogens (d) and on all the hydrogens in acetic acid molecule (d4). The energetic parameters of the reactant and the transition are in accordance with the theoretical results given in Ref. [4]. The computational methods will be described in detail in Section 2. Section 3 concludes numerical results and detailed discussions. Finally, concluding remarks and a summary of this work are presented in Section 4.

2. Computational methods

2.1. *Ab initio* calculations

This article contains four unimolecular dissociations included in Equations (5)–(7), as following:

$$cis\text{-acetic acid} \rightarrow TS1 \rightarrow CH_2CO + H_2O, \quad (5)$$

$$trans\text{-acetic acid} \rightarrow TS2 \rightarrow CH_4 + CO_2, \quad (6)$$

$$cis\text{-acetic acid} \rightarrow TS3 \rightarrow \text{enediol} \rightarrow TS4$$
$$\rightarrow CH_2CO + H_2O. \quad (7)$$
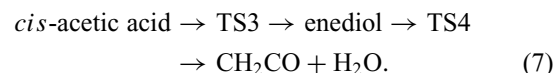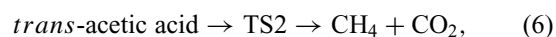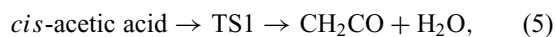
The geometry optimisations of the reactant CH_3COOH and transition states have been accomplished by the MP2 method with $6-311 + + G(3df,2p)$ basis set. The characterisation of stationary points, zero-point energy (ZPE) corrections, as well as the calculations of reaction rate constant

within the framework of the transition state theory (TST) and the Rice–Ramsperger–Kassel–Marcus (RRKM) theory are performed by the vibrational harmonic and anharmonic frequencies. All stationary points have been positively identified as local minima or transition states. The Gaussian 03 program is utilised for all *ab initio* calculations [23].

For the microcanonical system with energy E, in the RRKM theory, the unimolecular reaction rate constant can be expressed as [24]

$$k(E) = \frac{\sigma}{h} \frac{W^{\neq}(E - E^{\neq})}{\rho(E)}, \qquad (8)$$

where σ is the symmetry factor (here, we set $\sigma = 1$), h is Planck's constant, $\rho(E)$ stands for the density of the state of the reactant, $W^{\neq}(E)$ represents the total number of states for the transition state, and E and $E^{\neq}$ are the total energy and the activation energy in the microcanonical case, respectively. From the definition of $W(E)$ and $\rho(E)$, we can obtain [25–27]

$$W(E) = \sum_i H(E - E_i), \qquad (9)$$

$$\rho(E) = \frac{dW(E)}{dE}, \qquad (10)$$

where $H(E - E_i)$ denotes Heaviside function, E_i, are energy levels.

The Laplace transformation is employed for $W(E)$ and $\rho(E)$, we obtain [25–27]

$$\int_0^{\infty} dE e^{-\beta E} W(E) = \frac{Q(\beta)}{\beta} = L[W(E)], \qquad (11)$$

$$\int_0^{\infty} dE e^{-\beta E} \rho(E) = Q(\beta) = L[\rho(E)], \qquad (12)$$

where $\beta = 1/kT$, k is Boltzmann's constant, T is the temperature of the system and $Q(\beta)$ is the partition function of the system. That is, approximate $W(E)$ and $\rho(E)$ can be determined by Equations (11) and (12) by applying the inverse Laplace transformation after $Q(\beta)$ are given.

For a canonical system, the rate constant $k(T)$ for unimolecular reaction can be expressed as [25,27–29]

$$k(T) = \frac{kT}{h} \frac{Q^{\neq}(T)}{Q(T)} e^{-\frac{E^{\neq}}{kT}}, \qquad (13)$$

where $Q(T)$ and $Q^{\neq}(T)$ are the partition functions of the reactant and the activated complex, respectively. In this case, we get

$$Q^{\neq}(T) = \prod_i^{N-1} q_i^{\neq}(T), \qquad (14)$$

Table 2. The rate constants from *cis*-acetic acid (H) to TS1 (H) at different temperatures for the canonical system. The unit of rate constant is s⁻¹.

Temperature (K)	1000	1500	2000	2500	2800	3000	3200	3400	3600	3800	4000
Energy (kcal mol⁻¹)	13.62	27.11	42.29	58.37	68.30	74.99	81.74	88.53	95.36	102.22	109.11
Correspond (cm⁻¹)	4763.60	9481.72	14,790.93	20,414.91	23,887.93	26,227.75	28,588.57	30,963.37	33,352.16	35,751.45	38,161.22
Anharmonic rate constant (s⁻¹)	1.09×10^{-3}	8.55×10^2	9.31×10^5	6.75×10^7	4.28×10^8	1.19×10^9	2.90×10^9	6.33×10^9	1.26×10^{10}	2.30×10^{10}	3.93×10^{10}
Harmonic rate constant (s⁻¹)	4.84×10^{-4}	2.24×10^2	1.60×10^5	8.37×10^6	4.59×10^7	1.18×10^8	2.71×10^8	5.63×10^8	1.08×10^9	1.93×10^9	3.27×10^9
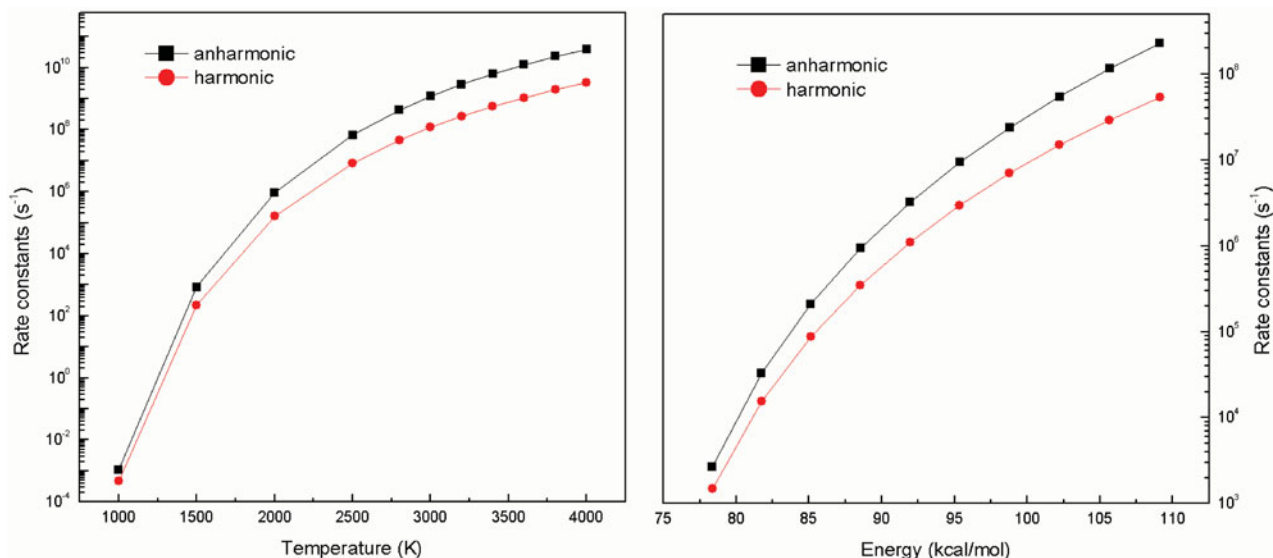
Figure 1. The canonical and microcanonical rate constants for *cis*-acetic (H) acid to TS1 (H). The unit of rate constant is s^{-1}.

$$Q(T) = \prod_i^N q_i(T), \qquad (15)$$

where N is the number of the vibrational modes of the reactant, $q_i^{\neq}(T)$ and $q_i(T)$ are the vibrational partition function of the transition state and the reactant for each mode.

The discussions above show that the partition function is considerable in the calculation of $k(E)$ and $k(T)$. Recently, the quantum chemical calculations can provide the information of cubic and quartic anharmonic potential functions not only for polyatomic molecules but also for clusters. We have applied these anharmonic potential functions to treat the intramolecular vibrational redistributions (or relaxations) of polyatomic molecules and clusters and solved the corresponding Schrödinger equations perturbatively to the second-order approximations which give us the same accuracy as given by Equation (16). This approach has been employed in this paper for the calculation of $W^{\neq}(E - E_0)$ and $\rho(E)$ in Ref. [30]. In this work, to calculate the partition function, Morse Oscillator (MO) is often used:

$$E_{n_i} = \left(n_i + \frac{1}{2}\right)\hbar\omega_i - x_i\left(n_i + \frac{1}{2}\right)^2\hbar\omega_i, \qquad (16)$$

where x_i is the MO parameter, and it can be expressed as $x_i = \frac{\hbar\omega_i}{4D_{ie}}$, in which D_{ie} represents the well depth of MO. In our study, x_i is obtained from anharmonic frequency calculations in Gaussian 03. ω_i is the frequency of the ith vibrational mode, and n_i is the vibration quantum number of the vibrational mode. The maximum value of n_i is

represented by $n_i^{\max}$. In this paper, we will discuss the anharmonic rate constant of the concerted exchange reaction in the CH$_3$COOH and its isomer.

In the calculation of the density of states, $E = -\left[\frac{\partial \ln Q}{\partial \beta}\right]$, harmonic and anharmonic degrees of freedom of the reactant are 18 ($3N - 6$, $N = 8$). To calculate the total number of states $W(E)$, harmonic and anharmonic imaginary frequencies are excluded and the degrees of freedom of the transition state are 17.

3. Results and discussions

The energetic parameters of the reactant and transition states about the unimolecular dissociation of the acetic acid are collected in Table 1. The data are obtained with the MP2/6-311++G (3df,2p) method. To obtain high accuracy and reliability, we recompute the single-point energies at CCSD(T)/6-311G(d,p) level, and then get the values of the energy barrier 75.19, 72.64, 44.73 and 66.42 kcal mol^{-1}, which are in accordance with the values obtained by Michael Page [4]. The results calculated with CCSD(T)/6-311++G(d,p) are used in the rate constants calculation.

3.1. Unimolecular dissociation of the cis-acetic acid radical (the channel which includes the TS1)

For this dissociation, the anharmonic and harmonic rate constants (H) for canonical case are presented in Table 2, with temperatures ranging from 1000 to 4000 K. From Table 2, it is clear that both the harmonic and anharmonic rate constants increase with the temperatures increasing.

Table 3. The rate constants from *cis*-acetic acid (H) to TS1 (H) at different energies for the microcanonical system. The unit of rate constant is s⁻¹.

Temperature (K)	3100	3200	3300	3400	3500	3600	3700	3800	3900	4000
Energy (kcal mol⁻¹)	78.36	81.74	85.13	88.53	91.94	95.36	98.79	102.22	105.66	109.11
Correspond (cm⁻¹)	27,406.41	28,588.57	29,774.22	30,963.37	32,156.02	33,352.16	34,551.80	35,751.45	36,954.59	38,161.22
Anharmonic rate constant (s⁻¹)	2.67×10^3	3.29×10^4	2.11×10^5	9.34×10^5	3.23×10^6	9.38×10^6	2.39×10^7	5.47×10^7	1.15×10^8	2.27×10^8
Harmonic rate constant (s⁻¹)	1.49×10^3	1.56×10^4	8.80×10^4	3.50×10^5	1.10×10^6	2.95×10^6	6.97×10^6	1.49×10^7	2.93×10^7	5.42×10^7

Table 4. The rate constants from *cis*-acetic acid-D to TS1-D at different temperatures for the canonical system. The unit of rate constant is s⁻¹.

	Temperature (K)	1000	1500	2000	2500	2800	3000	3200	3400	3600	3800	4000
d	Anharmonic rate Constant (s⁻¹)	1.18×10^{-3}	8.99×10^3	9.22×10^5	6.27×10^7	3.85×10^8	1.05×10^9	2.54×10^9	5.49×10^9	1.09×10^{10}	1.98×10^{10}	3.41×10^{10}
	Harmonic rate constant (s⁻¹)	4.96×10^{-4}	2.28×10^2	1.62×10^5	8.47×10^6	4.64×10^7	1.19×10^8	2.73×10^8	5.68×10^8	1.09×10^9	1.95×10^9	3.29×10^9
d3	Anharmonic rate constant (s⁻¹)	5.84×10^{-4}	4.91×10^2	5.30×10^5	3.80×10^7	2.42×10^8	6.79×10^8	1.68×10^9	3.73×10^9	7.58×10^9	1.43×10^{10}	2.51×10^{10}
	Harmonic rate constant (s⁻¹)	2.87×10^{-4}	1.51×10^2	1.13×10^5	6.10×10^6	3.38×10^7	8.74×10^7	2.01×10^8	4.19×10^8	8.06×10^8	1.45×10^9	2.45×10^9
d4	Anharmonic rate constant (s⁻¹)	6.21×10^{-4}	5.55×10^2	6.19×10^5	4.41×10^7	2.76×10^8	7.64×10^8	1.85×10^9	4.04×10^9	8.04×10^9	1.48×10^{10}	2.54×10^{10}
	Harmonic rate constant (s⁻¹)	2.82×10^{-4}	1.50×10^2	1.13×10^5	6.07×10^6	3.36×10^7	8.70×10^7	2.00×10^8	4.17×10^8	8.02×10^8	1.44×10^9	2.44×10^9

Table 5. The rate constants from *cis*-acetic acid-D to TS1-D at different energies for the microcanonical system. The unit of rate constant is s⁻¹.

d	Energy (kcal mol⁻¹)	76.36	79.75	83.15	86.56	89.98	93.41	96.84	100.29	103.74	107.19	110.65
	Correspond (cm⁻¹)	26,706.91	27,892.56	29,081.71	30,274.36	31,470.51	32,670.15	33,869.79	35,076.43	36,283.07	37,489.70	38,699.84
	Anharmonic rate constant (s⁻¹)	1.88×10^2	5.86×10^3	5.59×10^4	3.15×10^5	1.29×10^6	4.27×10^6	1.20×10^7	2.98×10^7	6.72×10^7	1.39×10^8	2.71×10^8
	Harmonic rate constant (s⁻¹)	1.10×10^2	2.77×10^3	2.31×10^4	1.16×10^5	4.31×10^5	1.30×10^6	3.36×10^6	7.74×10^6	1.62×10^7	3.16×10^7	5.76×10^7
d3	Energy (kcal mol⁻¹)	79.12	82.54	85.97	89.42	92.86	96.32	99.78	103.25	106.72	110.2	113.68
	Correspond (cm⁻¹)	27,672.22	28,868.37	30,068.01	31,274.65	32,477.79	33,687.92	34,898.06	36,111.69	37,325.32	38,542.45	39,759.58
	Anharmonic rate constant (s⁻¹)	4.06×10^2	6.70×10^3	5.21×10^4	2.67×10^5	1.03×10^6	3.28×10^6	8.98×10^6	2.18×10^7	4.85×10^7	9.97×10^7	1.92×10^8
	Harmonic rate constant (s⁻¹)	2.21×10^2	3.06×10^3	2.08×10^4	9.55×10^4	3.36×10^5	9.87×10^5	2.51×10^6	5.74×10^6	1.20×10^7	2.32×10^7	4.23×10^7
d4	Energy (kcal mol⁻¹)	77.04	80.48	83.93	87.38	90.84	94.31	97.79	101.27	104.75	108.24	111.73
	Correspond (cm⁻¹)	26,944.74	28,147.88	29,354.52	30,561.16	31,771.29	32,984.92	34,202.05	35,419.18	36,636.31	37,856.94	39,077.57
	Anharmonic rate constant (s⁻¹)	1.39×10^1	7.37×10^2	9.37×10^3	6.41×10^4	3.04×10^5	1.13×10^6	3.50×10^6	9.44×10^6	2.28×10^7	5.05×10^7	1.04×10^8
	Harmonic rate constant (s⁻¹)	9.91	4.08×10^2	4.47×10^3	2.70×10^4	1.15×10^5	3.88×10^5	1.10×10^6	2.74×10^6	6.14×10^6	1.27×10^7	2.43×10^7

Figure 2. The canonical and microcanonical rate constants (anharmonic) for *cis*-acetic-D acid to TS1-D. The unit of rate constant is s^{-1}.

Corresponding to Table 2, the rate constants (H) for the reaction are plotted in Figure 1. With the temperatures increasing from 1000 to 4000 K, the harmonic rate constants change from 4.84×10^{-4} to 3.27×10^{9} s^{-1}, while the anharmonic rate constants are in the range from 1.09×10^{-3} to 3.93×10^{10} s^{-1}. The gap between anharmonic rate constants and harmonic ones changes with the increasing temperatures. When the temperature is 1000 K, the anharmonic rate constant (1.09×10^{-3} s^{-1}) is 55.6%

higher than the harmonic rate constant (4.84×10^{-4} s^{-1}), and the anharmonic rate constant (3.93×10^{10} s^{-1}) is 91.7% higher than the harmonic rate constant (3.27×10^{9} s^{-1}) at 4000 K. It is worth noting the first six energy data in Table 2, as they are all lower than the calculated activation energy 75.19 kcal mol^{-1}. Hence, we have to calculate the rate constants in the microcanonical system at higher energy.
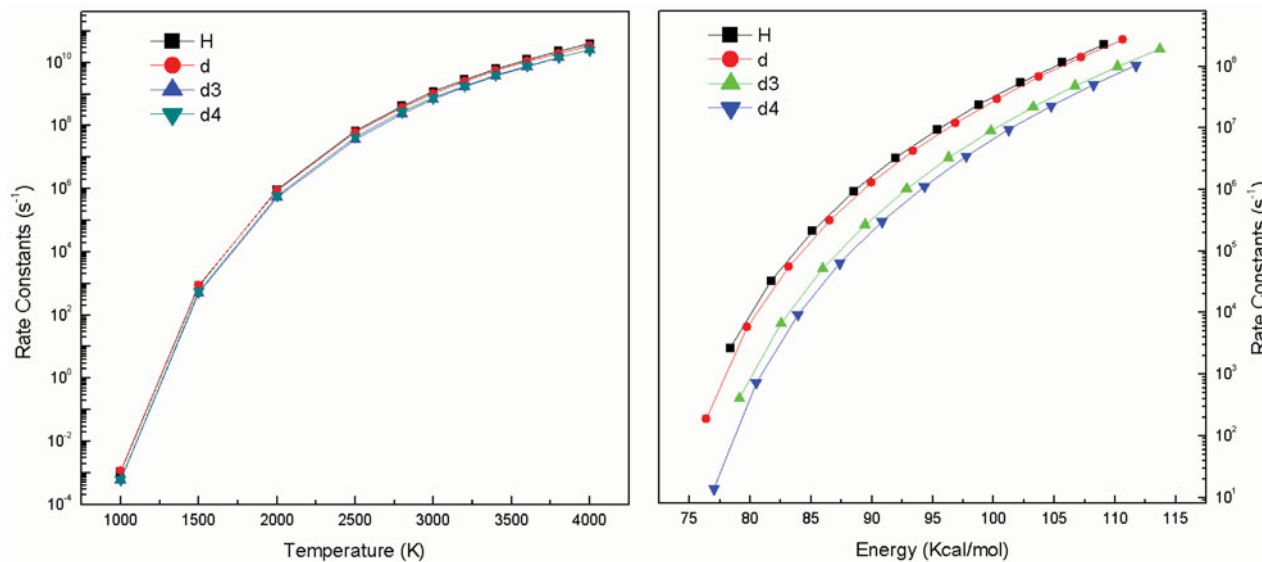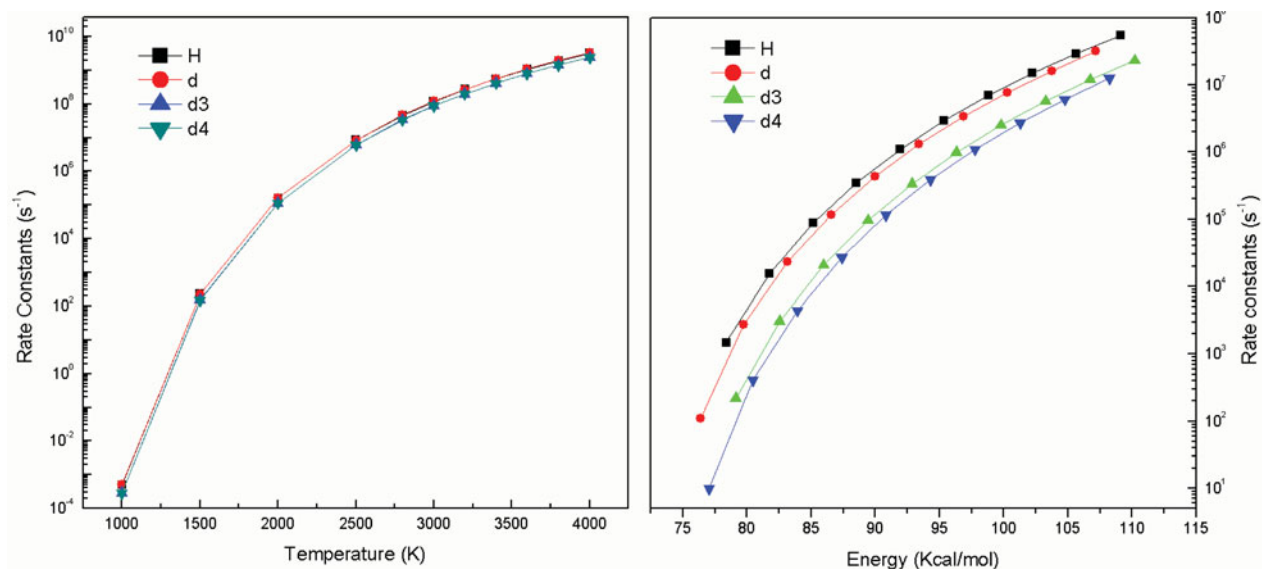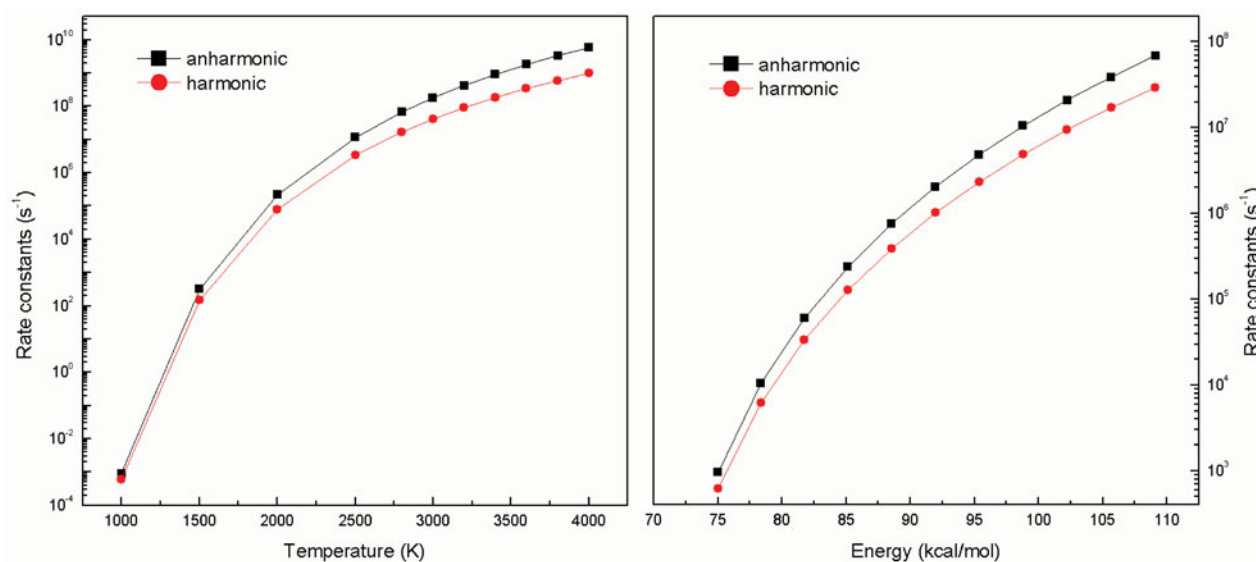

Figure 3. The canonical and microcanonical rate constants (harmonic) for *cis*-acetic-D acid to TS1-D. The unit of rate constant is s^{-1}.

Table 6. The rate constants from *cis*-acetic acid (H) to TS3 (H) at different temperatures for the canonical system. The unit of rate constant is s^{-1}.

Temperature (K)	1000	1500	2000	2500	2800	3000	3200	3400	3600	3800	4000
Energy (kcal mol^{-1})	13.62	27.11	42.29	58.37	68.30	74.99	81.74	88.53	95.36	102.22	109.11
Correspond (cm^{-1})	4763.60	9481.72	14,790.93	20,414.91	23,887.93	26,227.75	28,588.57	30,963.37	33,352.16	35,751.45	38,161.22
Anharmonic rate constant (s^{-1})	8.96×10^{-4}	3.15×10^2	2.15×10^5	1.17×10^7	6.70×10^7	1.78×10^8	4.20×10^8	9.04×10^8	1.79×10^9	3.33×10^9	5.82×10^9
Harmonic rate constant (s^{-1})	5.99×10^{-4}	1.50×10^2	7.79×10^4	3.37×10^6	1.70×10^7	4.18×10^7	9.21×10^7	1.84×10^8	3.43×10^8	5.97×10^8	9.84×10^8

Figure 4. The canonical and microcanonical rate constants for *cis*-acetic (H) acid to TS3 (H). The unit of rate constant is s^{-1}.

To calculate the energy corresponding to the above temperatures, we employ the relation between the total energy of a microcanonical system and the temperatures of a canonical system by

$$E = -\left[\frac{\partial \ln Q}{\partial \beta} \right] \quad (17)$$

with Equation (17), and the energy in the microcanonical system can be obtained. Then the total energies are 27,406.41 to 38,161.22 cm^{-1}, corresponding to the temperatures of 3100 to 4000 K, respectively, for this channel. Table 3 shows the harmonic and anharmonic rate constants (H) of the title reaction obtained with the YL method for microcanonical case.

From Table 3 and Figure 1, we can see that for the microcanonical system, the harmonic and anharmonic rate constants increase with the increasing of the total energies. With the energies increasing from 27,406.41 to 38,161.22 cm^{-1}, the harmonic rate constants increase from

Table 7. The rate constant from *cis*-acetic acid (H) to TS3(H) at different energies for the microcanonical system. The unit of rate constant is s^{-1}.

Energy (kcal mol^{-1})	74.99	78.36	81.74	85.13	88.53	91.94	95.36	98.79	102.22	105.66	109.11
Correspond (cm^{-1})	26,227.75	27,406.41	28,588.57	29,774.22	30,963.37	32,156.02	33,352.16	34,551.80	35,751.45	36,954.59	38,161.22
Anharmonic rate constant (s^{-1})	9.60×10^2	1.05×10^4	6.00×10^4	2.40×10^5	7.60×10^5	2.05×10^6	4.86×10^6	1.05×10^7	2.09×10^7	3.90×10^7	6.89×10^7
Harmonic rate constant (s^{-1})	6.24×10^2	6.22×10^3	3.35×10^4	1.28×10^5	3.91×10^5	1.02×10^6	2.34×10^6	4.88×10^6	9.42×10^6	1.71×10^7	2.93×10^7

Table 8. The rate constants from *cis*-acetic acid-D to TS3-D at different temperatures for the canonical system. The unit of rate constant is s⁻¹.

	Temperature (K)	1000	1500	2000	2500	2800	3000	3200	3400	3600	3800	4000
d	Anharmonic rate Constant (s⁻¹)	1.02×10^{-3}	3.59×10^{2}	2.47×10^{5}	1.37×10^{7}	7.97×10^{7}	2.15×10^{8}	5.16×10^{8}	1.13×10^{9}	2.28×10^{9}	4.30×10^{9}	7.66×10^{9}
	Harmonic rate constant (s⁻¹)	6.10×10^{-4}	1.51×10^{2}	7.86×10^{4}	3.40×10^{6}	1.71×10^{7}	4.21×10^{7}	9.26×10^{7}	1.86×10^{8}	3.45×10^{8}	6.00×10^{8}	9.88×10^{8}
d3	Anharmonic rate constant (s⁻¹)	4.54×10^{-4}	1.87×10^{2}	1.41×10^{5}	8.39×10^{6}	5.02×10^{7}	1.37×10^{8}	3.33×10^{8}	7.34×10^{8}	1.49×10^{9}	2.82×10^{9}	5.02×10^{9}
	Harmonic rate constant (s⁻¹)	3.33×10^{-4}	9.6×10^{1}	5.30×10^{4}	2.36×10^{6}	1.20×10^{7}	2.98×10^{7}	6.59×10^{7}	1.33×10^{8}	2.47×10^{8}	4.31×10^{8}	7.13×10^{8}
d4	Anharmonic rate constant (s⁻¹)	4.72×10^{-4}	1.90×10^{2}	1.38×10^{5}	7.85×10^{6}	4.61×10^{7}	1.24×10^{8}	3.01×10^{8}	6.59×10^{8}	1.33×10^{9}	2.52×10^{9}	4.48×10^{9}
	Harmonic rate constant (s⁻¹)	3.33×10^{-4}	9.60×10^{1}	5.29×10^{4}	2.36×10^{6}	1.20×10^{7}	2.98×10^{7}	6.58×10^{7}	1.32×10^{8}	2.47×10^{8}	4.31×10^{8}	7.12×10^{8}

Table 9. The rate constants from *cis*-acetic acid-D to TS3-D at different energies for the microcanonical system. The unit of rate constant is s⁻¹.

	Energy (kcal mol⁻¹)	72.98	76.36	79.75	83.15	86.56	89.98	93.41	96.84	100.29	103.74	107.19	110.65
d	Correspond (cm⁻¹)	25,524.76	26,706.91	27,892.56	29,081.71	30,274.36	31,470.51	32,670.15	33,869.79	35,076.43	36,283.07	37,489.70	38,699.84
	Anharmonic rate constant (s⁻¹)	7.96×10^{1}	2.09×10^{3}	1.78×10^{4}	9.01×10^{4}	3.37×10^{5}	1.03×10^{6}	2.70×10^{6}	6.29×10^{6}	1.34×10^{7}	2.66×10^{7}	4.93×10^{7}	8.70×10^{7}
	Harmonic rate constant (s⁻¹)	5.96×10^{1}	1.15×10^{3}	9.04×10^{3}	4.34×10^{4}	1.55×10^{5}	4.52×10^{5}	1.14×10^{6}	2.56×10^{6}	5.23×10^{6}	1.00×10^{7}	1.80×10^{7}	3.06×10^{7}
d3	Energy (kcal mol⁻¹)	75.70	79.12	82.54	85.97	89.42	92.86	96.32	99.78	103.25	106.72	110.20	
	Correspond (cm⁻¹)	26,476.08	27,672.22	28,868.37	30,068.01	31,274.65	32,477.79	33,687.92	34,898.06	36,111.69	37,325.32	38,542.45	
	Anharmonic rate constant (s⁻¹)	1.21×10^{2}	1.92×10^{3}	1.36×10^{4}	6.42×10^{4}	2.33×10^{5}	6.96×10^{5}	1.81×10^{6}	4.23×10^{6}	9.03×10^{6}	1.79×10^{7}	3.34×10^{7}	
	Harmonic rate constant (s⁻¹)	7.80×10^{1}	1.11×10^{3}	7.37×10^{3}	3.28×10^{4}	1.13×10^{5}	3.23×10^{5}	8.07×10^{5}	1.80×10^{6}	3.70×10^{6}	7.04×10^{6}	1.26×10^{7}	
d4	Energy (kcal mol⁻¹)	77.04	80.48	83.93	87.38	90.84	94.31	97.79	101.27	104.75	108.24	111.73	115.23
	Correspond (cm⁻¹)	26,944.74	28,147.88	29,354.52	30,561.16	31,771.29	32,984.92	34,202.05	35,419.18	36,636.31	37,856.94	39,077.57	40,301.69
	Anharmonic rate constant (s⁻¹)	2.36×10^{2}	2.72×10^{3}	1.68×10^{4}	7.25×10^{4}	2.47×10^{5}	7.12×10^{5}	1.80×10^{6}	4.09×10^{6}	8.54×10^{6}	1.67×10^{7}	3.07×10^{7}	5.37×10^{7}
	Harmonic rate constant (s⁻¹)	1.55×10^{2}	1.65×10^{3}	9.69×10^{3}	4.00×10^{4}	1.31×10^{5}	3.62×10^{5}	8.83×10^{5}	1.94×10^{6}	3.91×10^{6}	7.39×10^{6}	1.31×10^{7}	2.23×10^{7}

Table 10. The rate constants from enediol (H) to TS4 (H) at different temperatures for the canonical system. The unit of rate constant is s^{-1}.

Temperature (K)	2100	2200	2300	2400	2500	2600	2700	2800	2900	3000
Energy (kcal mol^{-1})	46.56	49.74	52.95	56.19	59.45	62.73	66.03	69.34	72.68	76.02
Correspond (cm^{-1})	16,284.36	17,396.57	18,519.26	19,652.45	20,792.64	21,939.82	23,093.99	24,251.67	25,419.83	26,588.00
Anharmonic rate constant (s^{-1})	6.17×10^8	1.08×10^9	1.81×10^9	2.94×10^9	4.59×10^9	6.98×10^9	1.03×10^{10}	1.49×10^{10}	2.11×10^{10}	2.93×10^{10}
Harmonic rate constant (s^{-1})	1.82×10^8	3.03×10^8	4.81×10^8	7.35×10^8	1.09×10^9	1.56×10^9	2.18×10^9	2.97×10^9	3.98×10^9	5.21×10^9

Table 11. The rate constants from enediol (H) to TS4 (H) at different energies for the microcanonical system. The unit of rate constant is s^{-1}.

Energy (kcal mol^{-1})	46.56	49.74	52.95	56.19	59.45	62.73	66.03	69.34	72.68	76.02
Correspond (cm^{-1})	16,284.36	17,396.57	18,519.26	19,652.45	20,792.64	21,939.82	23,093.99	24,251.67	25,419.83	26,588.00
Anharmonic rate constant (s^{-1})	7.13×10^4	7.91×10^5	4.22×10^6	1.55×10^7	4.46×10^7	1.09×10^8	2.38×10^8	4.70×10^8	8.67×10^8	1.50×10^9
Harmonic rate constant (s^{-1})	5.20×10^4	5.11×10^5	2.54×10^6	8.80×10^6	2.42×10^7	5.64×10^7	1.17×10^8	2.20×10^8	3.87×10^8	6.39×10^8

1.49×10^3 to 5.42×10^7 s^{-1}, while the anharmonic rate constants are in the range from 2.67×10^3 to 2.27×10^8 s^{-1}. The values of harmonic rate constants and the anharmonic ones increase with the increasing energies. When the total energy is 27,406.41 cm^{-1}, the anharmonic rate constant (2.67×10^3 s^{-1}) is 44.2% higher than the harmonic rate constant (1.49×10^3 s^{-1}), while the anharmonic rate constant (2.27×10^8 s^{-1}) is 76.1% higher than the harmonic rate constant (5.42×10^7 s^{-1}) at total energy 38,161.22 cm^{-1}.

In Table 4 and 5, isotopic effect results of this reaction are also given. The rate constants of the isotopic effect cases are illustrated in Figures 2 and 3. In the canonical case, as a whole, the isotopic effect is not obvious, and the result of the deuterated anharmonic rate constants by size is H > d > d4 > d3 (at the temperatures higher than 2000 K), for example, when temperature is 2000 K, the anharmonic rate constant for CH_3COOH case is 9.31×10^5 s^{-1}, the anharmonic rate constant for CH_3COOD case is 9.22×10^5 s^{-1}, for CD_3COOD case is 6.19×10^5 s^{-1} and for CD_3COOH case is 5.30×10^5 s^{-1}. The deuterated harmonic rate constants by size is d > H > d3 > d4, when temperature is 1000 K, the harmonic rate constant for d case is 4.96×10^{-4} s^{-1}, the harmonic rate constant for CH_3COOH case is 4.84×10^{-4} s^{-1}, for CD_3COOH case is 2.87×10^{-4} s^{-1} and for CD_3COOD case is 2.82×10^{-4} s^{-1}. In the microcanonical system, the isotopic effect is obvious, both the result of the deuterated harmonic rate constants and the result of the deuterated harmonic rate constants by size are H > d > d3 > d4, which can be reached from Figures 2 and 3 specifically.

3.2. Unimolecular dissociation of the cis-acetic acid radical (the channel includes the TS3)

For this reaction, the anharmonic and harmonic rate constants (H) for canonical case are presented in Table 6, with temperatures ranging from 1000 to 4000 K. Corresponding to Table 6, the rate constants (H) for this reaction are plotted in Figure 4. From Table 6, it is clear that both the harmonic and anharmonic rate constants increase with temperatures increasing from 1000 to 4000 K. The harmonic rate constants increase from 5.99×10^{-4} to 9.84×10^8 s^{-1}, while the anharmonic rate constants are in the range from 8.96×10^{-4} to 5.82×10^9 s^{-1} in Table 6. The anharmonic rate constants are higher than the harmonic ones at all the temperatures we calculated. When the temperature is 1000 K, the harmonic rate constant (5.99×10^{-4} s^{-1}) is 33.1% lower than the anharmonic rate constant (8.96×10^{-4} s^{-1}), while the harmonic rate constant (9.84×10^8 s^{-1}) is 83.1% lower than the anharmonic rate constant (5.82×10^9 s^{-1}) at temperature 4000 K. The first several energies are worth noting in Table 6 as they are all lower than the calculated activation energy of

72.64 kcal mol^{-1} . Hence, we have to calculate the rate constants in the microcanonical system at higher energies.

The total energies are 26,227.75–38,161.22 cm^{-1}, corresponding to the temperatures of 3000–4000 K using Equation (17), respectively. Table 7 shows the harmonic and anharmonic rate constants (H) of the reaction obtained from the YL method for the microcanonical case. The rate constants of the microcanonical total energies are also illustrated in Figure 4.

From Table 7 and Figure 4, we can see that in the microcanonical system the harmonic and anharmonic rate constants increase with the increasing of the total energies. With the energies increasing from 26,227.75 to 38,161.22 cm^{-1}, the harmonic rate constants increase from 6.24×10^2 to 2.93×10^7 s^{-1}, while the anharmonic rate constants are in the range from 9.60×10^2 to 6.89×10^7 s^{-1}. The anharmonic rate constants are higher than the harmonic ones at all ranges of energy. When total energy is 26,227.75 cm^{-1}, the harmonic rate constant (6.24×10^2 s^{-1}) is 35.0% lower than the anharmonic rate constant (9.60×10^2 s^{-1}), while the harmonic rate constant (2.93×10^7 s^{-1}) is 57.5% lower than the anharmonic rate constant (6.89×10^7 s^{-1}) at total energy 38,161.22 cm^{-1}.

In Table 8 and 9, the isotopic effect results of this reaction are also given. The rate constants for the isotopic effect cases are illustrated in Figures 5 and 6. In the canonical case, as a whole, the isotopic effect is not obvious and the result of the deuterated anharmonic rate constants by size is d > H > d3 > d4 (the temperatures are higher than 2000 K). For example, when temperature is 2000 K, the anharmonic rate constant for CH_3COOD case is 2.47×10^5 s^{-1}, the anharmonic rate constant for CH_3COOH case is 2.15×10^5 s^{-1}, for CD_3COOH case is 1.41×10^5 s^{-1} and for CD_3COOD case is 1.38×10^5 s^{-1}; the result of the deuterated harmonic rate constants by size is d > H > d3 > d4, when temperature is 2000 K, the harmonic rate constant for CH_3COOD case is 7.86×10^4 s^{-1}, the harmonic rate constant for CH_3COOH case is 7.79×10^{-4} s^{-1}, for CD_3COOH case is 5.30×10^{-4} s^{-1} and for CD_3COOD case is 5.29×10^{-4} s^{-1}. In the microcanonical system, the isotopic effect is obvious and both the results of the deuterated harmonic rate constants and the results of the deuterated harmonic rate constants by size are H > d > d3 > d4, which can be reached from Figures 5 and 6 specifically.

3.3. Unimolecular dissociation of the enediol radical (the channel includes the TS4)

For this reaction, the anharmonic and harmonic rate constants for canonical case are presented in Table 10, with temperatures ranging from 2100 to 3000 K. Corresponding to Table 10, the rate constants for the title reaction are plotted in Figure 7. From Table 10, it is clear that both the harmonic and anharmonic rate constants increase
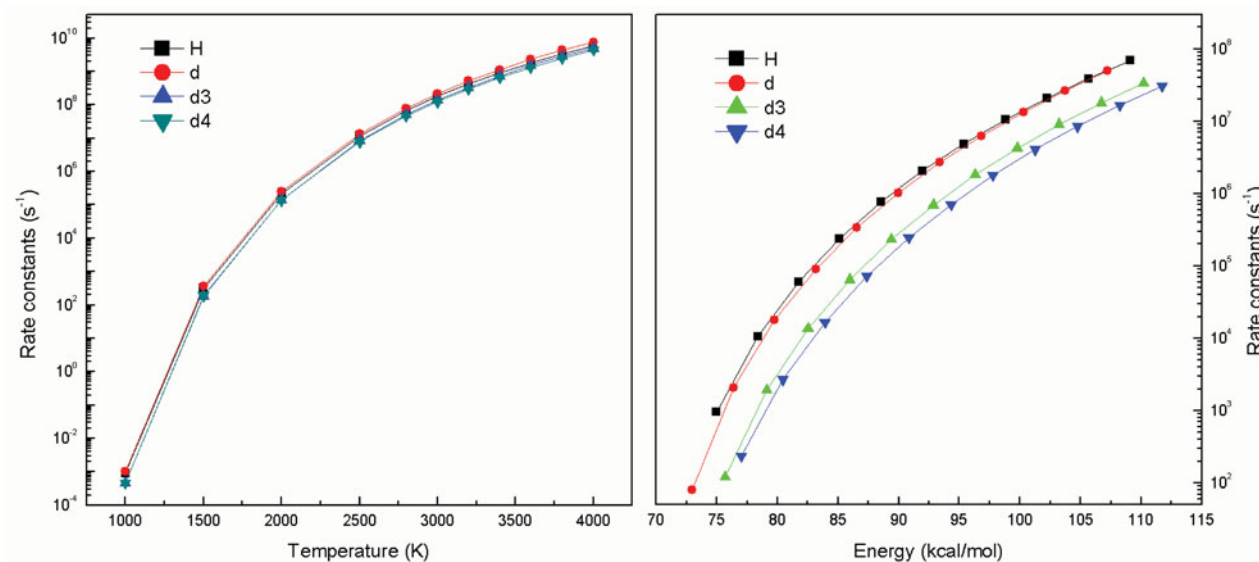
Figure 5. The canonical and microcanonical rate constants (anharmonic) for *cis*-acetic-D acid to TS3-D. The unit of rate constant is s^{-1}.

with temperatures increasing from 2100 to 3000 K. The harmonic rate constants increase from 1.82×10^8 to 5.21×10^9 s^{-1}, while the anharmonic rate constants are in the range from 6.17×10^8 to 2.93×10^{10} s^{-1}. The anharmonic rate constants are higher than the harmonic ones at all range of temperatures. When the temperature is 2100 K, the harmonic rate constant (1.82×10^8 s^{-1}) is 70.5% lower than the harmonic rate constant (6.17×10^8 s^{-1}), while the harmonic rate constant (5.21×10^9 s^{-1}) is 82.2% lower than the anharmonic rate constant (2.93×10^{10} s^{-1}) at the temperature 3000 K.

The total energies are 16,284.36–26,588.00 cm^{-1}, corresponding to the temperatures of 2100–3000 K using

Equation (17). Table 11 shows the harmonic and anharmonic rate constants of the title reaction obtained with the YL method for microcanonical case. The rate constants of the microcanonical total energies are also illustrated in Figure 7.

From Table 11 and Figure 7, we can see that for the microcanonical system the harmonic and anharmonic rate constants increase with the increase in total energy. With the energy increasing from 16,284.36 to 26,588.00 cm^{-1}, the harmonic rate constants increase from 5.20×10^4 to 6.39×10^8 s^{-1}, while the anharmonic rate constants are in the range from 7.13×10^4 to 1.50×10^9 s^{-1}. The anharmonic rate constants are higher than the harmonic ones at all
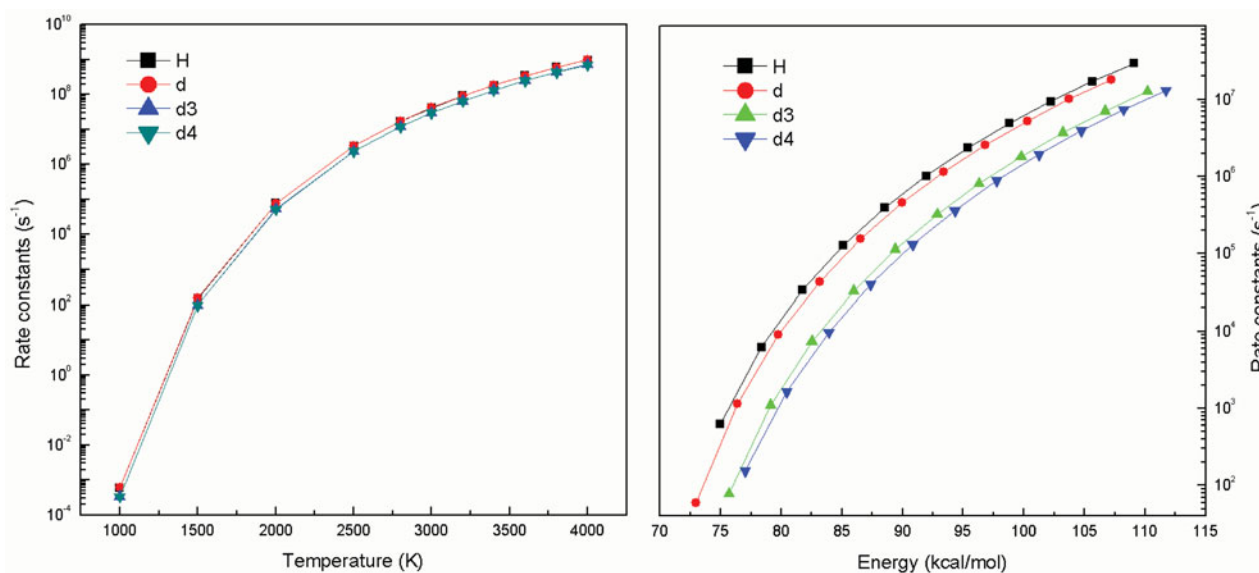

Figure 6. The canonical and microcanonical rate constants (harmonic) for *cis*-acetic-D acid to TS3-D. The unit of rate constant is s^{-1}.
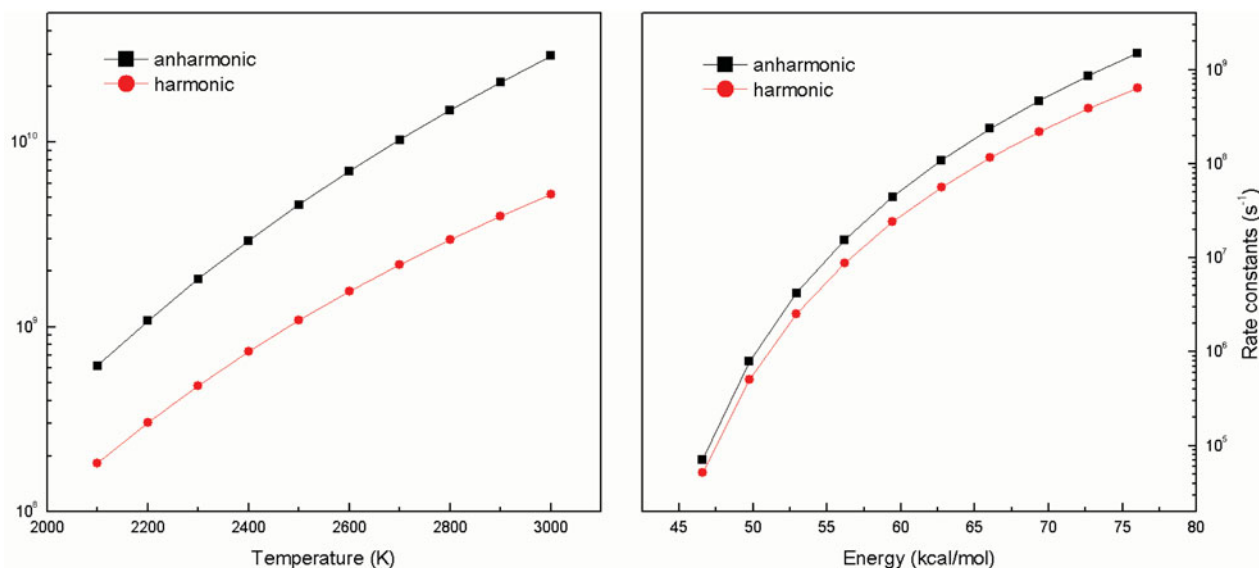
Figure 7. The canonical and microcanonical rate constants for enediol (H) to TS4 (H). The unit of rate constant is s^{-1}.

range of energy. When the total energy is 16,284.36 cm^{-1}, the harmonic rate constant (5.20×10^4 s^{-1}) is 27.1% lower than the anharmonic rate constant (7.13×10^4 s^{-1}), while the harmonic rate constant (6.39×10^8 s^{-1}) is 57.4% lower than the anharmonic rate constant (1.50×10^9 s^{-1}) at total energy 26,588.00 cm^{-1}.

In Table 12 and 13, isotopic effect results of this effect are also given. The rate constants for the isotopic effect cases are illustrated in Figures 8 and 9. For the canonical case, the isotopic effect is obvious, and it is supposed that C–O bond scission has an effect on it. The result of the deuterated anharmonic rate constants by size is d3 > H > d4 > d. However, compared with the results of H, there is little

difference among the results of CD_3COOD; however, the difference between the results of CH_3COOH and the results of CH_3COOD is in the range from 13.79% to 15.02%, and the results of H are about 43.16% to 44.63% lower than the deuterated results of CD_3COOH case. For example, when the temperature is 2100 K, the anharmonic rate constant for CD_3COOH case is 1.06×10^9 s^{-1}, and the anharmonic rate constant for CH_3COOH case is 6.17×10^8 s^{-1}, for CD_3COOD case is 6.07×10^8 s^{-1} and for CH_3COOD case is 5.22×10^8 s^{-1}, The result of the deuterated harmonic rate constants by size is H > d3 > d > d4; there is little difference among the results of the harmonic rate constants between the results of CH_3COOH and CD_3COOH case, nevertheless
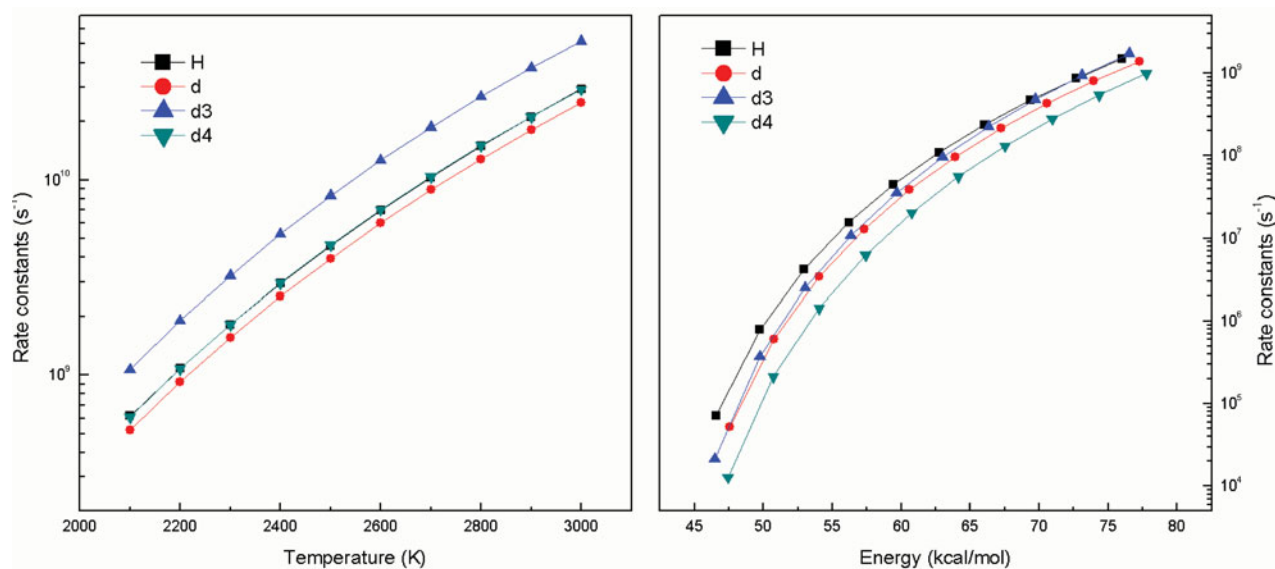

Figure 8. The canonical and microcanonical rate constants (anharmonic) for enediol-D to TS4-D. The unit of rate constant is s^{-1}.
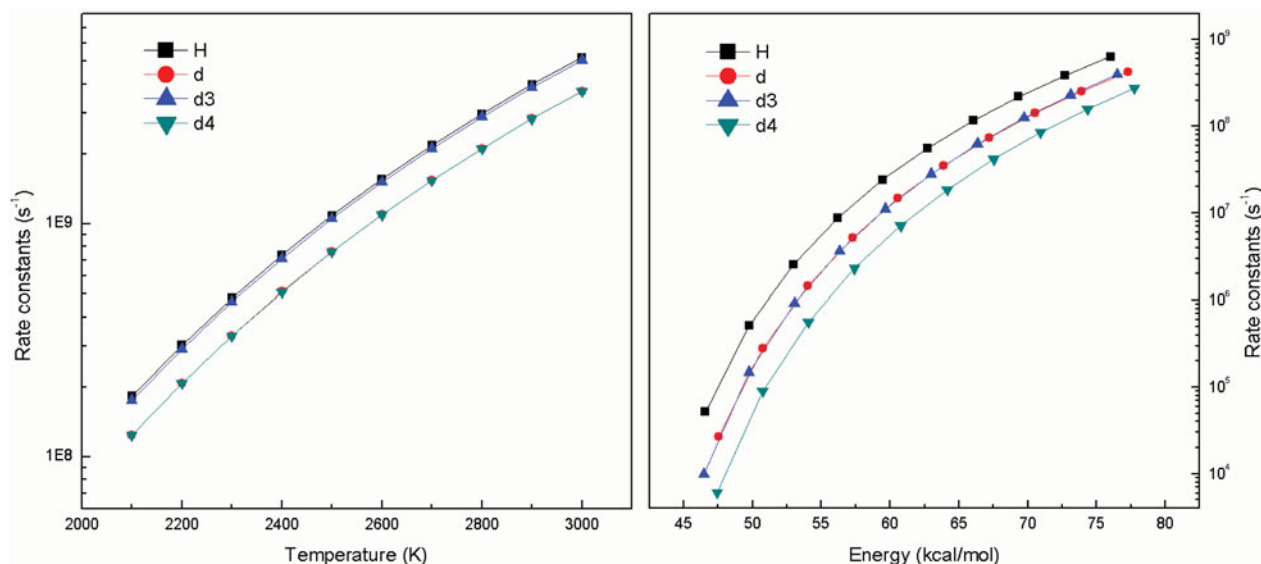
Figure 9. The canonical and microcanonical rate constants (harmonic) for enediol-D to TS4-D. The unit of rate constant is s^{-1}.

the difference between the results of CH$_3$COOH case and CH$_3$COOD case is in the range from 28.41% to 31.78%, The results of CH$_3$COOH and the deuterated results of CD$_3$COOD case is in the range from 28.41% to 31.35%. For example, when the temperature is 2100 K, the harmonic rate constant for CH$_3$COOH is 1.82×10^8 s^{-1}, and the harmonic rate constant for CD$_3$COOH case is 1.76×10^8 s^{-1}, for CH$_3$COOD case is 1.24×10^{-4} s^{-1} and for CD$_3$COOD case is 1.24×10^{-4} s^{-1}. In the microcanonical system, both the result of the deuterated harmonic rate constants and the result of the deuterated harmonic rate constants by size are H > d3 > d > d4, this conclusion can be reached from Figures 8 and 9 specifically.

3.4. Unimolecular dissociation of the trans-acetic acid radical (the channel includes the TS2)

This reaction, the anharmonic and harmonic rate constants for canonical case are presented in Table 14, with temperatures ranging from 1000 to 4000 K. Corresponding to Table 14, the rate constants for the title reaction are plotted in Figure 10. From Table 14, it is clear that both the harmonic and anharmonic rate constants increase with the increasing temperatures. With the temperatures increasing from 1000 to 4000 K, the harmonic rate constants increase from 0.43×10^{-2} to 8.91×10^9 s^{-1}, while the anharmonic rate constants are in the range from 0.52×10^{-2} to 1.66×10^{10} s^{-1}. The anharmonic rate constants are higher

Figure 10. The canonical and microcanonical rate constants for *trans*-acetic acid (H) to TS2 (H). The unit of rate constant is s^{-1}.

Figure 11. The canonical and microcanonical rate constants (anharmonic) for *trans*-acetic acid-D to TS2-D. The unit of rate constant is s^{-1}.

than the harmonic ones at all range of temperatures. When the temperature is 1000 K, the harmonic rate constant $(0.43 \times 10^{-2} \text{ s}^{-1})$ is 17.3% lower than the harmonic rate constant $(0.52 \times 10^{-2} \text{ s}^{-1})$, while the harmonic rate constant $(8.91 \times 10^{9} \text{ s}^{-1})$ is 46.3% lower than the anharmonic rate constant $(1.66 \times 10^{10} \text{ s}^{-1})$ at the temperature 4000 K. The first several energies are worth noting in Table 14 as they are all lower than the calculated activation energy of 66.42 kcal mol^{-1}. Hence, we have to calculate the rate constants in the microcanonical system at higher energies.

The total energies are 23,940.39–37,007.05 cm^{-1}, corresponding to the temperatures from 2800 to 3900 K, respectively, using Equation (17). Table 15 shows the harmonic and anharmonic rate constants of the title reaction obtained with the YL method for microcanonical case. The rate constants of the microcanonical total energies are also illustrated in Figure 10.

From Table 15 and Figure 10, for the microcanonical system, we can see that the harmonic and anharmonic rate constants increase with the increasing total energies. With
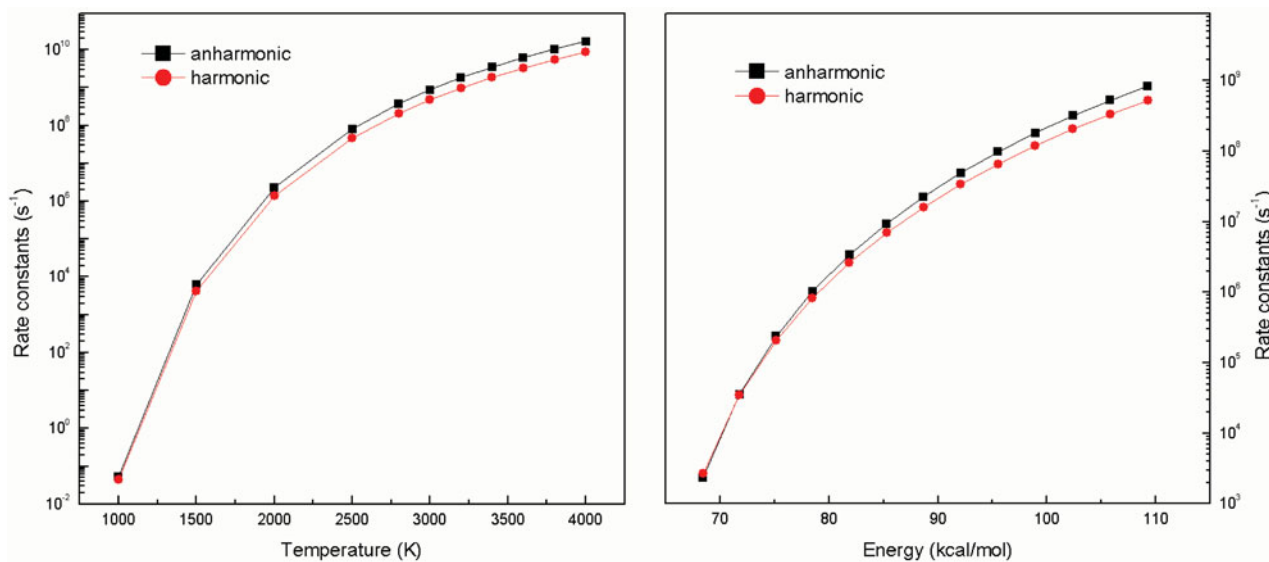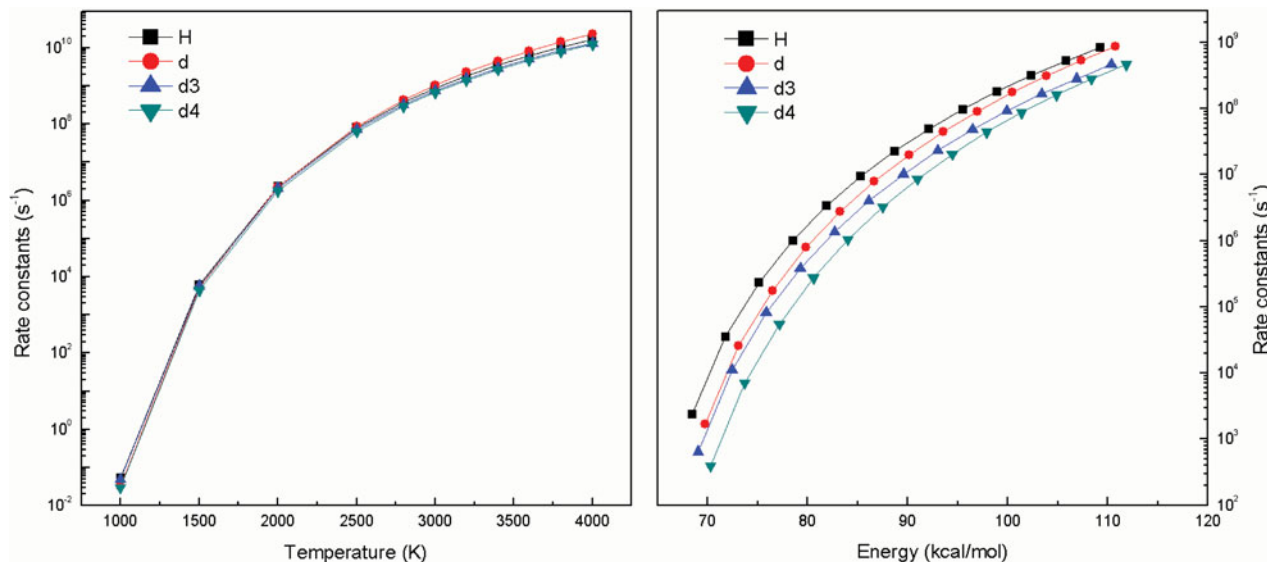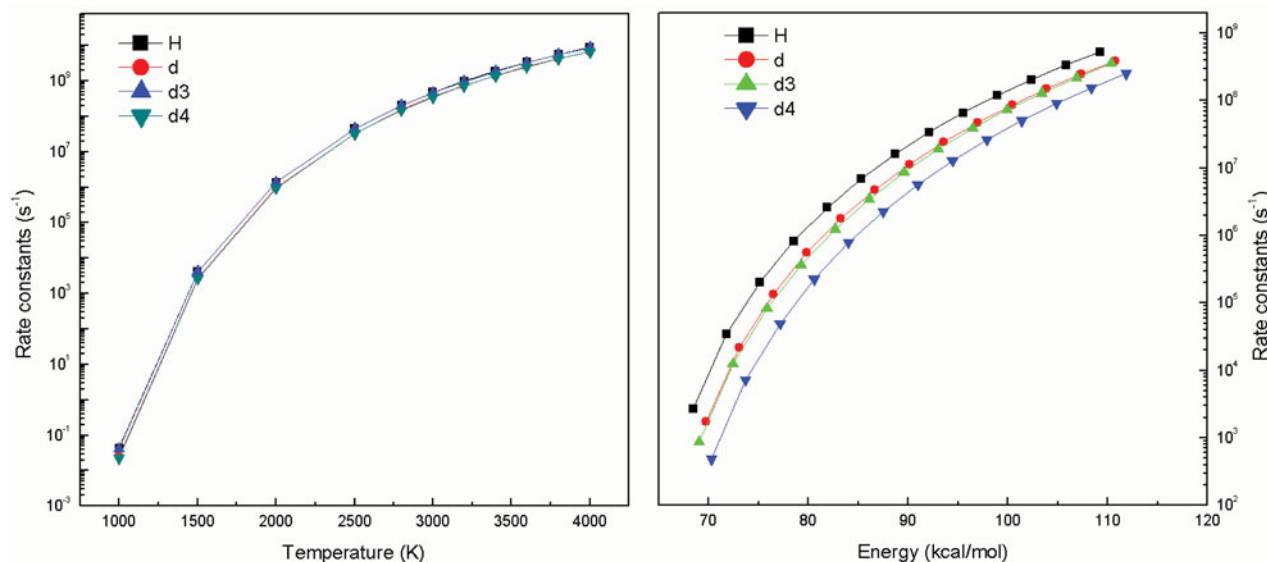

Figure 12. The canonical and microcanonical rate constants (harmonic) for *trans*-acetic acid-D to TS2-D. The unit of rate constant is s^{-1}.

Table 12. The rate constants from enediol-D to TS4-D at different temperatures for the canonical system. The unit of rate constant is s^{-1}.

	Temperature (K)	2100	2200	2300	2400	2500	2600	2700	2800	2900	3000
d	Anharmonic rate constant (s^{-1})	5.22×10^8	9.21×10^8	1.55×10^9	2.52×10^9	3.95×10^9	6.01×10^9	8.88×10^9	1.28×10^{10}	1.80×10^{10}	2.49×10^{10}
	Harmonic rate constant (s^{-1})	1.24×10^8	2.08×10^8	3.33×10^8	5.12×10^8	7.61×10^8	1.10×10^9	1.54×10^9	2.11×10^9	2.84×10^9	3.73×10^9
d3	Anharmonic rate constant (s^{-1})	1.06×10^9	1.90×10^9	3.23×10^9	5.27×10^9	8.29×10^9	1.26×10^{10}	1.86×10^{10}	2.68×10^{10}	3.76×10^{10}	5.16×10^{10}
	Harmonic rate constant (s^{-1})	1.76×10^8	2.92×10^8	4.65×10^8	7.11×10^8	1.05×10^9	1.51×10^9	2.12×10^9	2.89×10^9	3.87×10^9	5.07×10^9
d4	Anharmonic rate constant (s^{-1})	6.07×10^8	1.07×10^9	1.82×10^9	2.95×10^9	4.63×10^9	7.04×10^9	1.04×10^{10}	1.50×10^{10}	2.11×10^{10}	2.92×10^{10}
	Harmonic rate constant (s^{-1})	1.24×10^8	2.08×10^8	3.32×10^8	5.11×10^8	7.61×10^8	1.10×10^9	1.54×10^9	2.11×10^9	2.83×10^9	3.73×10^9

Table 13. The rate constants from enediol-D to TS4-D at different energies for the microcanonical system. The unit of rate constant is s^{-1}.

d

Energy (kcal mol^{-1})	47.55	50.77	54.02	57.29	60.58	63.89	67.22	70.56	73.92	77.29	—
Correspond (cm^{-1})	16,630.61	17,756.81	18,893.50	20,037.18	21,187.86	22,345.53	23,510.20	24,678.36	25,853.52	27,032.18	—
Anharmonic rate constant (s^{-1})	5.22×10^4	6.09×10^5	3.40×10^6	1.29×10^7	3.85×10^7	9.66×10^7	2.14×10^8	4.30×10^8	8.00×10^8	1.40×10^9	—
Harmonic rate constant (s^{-1})	2.67×10^4	2.77×10^5	1.45×10^6	5.19×10^6	1.47×10^7	3.52×10^7	7.44×10^7	1.43×10^8	2.55×10^8	4.26×10^8	—

d3

Energy (kcal mol^{-1})	46.48	49.74	53.03	56.33	59.66	63.00	66.36	69.74	73.12	76.52	79.93
Correspond (cm^{-1})	16,256.38	17,396.57	18,547.24	19,701.42	20,866.09	22,034.25	23,209.41	24,391.57	25,573.72	26,762.87	27,955.52
Anharmonic rate constant (s^{-1})	2.14×10^4	3.72×10^5	2.52×10^6	1.08×10^7	3.53×10^7	9.55×10^7	2.26×10^8	4.81×10^8	9.40×10^8	1.72×10^9	2.98×10^9
Harmonic rate constant (s^{-1})	9.88×10^3	1.48×10^5	9.19×10^5	3.65×10^6	1.12×10^7	2.83×10^7	6.28×10^7	1.26×10^8	2.31×10^8	4.00×10^8	6.50×10^8

d4

Energy (kcal mol^{-1})	47.44	50.74	54.06	57.40	60.76	64.14	67.53	70.93	74.34	77.77	81.20	115.23
Correspond (cm^{-1})	16,592.14	17,746.32	18,907.49	20,075.65	21,250.81	22,432.97	23,618.62	24,807.77	26,000.42	27,200.06	28,399.70	40,301.69
Anharmonic rate constant (s^{-1})	1.28×10^4	2.13×10^5	1.44×10^6	6.21×10^6	2.04×10^7	5.56×10^7	1.32×10^8	2.79×10^8	5.45×10^8	9.93×10^8	1.71×10^9	5.37×10^7
Harmonic rate constant (s^{-1})	6.11×10^3	9.03×10^4	5.68×10^5	2.32×10^6	7.21×10^6	1.87×10^7	4.21×10^7	8.54×10^7	1.59×10^8	2.77×10^8	4.56×10^8	2.23×10^7

Table 14. The rate constants from *trans*-acetic acid (H) to TS2(H) at different temperatures for the canonical system. The unit of rate constant is s^{-1}.

Temperature (K)	1000	1500	2000	2500	2800	3000	3200	3400	3600	3800	4000
Energy (kcal mol^{-1})	13.74	27.25	42.43	58.52	68.45	75.14	81.89	88.68	95.51	102.37	109.26
Correspond (cm^{-1})	4805.57	9530.69	14,839.89	20,467.37	23,940.39	26,280.22	28,641.03	31,015.83	33,404.62	35,803.91	38,213.69
Anharmonic rate constant (s^{-1})	0.52×10^{-2}	6.25×10^{3}	2.31×10^{6}	8.14×10^{7}	3.75×10^{8}	8.74×10^{8}	1.83×10^{9}	3.52×10^{9}	6.26×10^{9}	1.05×10^{10}	1.66×10^{10}
Harmonic rate constant (s^{-1})	0.43×10^{-2}	4.20×10^{3}	1.38×10^{6}	4.54×10^{7}	2.04×10^{8}	4.72×10^{8}	9.83×10^{8}	1.88×10^{9}	3.34×10^{9}	5.60×10^{9}	8.91×10^{9}

Table 15. The rate constants from *trans*-acetic acid (H) to TS2 (H) at different energies for the microcanonical system. The unit of rate constant is s^{-1}.

Energy (kcal mol^{-1})	68.45	71.79	75.14	78.51	81.89	85.28	88.68	92.09	95.51	98.93	102.37	105.81
Correspond (cm^{-1})	23,940.39	25,108.55	26,280.22	27,458.87	28,641.03	29,826.68	31,015.83	32,208.48	33,404.62	34,600.77	35,803.91	37,007.05
Anharmonic rate constant (s^{-1})	2.35×10^{3}	3.55×10^{4}	2.35×10^{5}	1.02×10^{6}	3.39×10^{6}	9.38×10^{6}	2.26×10^{7}	4.91×10^{7}	9.78×10^{7}	1.81×10^{8}	3.17×10^{8}	5.28×10^{8}
Harmonic rate constant (s^{-1})	2.66×10^{3}	3.44×10^{4}	2.05×10^{5}	8.27×10^{5}	2.61×10^{6}	6.90×10^{6}	1.61×10^{7}	3.38×10^{7}	6.57×10^{7}	1.19×10^{8}	2.05×10^{8}	3.36×10^{8}

Table 16. The rate constants from *trans*-acetic acid-D to TS2-D at different temperatures for the canonical system. The unit of rate constant is s⁻¹.

	Temperature (K)	1000	1500	2000	2500	2800	3000	3200	3400	3600	3800	4000
d	Anharmonic rate constant(d1) (s⁻¹)	0.33×10^{-1}	5.12×10^{3}	2.23×10^{6}	8.90×10^{6}	4.36×10^{8}	1.06×10^{9}	2.29×10^{9}	4.53×10^{9}	8.29×10^{9}	1.42×10^{10}	2.31×10^{10}
	Harmonic rate constant(d1) (s⁻¹)	0.25×10^{-1}	2.81×10^{3}	9.87×10^{5}	3.37×10^{7}	1.54×10^{7}	3.58×10^{8}	7.49×10^{8}	1.44×10^{9}	2.57×10^{9}	4.32×10^{9}	6.89×10^{9}
d3	Anharmonic rate constant(d3) (s⁻¹)	0.49×10^{-1}	5.75×10^{3}	2.07×10^{6}	7.11×10^{6}	3.22×10^{8}	7.41×10^{8}	1.54×10^{9}	2.91×10^{9}	5.12×10^{9}	8.46×10^{9}	1.33×10^{10}
	Harmonic rate constant(d3) (s⁻¹)	0.42×10^{-1}	4.12×10^{3}	1.36×10^{6}	4.50×10^{7}	2.02×10^{8}	4.68×10^{8}	9.74×10^{8}	1.86×10^{9}	3.31×10^{9}	5.55×10^{9}	8.84×10^{9}
d4	Anharmonic rate constant(d4) (s⁻¹)	0.30×10^{-1}	4.48×10^{3}	1.78×10^{6}	6.36×10^{6}	2.91×10^{8}	6.75×10^{8}	1.41×10^{9}	2.67×10^{9}	4.72×10^{9}	7.83×10^{9}	1.23×10^{10}
	Harmonic rate constant(d4) (s⁻¹)	0.22×10^{-1}	2.65×10^{3}	9.44×10^{5}	3.25×10^{7}	1.49×10^{8}	3.47×10^{8}	7.27×10^{8}	1.39×10^{9}	2.50×10^{9}	4.20×10^{9}	6.72×10^{9}

Table 17. The rate constants from *trans*-acetic acid-D to TS2-D at different energies for the microcanonical system. The unit of rate constant is s⁻¹.

d	Energy (kcal mol⁻¹)	69.73	73.09	76.47	79.86	83.26	86.68	90.10	93.53	96.96	100.41	103.86	107.31
	Correspond (cm⁻¹)	24,388.07	25,563.23	26,745.38	27,931.04	29,120.19	30,316.33	31,512.48	32,712.12	33,911.76	35,118.40	36,325.04	37,531.67
	Anharmonic rate constant (s⁻¹)	1.71×10^{3}	2.58×10^{4}	1.77×10^{5}	8.01×10^{5}	2.77×10^{6}	7.97×10^{6}	1.99×10^{7}	4.45×10^{7}	9.13×10^{7}	1.75×10^{8}	3.15×10^{8}	5.39×10^{8}
	Harmonic rate constant (s⁻¹)	1.72×10^{3}	2.20×10^{4}	1.34×10^{5}	5.54×10^{5}	1.78×10^{6}	4.80×10^{6}	1.13×10^{7}	2.41×10^{7}	4.72×10^{7}	8.66×10^{7}	1.50×10^{8}	3.91×10^{8}
d3	Energy (kcal mol⁻¹)	69.06	72.45	75.86	79.27	82.7	86.13	89.57	93.02	96.48	99.94	103.40	106.88
	Correspond (cm⁻¹)	24,153.74	25,339.39	26,532.04	27,724.68	28,924.33	30,123.97	31,327.11	32,533.75	33,743.88	34,954.02	36,164.15	37,381.28
	Anharmonic rate constant (s⁻¹)	6.48×10^{2}	1.11×10^{4}	8.18×10^{4}	3.84×10^{5}	1.37×10^{6}	4.02×10^{6}	1.02×10^{7}	2.32×10^{7}	4.80×10^{7}	9.22×10^{7}	1.66×10^{8}	2.84×10^{8}
	Harmonic rate constant (s⁻¹)	8.64×10^{2}	1.25×10^{4}	8.29×10^{4}	3.64×10^{5}	1.24×10^{6}	3.49×10^{6}	8.60×10^{6}	1.90×10^{7}	3.86×10^{7}	7.30×10^{7}	1.30×10^{8}	2.19×10^{8}
d4	Energy (kcal mol⁻¹)	70.32	73.74	77.16	80.60	84.05	87.51	90.97	94.44	97.91	101.39	104.88	108.37
	Correspond (cm⁻¹)	24,594.42	25,790.57	26,986.71	28,189.85	29,396.49	30,606.62	31,816.76	33,030.39	34,244.02	35,461.15	36,681.78	37,902.41
	Anharmonic rate constant (s⁻¹)	3.96×10^{2}	7.12×10^{3}	5.53×10^{4}	2.78×10^{5}	1.06×10^{6}	3.28×10^{6}	8.72×10^{6}	2.06×10^{7}	4.41×10^{7}	8.72×10^{7}	1.61×10^{8}	2.81×10^{8}
	Harmonic rate constant (s⁻¹)	4.87×10^{2}	7.29×10^{3}	4.99×10^{4}	2.27×10^{5}	7.92×10^{5}	2.29×10^{6}	5.75×10^{6}	1.29×10^{7}	2.65×10^{7}	5.07×10^{7}	9.12×10^{7}	1.56×10^{8}

the energies increasing from 23,940.39 to 37,007.05 cm^{-1}, the harmonic rate constants increase from 2.66×10^3 to 3.36×10^8 s^{-1}, while the anharmonic rate constants are in the range from 2.35×10^3 to 5.28×10^8 s^{-1}. The anharmonic rate constants are higher than the harmonic ones except when the energy is 23,940.39 cm^{-1}. When total energy is 25,108.55 cm^{-1}, the harmonic rate constant $(3.44 \times 10^4$ s$^{-1})$ is 3.1% lower than the anharmonic rate constant $(3.55 \times 10^4$ s$^{-1})$, while the harmonic rate constant $(3.36 \times 10^8$ s$^{-1})$ is 36.4% lower than the anharmonic rate constant $(5.28 \times 10^8$ s$^{-1})$ at total energy 37,007.05 cm^{-1}. It can be seen that, the anharmonic effect is not obvious at the first several energies, but in the case of high energies that it is not negligible. In other words, the anharmonic effect is not such obvious as the other Three.

In Table 16 and 17, isotopic effect results of this reaction are also given. The rate constants for the isotopic effect cases are illustrated in Figures 11 and 12. For the canonical case, the isotopic effect is not obvious and the d4's result of the deuterate anharmonic rate constants is the smallest among the four values, but the other three data have no regular size. The result of the deuterated harmonic rate constants by size is H > d3 > d > d4, for example, when temperature is 4000 K, the harmonic rate constant for CH$_3$COOH case is 8.91×10^9 s^{-1}, the harmonic rate constant for CD$_3$COOH case is 8.84×10^9 s^{-1}, for CH$_3$COOD case is 6.89×10^9 s^{-1} and for CD$_3$COOD case is 6.72×10^{-4} s^{-1}. In the microcanonical system, both the result of the deuterated harmonic rate constants and the result of the deuterated harmonic rate constants by size are H > d > d3 > d4, and this conclusion can be reached from Figures 11 and 12 specifically.

For all the four unimolecular reactions, for the results of CH$_3$COOH or the deuterated results, we can see that the harmonic and anharmonic rate constants increase with the temperatures and total energies increasing in the canonical or the microcanonical system. In other words, the anharmonic effect becomes more significant with the temperatures and energies increasing, which cannot be neglected, while the anharmonic effect on the reaction *trans*-acetic acid → TS2 radical is the smallest one. The rate constants of the deuterated results are smaller than the results of H for all the four reactions. In the results of the CH$_3$COOH and the deuterated ones, the anharmonic effect becomes manifest along with the increase of temperatures or total energies. In the microcanonical system, the results of H are always the biggest ones among the deuterated rate constants of the four reactions.

Various systems and reactions give different results. We can find lots of examples in our previous papers [22]. The increasing ratio of total number of states $W(E)$ and density of state $\rho(E)$ are different. For anharmonic rate constants and harmonic rate constants, we cannot expect which one is higher than the other one.

4. Conclusions

In this paper, the anharmonic and harmonic rate constants have been calculated for canonical and microcanonical case of the four reactions with the YL method. The anharmonic effect on the decomposition reactions has been examined at MP2/6-311 + + G(3df,2p) level. All the values of barrier height (H) coincide with the earlier theoretical work [4] very well.

For the reaction *cis*-acetic acid → TS1, we obtain the barrier height (H) 75.19 kcal mol^{-1}, which is in accordance with the earlier theoretical (76.4 kcal mol^{-1})work by Page [4]. In both canonical and microcanonical cases, the rate constants increase with the total energies or the temperatures increasing basically. However, the difference between the two kinds of rate constants is notable. Therefore, we can draw the conclusion that the anharmonic effect is obvious in either canonical or microcanonical system, and the deuterated results are also like this.

For the reaction *cis*-acetic acid → TS3, we obtain the barrier height (H) 72.64 kcal/mol, which is in great agreement with the earlier theoretical (73.1 kcal mol^{-1}) work by Page [4]. In both canonical and microcanonical cases, the rate constants increase with the total energies increasing basically. The harmonic and anharmonic rate constants are different at all the temperatures and energies. What is more, the difference increases with the total energies increasing. Therefore, we can draw conclusion that the anharmonic effect is so significant that it cannot be neglected in either canonical or microcanonical system, also the CH$_3$COOH results and the deuterated results.

For the reaction enediol → TS4, we obtain the barrier height (H) 44.73 kcal mol^{-1}, which is in reasonable agreement with the earlier theoretical (44.8 kcal mol^{-1}) work in Ref. 4. In both canonical and microcanonical cases, the rate constants increase with the total energies increasing basically, and the anharmonic rate constants are higher than those for harmonic cases, especially in the case of high total energies and temperatures, which indicates that the anharmonic effect of this reaction is significant. Therefore, we can draw a conclusion that the anharmonic effect is so significant that it cannot be neglected in either canonical or microcanonical system.

For the reaction *trans*-acetic acid → TS2, we obtain the barrier height (H) 66.42 kcal mol^{-1}, which is in reasonable agreement with the earlier theoretical (66.9 kcal mol^{-1}) results in Ref. 4. In both canonical and microcanonical cases, the rate constants increase with the total energies increasing basically. However, the harmonic and anharmonic rate constants (H) produce similar results when the temperatures and energies are low, and the difference between the two kinds of rate constants is obvious at high energies and temperatures. What is more, the difference gradually becomes more and more obvious with the total energies increasing. Therefore, we can draw a conclusion that the

anharmonic effect is so significant that it is not negligible in either canonical or microcanonical system, also the non-deuterated results.

For all the four reactions, compared with the non-deuterated results, the deuterated results differ from each other in the microcanonical system, and for the canonical system, except the reaction enediol $\rightarrow$ TS4, the isotopic effect of the four reactions is not obvious. As the C–H bond scission in each reaction is different, the three deuterated results on the different positions would result in the different deuterated results. Moreover, at different temperatures, the deuterated results for each reaction are also different.

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