



Anharmonic Effect Study of Formaldehyde Unimolecular Reaction

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The rate constants of the unimolecular dissociation and isomerization reactions of the formaldehyde were calculated based on the harmonic and anharmonic oscillator models. The anharmonic effect was examined. *ab initio* Calculations were carried out at MP2/aug-cc-pVTZ level. The results show that the rate constant for the H elimination is the largest, *i.e.* the H-elimination is predominant channel for unimolecular reaction of HCHO. In addition, in the canonical system, the anharmonic effect is not obvious while, the one is visible in the microcanonical case. It is indicated that the anharmonic Rice-Ramsperger-Kassel-Marcus theory can provide a reasonably good description for formaldehyde unimolecular reaction.

Keywords: Anharmonic effect, Unimolecular reaction, Rate constant, Rice-Ramsperger-Kassel-Marcus theory.

INTRODUCTION

Formaldehyde has received continuous interest over last 40 years both the experimental and theoretical studies¹⁻¹³. On one hand, its abundance and importance in the environment have stimulated macroscopic kinetic and microscopic spectroscopic studies. On the other hand, formaldehyde provides a typical example for detailed studies of unimolecular reactions of small polyatomic molecules. As is well known, *ab initio* theoretical calculations of formaldehyde note that the ground electronic state correlates with molecular products (H₂ + CO) and radicals (H + HCO), while the electronically excited state S₁ correlates with excited state HCO. Recently, a new mechanism of formaldehyde decomposition has been discovered, termed "the roaming atom" mechanism¹⁴⁻¹⁶. The discovery has shown that it is possible to have multiple pathways for a reaction leading to the same product. Furthermore, the existence of the *trans*-HCOH isomer of formaldehyde is supported by theoretical¹ and experimental¹⁷ studies, which suggest that, near the decomposition threshold, a rearrangement reaction could take place, followed by a geometric isomerization.

Although many efforts have been made to research the decomposition and isomerization for formaldehyde, the study of the anharmonic effect of the reactions is very rare. At present, many chemists observed significant anharmonic effects in dissociation of clusters and molecular systems and the requirement for the anharmonic correction to previous reaction rate theories has been emphasized by several authors¹⁸⁻²⁹. In our previous papers, we have successfully studied the anharmonic

effect on the decomposition reaction³⁰⁻³⁵ and the concerted exchange reaction of the small cyclic water clusters³⁶. Our purpose in this paper is twofold, the one is to calculate rate constants of the dissociation and isomerization reactions of formaldehyde with anharmonic Rice-Ramsperger-Kassel-Marcus (RRKM) theory³⁰. The other is to analyze the anharmonic effect for the two kinds of reactions. The method we applied was presented by Yao and Lin, which can carry out the first principle calculations about the rate constants of molecular reactions within the framework of the transition state theory (TST).

COMPUTATIONAL METHODS

***ab initio* Calculations:** The reactions considered here are



First of all, the geometries of reactants and transition states have been optimized at MP2/aug-cc-pVTZ level using Gaussian 03 program³⁷. Then, the vibrational harmonic and anharmonic frequencies, calculated at the same level, are used for characterization of stationary points and ZPE (zero-point energy) corrections and for the calculations of the rate constant, within the framework of the TST and the RRKM theory, respectively. As distinct transition state for the H loss does not exist in reaction (IV). Variational transition state theory (VTST) is applied to obtain the transition state with the dividing surface

method. So, all stationary points have been positively identified as local minima or transition states. To obtain more accurate energy, the single point energy is recalculated at the CCSD(T)/aug-cc-pVTZ level.

Anharmonic Rice-Ramsperger-Kassel-Marcus (RRKM)

theory: According to the RRKM theory, the unimolecular reaction rate constant in the microcanonical system can be expressed as³⁸

$$k(E) = \frac{\sigma}{h} \frac{W^\ddagger(E - E^\ddagger)}{\rho(E)} \quad (1)$$

where σ is the symmetry factor (here we set $\sigma = 1$), h is Planck's constant, $\rho(E)$ represents the density of states of the reactant and $W^\ddagger(E - E^\ddagger)$ is the total number of states for the transition state. E^\ddagger and E represent the total energy given to the system and the activation energy, respectively. Thus, as is expected in a statistical treatment, the RRKM theory simply states that the rate constant is proportional to the fraction of molecules with an internal energy E meeting the reaction requirement regardless of how the molecule has been activated to that energy³⁹⁻⁴¹. It should be emphasized that conventionally $W^\ddagger(E - E^\ddagger)$ and $\rho(E)$ are evaluated in the Morse oscillator potential. In general, from the definitions of $W(E)$ and $\rho(E)$ they can be expressed as

$$k(E) = \frac{s}{h} \frac{W^1(E - E^1)}{r(E)} \quad (2)$$

$$\rho(E) = \frac{dW(E)}{dE} \quad (3)$$

here $H(E - E_i)$ denotes the Heaviside function, energy levels E_i are calculated explicitly. Applying the Laplace transformation to eqns. 2 and 3, we obtain

$$\int_0^\infty dE e^{-\beta E} W(E) = \frac{Q(\beta)}{\beta} = L[W(E)] \quad (4)$$

$$\int_0^\infty dE e^{-\beta E} \rho(E) = Q(\beta) = L[\rho(E)] \quad (5)$$

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. In other words $W(E)$ and $\rho(E)$ can be obtained from eqns. 4 and 5 by the inverse Laplace transformation, which in turn can be expressed in terms of contour integrals. The contour integrals involved in the inverse Laplace transformation can be evaluated by using the first- and second-order saddle-point approximation method. The detail of derivation can be found³⁰⁻³². According to the TST, for a canonical system, the rate constant is given by

$$k_r(T) = \frac{kT}{h} \frac{Q^\ddagger(T)}{Q(T)} e^{-\frac{E_a^\ddagger}{kT}} \quad (6)$$

where $Q(T)$ and $Q^\ddagger(T)$ represent the partition functions for the reactant and activated complex, respectively. In this case, we have

$$Q^1(T) = \prod_i^{N-1} q_i^1(T) \quad (7)$$

$$Q(T) = \prod_i^N q_i(T) \quad (8)$$

where N is the number of the vibrational modes of the reactant and $q_i^\ddagger(T)$ and $q_i(T)$ are the vibrational partition functions for the transition state and the reactant for each mode, respectively.

The above discussion suggests that the partition function plays an important role in calculating the total number of states, the density of states and the rate constants. To investigate the anharmonic effect on a unimolecular reaction, the anharmonic number and the density of states of a system of separate Morse oscillators take a particularly simple form. For the Morse oscillator, we have

$$E_{n_i} = (n_i + \frac{1}{2})\hbar\omega_i - x_i(n_i + \frac{1}{2})^2\hbar\omega_i \quad (9)$$

where E_{n_i} is the energy of the i th vibrational mode and calculated explicitly by quantum numbers. ω_i is the frequency of the i th 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} and $n_i^{\max} = 1/2x_i - 1/2$. In other words, the anharmonic effect has two features: one is that the energy spacings are not equal and the other is the existence of a maximum quantum number n_i^{\max} . The anharmonic constant for various molecules can be determined from anharmonic frequency calculation in Gaussian 03.

RESULTS AND DISCUSSION

Table-1 summarizes optimized structures of formaldehyde (H_2CO), *trans*-HCOH, TS1, TS2 and TS3 (Fig. 1). And some theoretical and experimental results^{1,4,5,11} are also listed for comparison.

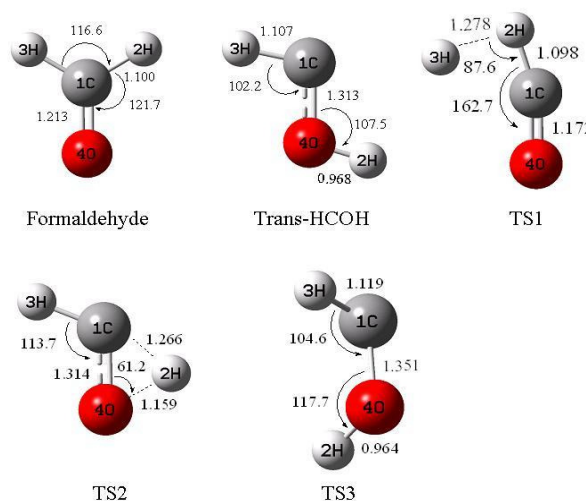


Fig. 1. The optimized structures of formaldehyde, *trans*-HCOH, TS1, TS2 and TS3 at the MP2/aug-cc-pVTZ level [bond lengths (Å) and angles (°)]

Dissociation reaction (I): For the formaldehyde molecule, the optimized geometry and vibrational frequencies show excellent agreement with experimental data^{1,2}. In addition, internal coordinates calculated are close to the corresponding data calculated at other levels of theory, for example, MP2/6-311G, B3LYP/6-311G⁸, MCSCF/D95¹⁰ and QCISD/D95 (d, p)¹¹.

TABLE-1
GEOMETRIC PROPERTIES OF FORMALDEHYDE, TRANS-HCOH,
TS1, TS2 AND TS3, BOND LENGTH (Å) AND ANGLES (°)

H ₂ CO	R (1C4O)	R (1C2H)	θ (4O1C2H)	θ (2H1C3H)	α	
MP2	1.213	1.100	121.7	116.6	180.0	
Ref. 1	1.203	1.100	121.8	116.3	180.0	
Ref. 11	1.184	1.091	122.1	115.7	180.0	
<i>trans</i> -HCOH	R (1C4O)	R (1C3H)	R (4O2H)	θ (4O1C3H)	θ (1C4O2H)	α
MP2	1.313	1.107	0.968	102.2	107.5	180.0
Ref. 4	1.337	1.098	0.953	103.8	114.4	180.0
Ref. 11	1.331	1.118	0.969	101.4	107.4	180.0
TS1	R (1C4O)	R (1C2H)	R (2H3H)	θ (4O1C2H)	θ (3H2H1C)	α
MP2	1.172	1.098	1.278	162.7	87.6	180.0
Ref. 5	1.190	1.100	1.371	163.7	87.4	180.0
Ref. 11	1.191	1.094	1.589	161.9	51.5	180.0
TS2	R (1C4O)	R (1C2H)	R (4O2H)	θ (4O1C3H)	θ (1C4O2H)	α
MP2	1.314	1.266	1.159	113.7	61.2	180.0
Ref. 5	1.316	1.262	1.198	117.3	55.0	180.0
Ref. 11	1.232	1.111	1.183	114.4	59.2	180.0
TS3	R (1C4O)	R (1C3H)	R (4O2H)	θ (4O1C3H)	θ (1C4O2H)	α
MP2	1.351	1.119	0.964	104.6	117.7	90.8
Ref. 5	1.376	1.111	0.951	105.1	128.7	89.0
Ref. 11	1.372	1.131	0.963	104.0	116.0	91.0

TABLE-2
HARMONIC VIBRATIONAL FREQUENCIES (cm⁻¹) OF FORMALDEHYDE, *trans*-HCOH AND TS1, TS2 AND TS3 CALCULATED AT
MP2/aug-cc-pVTZ LEVEL. THE CRITICAL ENERGIES WITH ZPE CORRECTION ARE OBTAINED AT CCSD(T)/aug-cc-pVTZ LEVEL

H ₂ CO	ω ₁	ω ₂	ω ₃	ω ₄	ω ₅	ω ₆	E
MP2	3047	2973	1753	1550	1267	1197	0
Ref. 2	3008	2944	1763	1562	1281	1191	0
Ref. 11	3198	3130	2016	1598	1282	1182	0
<i>trans</i> -HCOH	ω ₁	ω ₂	ω ₃	ω ₄	ω ₅	ω ₆	E
MP2	3745	2947	1513	1343	1211	1113	51.5
Ref. 4	4075	3158	1877	1264	1101	1093	
Ref. 11	3828	2928	1543	1321	1224	1093	55.7
TS1	ω ₁	ω ₂	ω ₃	ω ₄	ω ₅	ω ₆	E
MP2	1947 <i>i</i>	3152	1851	1367	911	804	81.3
Ref. 5	1853 <i>i</i>	3207	1815	1282	849	791	
Ref. 11	2001 <i>i</i>	3251	1832	1466	868	857	86.7
TS2	ω ₁	ω ₂	ω ₃	ω ₄	ω ₅	ω ₆	E
MP2	2089 <i>i</i>	2962	2647	1402	1324	819	81.7
Ref. 5	2705 <i>i</i>	3298	2752	1568	1221	4323	
Ref. 11	2236 <i>i</i>	2981	2664	1413	1292	693	83.9
TS3	ω ₁	ω ₂	ω ₃	ω ₄	ω ₅	ω ₆	E
MP2	1495 <i>i</i>	3854	2813	1416	1200	683	78.2
Ref. 11	1548 <i>i</i>	3907	2784	1415	1185	755	79.3

As shown in Table-1, the 1C4O and 1C2H bond distances show little variation, *i.e.* 1.212 Å and 1.101 Å at formaldehyde and 1.172 Å and 1.098 Å at TS1, respectively. The 2H3H and 1C3H bond distances are 1.872 Å and 1.100 Å at the reactant, respectively, while they reach 1.278 Å and 1.649 Å at TS1, *i.e.*, the formation of the 2H3H bond and dissociation of the 1C3H bond. So, the reaction coordinate for the decomposition reaction is composed of the increase in the 1C3H bond distance and 1C2H3H angle and the decrease in 2H3H bond distance. Furthermore, our calculated critical energy is 78.7 kcal/mol (with ZPE correction) at CCSD(T)/aug-cc-pVTZ, which is in good agreement with the best experimental value (79.2 ± 0.8) kcal/mol⁷, and other values, as 79.1 kcal/mol (MP4SDTD/6-311G)⁸, 81.0 kcal/mol (QCISD/6-311++G)⁹, 83.2 kcal/mol (MC10/D95)¹⁰ and 86.7 kcal/mol (QCISD/D95(d, p))¹¹.

On the basis of the above *ab initio* calculation results, we calculate harmonic and anharmonic dissociation rate constants for the microcanonical and canonical cases, respectively. The results are given in Tables 3 and 4 and illustrated in Fig. 2, respectively. For comparison, the results of Martins *et al.*¹⁰ and Bauerfeldt *et al.*¹¹ are also displayed in tables and figure, respectively. From Fig. 2 (a), it can be seen that the rate constants sharply increase with the increasing temperature, especially less than 1000 K. Table-3 shows the harmonic rate constants are smaller than the anharmonic ones. The result is opposite to the one in the microcanonical system. For the microcanonical case, the dissociation occurs as the total energy reaches the activation energy, whether in the harmonic or anharmonic model. Moreover, as shown in Fig. 2 (b), the harmonic and anharmonic rate constants sharply increase as the total energy

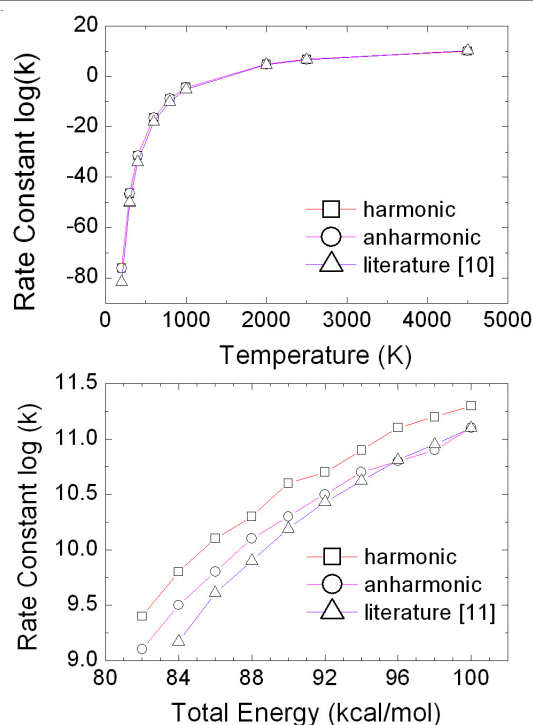


Fig. 2. Decomposition rate constants of formaldehyde $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ in the canonical (top) and microcanonical (bottom) cases. The unit of rate constant k is s^{-1}

energy becomes slightly higher than the activation energy. The result suggests that, due to activation energies in the dissociation of H_2CO , there exists a distinct threshold behavior in the plot of $k(E)$ as the function of E . The detailed data can be obtained from Table-4. Furthermore, the results show that the anharmonic effect is very significant for the microcanonical system, while, in the canonical case, the one is not obvious.

On the other hand, by comparing our results with the literature ones, we find that the calculated rate constants, whether in the canonical or the microcanonical case, are larger than literature ones. But, Fig. 2 showed a distinct picture that deviation between our calculated rate constants and literature ones becomes small when the total energy or temperature increases. The anharmonic rate constants are closer to the literature results. So, the anharmonic effect should be considered for reaction (I).

Isomerization reaction (II): For the reaction (II), the 1C4O and 1C3H bond distances show little variation, 1.212 Å

and 1.101 Å at formaldehyde, 1.312 Å and 1.105 Å at TS2, respectively. The 4O2H and 1C2H bond distances reach 1.169 Å and 1.166 Å, respectively and the 1C4O2H angle reaches 61.2° at TS2. These changes suggest the movement of the hydrogen atom in molecular plane, dissociating of the 1C2H bond and forming of the 4O2H bond. The isomerization barrier values including ZPE are 79.7 kcal/mol, calculated at CCSD(T) levels. Our value agrees with the literature values 80.0 kcal/mol and 83.9 kcal/mol¹¹, which calculated at B3LYP/D95(d, p) and QCISD/D95(d, p), respectively.

The harmonic and anharmonic rate constants calculated are plotted in Fig. 3 and listed in Tables-3 and 4, respectively, for canonical and microcanonical cases. For comparison, the results Bauerfeldt *et al.*¹¹ is plotted in Fig. 3. (b). The rate constants increase with the increasing temperature or total energy. It can be seen that the anharmonic rate constants are smaller than the harmonic ones, whether in the canonical or microcanonical case. The result is different from the one for reaction (I). Moreover, the difference between the harmonic and the anharmonic rate constants increases with the increasing temperature or total energy. That is, the anharmonic effect becomes obvious as temperature or total energy increases. Meanwhile, it is found that the difference is larger in the microcanonical case than in the canonical one, *i.e.* the anharmonic effect in the microcanonical case is more significant.

Isomerization reaction (III): The geometric isomerization *trans*-HCOH \rightarrow *cis*-HCOH occurs by an out-of-plane rotation of the hydrogen atom. Little change is found among bond distances at the TS3 and the potential minima. The dihedral angle undergoes the largest variation, reaching 90.8° at TS3. Then, critical energy found for the geometric isomerization *trans*-HCOH \rightarrow *cis*-HCOH in this work is, 26.8 kcal/mol at CCSD(T) levels.

According to the *ab initio* calculation results, the canonical and microcanonical rate constants for isomerization are presented in Fig. 4 and tabulated in Tables 3 and 4. The literature results¹¹ also are plotted in Fig. 4. (b). The harmonic and anharmonic rate constants increase with the increasing temperature or total energy. For the canonical system, the magnitude of the harmonic rate constants is smaller than the anharmonic ones, while, in the microcanonical system, the harmonic rate constant is larger than the anharmonic one under 42.0 kcal/mol and smaller than the anharmonic one over 42.0 kcal/mol. And the difference between the harmonic and the anharmonic

TABLE-3
RATE CONSTANTS OF REACTIONS I-IV FOR DIFFERENT TEMPERATURES IN CANONICAL SYSTEM. THE UNITS OF TEMPERATURE AND RATE CONSTANT ARE K AND s^{-1} , RESPECTIVELY

Temp.	$\text{H}_2\text{CO} \rightarrow \text{H}_2\text{CO}$			$\text{H}_2\text{CO} \rightarrow \text{H} + \text{HCO}$		$\text{H}_2\text{CO} \rightarrow \text{trans-HCOH}$		$\text{trans-HCOH} \rightarrow \text{cis-HCOH}$	
	Harmonic	Anharmonic	Ref [10]	Harmonic	Anharmonic	Harmonic	Anharmonic	Harmonic	Anharmonic
200.0	7.44×10^{-77}	7.45×10^{-77}	2.37×10^{-82}	6.52×10^{-71}	5.37×10^{-71}	2.87×10^{-77}	2.87×10^{-77}	2.63×10^{-17}	2.63×10^{-17}
298.5	2.20×10^{-47}	2.21×10^{-47}	6.28×10^{-51}	4.99×10^{-43}	3.87×10^{-43}	1.15×10^{-47}	1.15×10^{-47}	1.74×10^{-7}	1.76×10^{-7}
300.0	4.39×10^{-47}	4.40×10^{-47}	1.31×10^{-50}	9.59×10^{-43}	7.44×10^{-43}	2.30×10^{-47}	2.30×10^{-47}	2.20×10^{-7}	2.21×10^{-7}
400.0	2.79×10^{-32}	2.82×10^{-32}	1.03×10^{-34}	1.44×10^{-28}	1.11×10^{-28}	2.27×10^{-32}	2.27×10^{-32}	2.23×10^{-2}	2.26×10^{-2}
600.0	3.90×10^{-17}	3.96×10^{-17}	9.55×10^{-19}	2.70×10^{-14}	2.24×10^{-14}	2.58×10^{-17}	2.58×10^{-17}	2.58×10^3	2.69×10^3
800.0	1.41×10^{-9}	1.44×10^{-9}	1.06×10^{-10}	4.17×10^{-7}	3.83×10^{-7}	9.49×10^{-10}	9.45×10^{-10}	9.45×10^5	1.02×10^6
1000.0	5.14×10^{-5}	5.28×10^{-5}	7.66×10^{-6}	9.15×10^{-3}	8.96×10^{-3}	3.42×10^{-5}	3.39×10^{-5}	3.36×10^7	3.75×10^7
2000.0	8.27×10^4	8.28×10^4	5.30×10^4	6.87×10^6	4.41×10^6	5.04×10^4	4.84×10^4	4.63×10^{10}	6.10×10^{10}
2500.0	5.98×10^6	6.39×10^6	5.21×10^6	4.33×10^8	2.39×10^8	3.52×10^6	3.33×10^6	1.99×10^{11}	2.74×10^{11}
4500.0	1.25×10^{10}	1.43×10^{10}	1.93×10^{10}	7.22×10^{11}	2.59×10^{11}	6.86×10^9	6.05×10^9	2.70×10^{12}	3.33×10^{12}

TABLE-4
RATE CONSTANTS OF REACTIONS I-IV FOR DIFFERENT TOTAL ENERGIES IN MICROCANONICAL SYSTEM.
THE UNITS OF TOTAL ENERGY AND RATE CONSTANT ARE kcal/mol AND s^{-1} . E DENOTES THE TOTAL ENERGY

E	$H_2CO \rightarrow H_2 + CO$			$H_2CO \rightarrow H + HCO$			$H_2CO \rightarrow trans\text{-HCOH}$			$trans\text{-HCOH} \rightarrow cis\text{-HCOH}$			
	H	A	Ref. 11	H	A	Ref. 11	H	A	Ref. 11	H	A	Ref. 11	E
78.0				4.15×10^{10}	3.43×10^{10}					1.54×10^{11}	0.98×10^{11}		28.0
80.0				1.50×10^{11}	9.66×10^{10}					2.84×10^{11}	2.08×10^{11}	2.47×10^{11}	30.0
82.0	2.75×10^9	1.23×10^9		3.56×10^{11}	1.93×10^{11}		2.92×10^9	1.59×10^9		4.64×10^{11}	3.69×10^{11}	4.63×10^{11}	32.0
84.0	5.88×10^9	3.05×10^9	1.49×10^9	6.96×10^{11}	3.33×10^{11}		4.31×10^9	2.13×10^9	2.00×10^9	6.85×10^{11}	5.84×10^{11}	7.81×10^{11}	34.0
86.0	1.21×10^{10}	6.50×10^9	4.06×10^9	1.21×10^{12}	5.21×10^{11}	1.16×10^{10}	8.23×10^9	4.22×10^9	4.75×10^9	9.45×10^{11}	8.54×10^{11}	1.05×10^{12}	36.0
88.0	2.17×10^{10}	1.19×10^{10}	8.02×10^9	1.94×10^{12}	7.63×10^{11}	8.62×10^{10}	1.42×10^{10}	7.37×10^9	9.57×10^9	1.24×10^{12}	1.18×10^{12}	1.86×10^{12}	38.0
90.0	3.57×10^{10}	1.98×10^{10}	1.55×10^{10}	2.93×10^{12}	1.06×10^{12}	2.30×10^{11}	2.26×10^{10}	1.18×10^{10}	1.61×10^{10}	1.58×10^{12}	1.55×10^{12}	1.96×10^{12}	40.0
92.0	5.49×10^{10}	3.06×10^{10}	2.72×10^{10}	4.21×10^{12}	1.42×10^{12}	4.08×10^{11}	3.40×10^{10}	1.77×10^{10}	2.83×10^{10}	1.94×10^{12}	1.96×10^{12}	2.73×10^{12}	42.0
94.0	8.00×10^{10}	4.48×10^{10}	4.20×10^{10}	5.83×10^{12}	1.85×10^{12}	7.19×10^{11}	4.86×10^{10}	2.52×10^{10}	4.22×10^{10}	2.33×10^{12}	2.41×10^{12}	3.11×10^{12}	44.0
96.0	1.12×10^{11}	6.28×10^{10}	6.41×10^{10}	7.81×10^{12}	2.33×10^{12}	1.15×10^{12}	6.68×10^{10}	3.45×10^{10}	6.12×10^{10}	2.75×10^{12}	2.89×10^{12}	4.03×10^{12}	46.0
98.0	1.51×10^{11}	8.52×10^{10}	8.99×10^{10}	1.02×10^{13}	2.90×10^{12}	1.75×10^{12}	8.92×10^{10}	4.58×10^{10}	8.38×10^{10}	3.19×10^{12}	3.39×10^{12}	4.49×10^{12}	48.0
100.0	1.99×10^{11}	1.12×10^{11}	1.25×10^{11}	1.30×10^{13}	3.52×10^{12}	2.49×10^{12}	1.16×10^{11}	5.90×10^{10}	1.14×10^{11}	3.65×10^{12}	3.91×10^{12}	5.25×10^{12}	50.0

H = Harmonic; A = Anharmonic

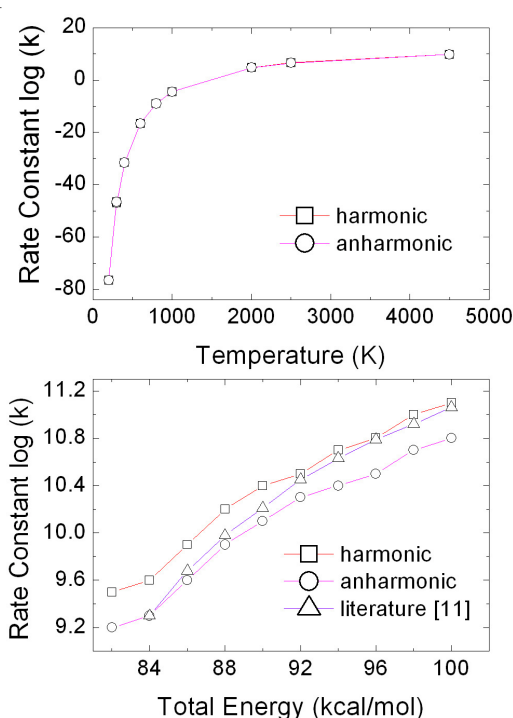


Fig. 3. The same as Fig. 2, but for the isomerization of formaldehyde $HCHO \rightarrow trans\text{-HCOH}$

rate constants increases for the canonical system, but, the difference decreases for the microcanonical system. The rate constants calculated in present work are in reasonable agreement with the predicted values within the literature¹¹.

H loss reaction (IV): As is expected, no intrinsic barrier exists for the H loss of formaldehyde. So, VTST is used to obtain the transition state in the reaction. To locate variational transition states, the PES scan with varying the C-H bond distance was carried out. Fifty optimized geometries were calculated corresponding to the C-H distances from 1.70 Å to 6.70 Å with a step of 0.1 Å. For obtaining more accurate positions of the variational transition states, an additional 20 optimized geometries were calculated with C-H distances from 2.85 Å to 3.85 Å with a step of 0.05 Å. Using the dividing surface method, the transition state, for the H loss of formaldehyde is located at the C-H distance of 3.62 Å at the CCSD(T)/aug-cc-pVTZ level. The energy with ZPE calculated is 75.4 kcal/mol.

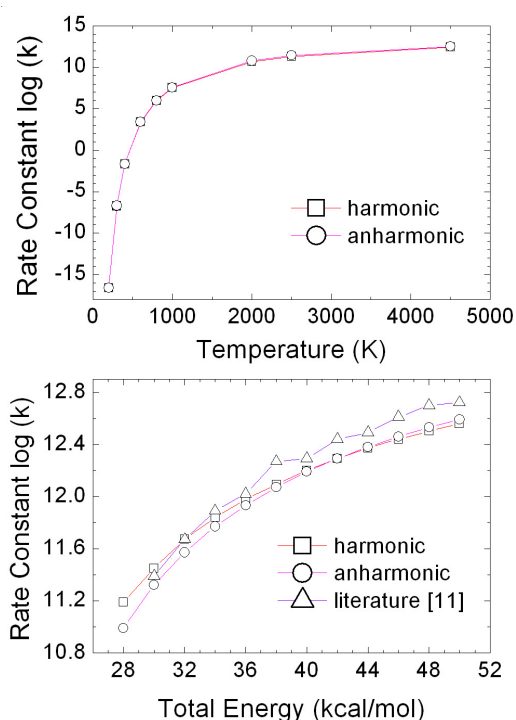


Fig. 4. The same as Fig. 2, but for the isomerization of $trans\text{-HCOH} \rightarrow cis\text{-HCOH}$

The harmonic and anharmonic dissociation rate constants are plotted in Fig. 5. The literature results¹¹ are also plotted in Fig. 5. (b). As shown in Fig. 5, the rate constant increases with the increasing temperature or energy. Moreover, the anharmonic rate constants are smaller than the harmonic ones, whether in the canonical or microcanonical case. Meanwhile, the deviation between harmonic and anharmonic rate constants becomes large when the total energy or temperature increases. It is noted that the difference in the dependence of harmonic and anharmonic rate constant is caused by the use of different models and harmonic and anharmonic potentials, which are utilized to simulate the vibrational bonds. For the different models and vibrational states, the total number and density of states are counted, which affects the reaction rate constant. In addition, by comparing our results with the literature ones, we find that the calculated rate constants are much higher than the literature ones at low energy. But, the difference between

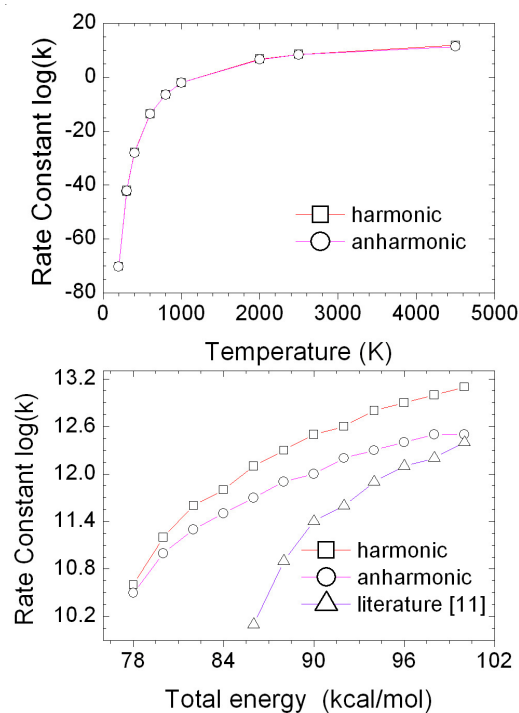


Fig. 5. The same as Fig. 2, but for $\text{HCHO} \rightarrow \text{H} + \text{HCO}$

them becomes smaller with the increasing temperature or energy. The result shows that the anharmonic constants are nearer to the ones with literature¹¹. Thus, the anharmonic effect should be considered in this reaction.

Conclusion

In this paper, we have calculated the anharmonic and harmonic rate constants of the decomposition and isomerization reactions for formaldehyde with anharmonic RRKM theory. Specially, we investigate the anharmonic effect of the rate constant. The calculated rate constants are in good agreement with the other theoretical and experimental results.

The rate constants for the reactions (I)-(IV) increase with the increasing temperature or total energy. In the microcanonical case, the harmonic rate constants are larger to the anharmonic ones, except for reaction III; the anharmonic effect is visible while in the canonical case, the one is not obvious. Then again, the rate constant is largest for reaction IV. That is, H-elimination is predominant. The reactions I and II are competitive over the whole range of temperature or total energy: First of all, the difference of critical energy is very small, the decomposition reaction 78.7 kcal/mol and the isomerization reaction 79.7 kcal/mol. Then, although the magnitude of the decomposition rate constants is a fit larger than the one of the isomerization rate constants, the difference between them is very small; At last, in the microcanonical case, the decomposition rate constants over the total range of energy is larger than the isomerization ones, except that the energy is equal to 82 kcal/mol. It should be noted that the contribution of rotational degrees of freedom can be taken into account in our method for the RRKM calculation through the calculation of rotational partition function. We can even take into account the effect of vibration-rotation interaction. This will be carried out in our future work.

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