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Ab Initio Dynamics of Unimolecular Decomposition of *β*-propiolactone and *β*-propiolactam

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Abstract

Using the potential energy surface and molecular properties obtained at the accurate composite W1U method, time-resolved temperature- and pressure-dependent behaviors of the thermal decomposition of β-propiolactone and β-propiolactam (for 500 – 2000 K & 0.001 – 760 torr) were charaterized using the integrated deterministic/stochastic model within the master equation/Rice–Ramsperger–Kassel–Marcus (ME/RRKM) framework. The integrated model helps to confidently explain and predict the different kinetic behaviors of the two similar-ring systems, which is consistent with experimental data, namely, β-propiolactone only decomposes to $C_2H_4 + CO_2$ while β-propiolactam can form both $C_2H_4 + HNCO$ (main product) and $CH_2CO + CH_2NH$ (minor product).

Introduction

The small oxygen-containing ring compounds are often used in synthetic and pharmaceutical chemistry [1-3] and can also appear as intermediates via the oxidation of hydrocarbon radicals [4-8]. These structures exhibiting a high degree of ring strain are typically sensitive to thermal decomposition, even at relatively low temperatures, due to their instability [9, 10]. The cyclic ester, β-propiolactone (2-oxetanone) has been received much attention [11-14] due to being an archetype of such small, ring-strained compounds. These studies had shown that β-propiolactone undergoes thermal decarboxylation to form ethene (C_2H_4) and carbon dioxide (CO_2) as the only products [11-13], which is believed to take place through an asynchronous concerted process by the theoretical investigations [15-17]. Having the similar structure, the nitrogen analogue of β-propiolactone, β-propiolactam (2-azetidinone), is an essential structural moiety for antibacterial activity [18, 19]. Despite their importance, there has been only one report in the literature on the thermal decomposition of β-propiolactam, in which C_2H_4, isocyanic acid (HNCO), ketene (CH_2CO) and formaldehyde (CH_2O) were detected by Lim *et al.* [11], using photoelectron spectroscopy (PE) method.

To our best knowledge, there is no *ab initio* study on the kinetics of both two of the title reactions to clarify/verify the previously experimental observation as well as give more in-depth understanding of the kinetic behaviors for two decomposition reactions of β-propiolactone and β-propiolactam - two small presented lactone and lactam families. Therefore, in this study, we carried out highly accurate *ab initio* calculations and state-of-the-art combined *deterministic* and *stochastic* statistical rate theory in the framework of RRKM/ME to provide reliable and comprehensive kinetic/thermodynamic data for the two title reactions in a wide range of

conditions. It is hoped to provide a detailed picture about the decomposition in order to control and optimize the applications of the two substances and related species.

Computational Details

All geometry structures of reactants, products and TSs were obtained at B3LYP/cc-pVTZ+d level of theory [20-22]. The calculated B3LYP/cc-pVTZ+d vibrational frequencies with the scaling factor of 0.985 [23-25] were used to calculate the zero-point energy (ZPE) corrections in the calculations of thermochemical properties. To estimate the accuracy of energy, we used Martin's W1U composite method [23-25] to approximate infinite-basis-set CCSD(T) whose procedure can be found in the work of Szőri *et al.* [26]. For all transition states, intrinsic reaction coordinate (IRC) [27, 28] calculations were also carried out at the B3LYP/cc-pVTZ+d to confirm the correct minima. The results obtained from W1U calculations, were then compared with less accurate composite methods such as CBS-QB3 [29], CBS-APNO [30], G3 [31] and G4 [32] levels of theory. All these calculations were performed by the Gaussian 09 quantum chemistry package [33].

Thermodynamic and kinetic analyses, using both deterministic and stochastic models, were carried out using the Multi-Species Multi-Channels (MSMC) code [34] accompanied with the aid of the MSMC-GUI [35], with updates and enhancements in stochastic profiles simulation and rate constant extraction. In the calculations, overall rotations were treated classically and vibrations were treated quantum mechanically within the harmonic oscillator (HO) approximation and the tunneling effect was treated using the 1-D Eckart model [36]. The energy-transfer process was computed on the basis of the exponential-down model with

$$\langle E_{down} \rangle = 250.0 \times \left(\frac{T}{298} \right)^{0.8} \text{cm}^{-1} \text{ for N}_2 \text{ as the bath gas [37]. The Lennard-Jones (L-J) parameters}$$

ε / k_B = 71.4 K and σ = 3.798 Å were used for N$_2$ [38] while ε / k_B = 357 K and σ = 5.18 Å were taken from the data of furan (C$_4$H$_4$O – M = 68) [39] to represent both β-propiolactone (C$_3$H$_4$O$_2$ – M = 72) and β-propiolactam (C$_3$H$_5$NO – M = 71). To investigate the significance of the variational effects, the canonical Variational TST (cVTST) calculations were carried out for all reaction channels. Specifically, for each reaction channel at a specific temperature, the high-pressure rate constants k^{TST} for a set of N variational transition states (VTS) along the reaction coordinate were calculated and the canonical variational TST rate constant was defined as $k^{cVTST}(T) = \min\left\{k_i^{TST}(T), i = 1..N\right\}$ with the extrapolation using the cubic spline method [40]. The value of N was chosen so that a converged result (less than 1% difference) was obtained between the two consecutive calculations, N and (N + 1).

Results and Discussion

The β-propiolactone and β-propiolactam molecules can decompose via two 4-membered-ring transition states (**TS1**, **TS2** from β-propiolactone and **TS3**, **TS4** from β-propiolactam, respectively) to form C$_2$H$_4$ + CO$_2$ (**P1**), CH$_2$CO + CH$_2$O (**P2**), C$_2$H$_4$ + HNCO (**P3**) and CH$_2$CO + CH$_2$NH (**P4**), respectively, presented in Figure 1 and Figure S1 in the accompanied Supplementary Information (SI) material.
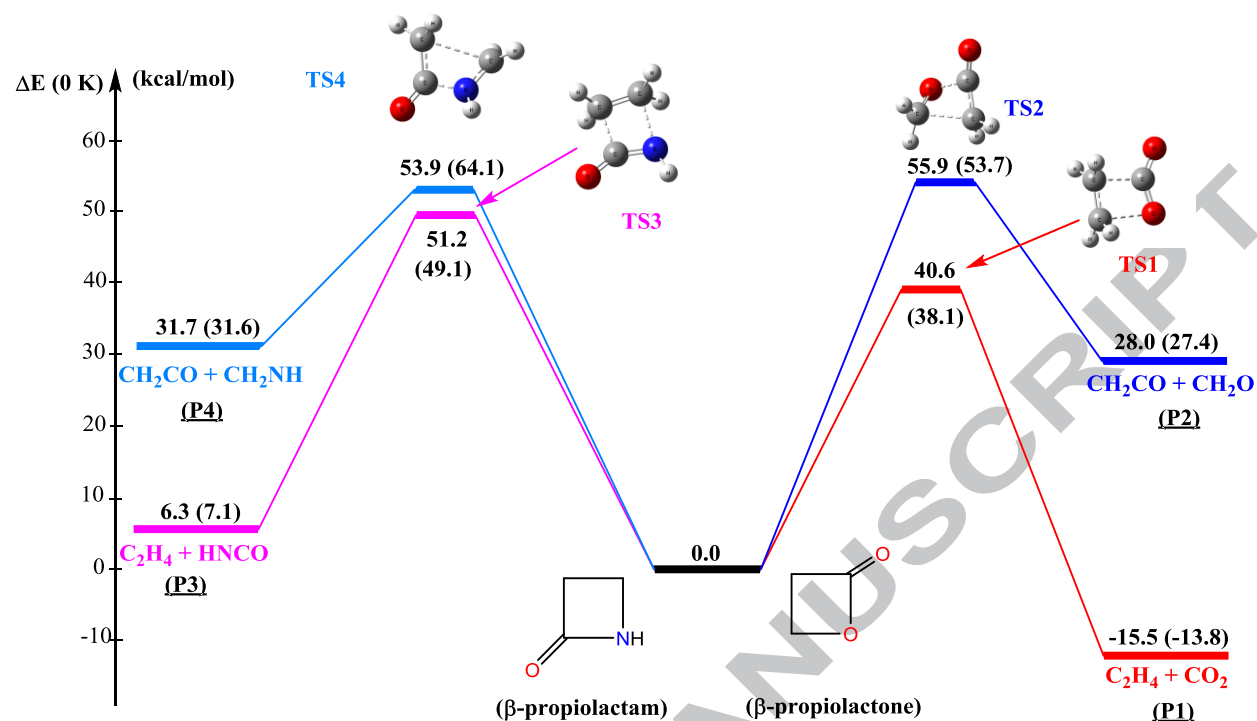
Figure 1: Potential energy surface (+ ZPE correction) of possible channels for the unimolecular decomposition reactions of *β*-propiolactone → products (*right*) and *β*-propiolactam → products (*left*) at W1U level of theory. Values in the parentheses are from the work of Lim *et al.* [11]. All values are in kcal/mol.

The optimized geometries are consistent with those of the literature data with average errors of ~ 0.1 Å and ~ 1° in bonds and angles, respectively. In particular, the geometries of the **TS1**, **TS2** and **TS3** obtained at the B3LYP/cc-pVTZ+d level in this study are very similar to the values obtained from the lower method, B3LYP/6-31G**, reported by Lim *et al.* [11]; however, there is a large difference between our calculated geometries and Lim's data [11] in **TS4** with maximum errors of ~ 0.2 Å and ~16° in bonds and angles, respectively, shown in Figure S2, that leads to the maximum difference of the energy of **TS4** between the calculated results and Lim's data [11] being about 10.2 kcal/mol. It is expected due to the small basis set, namely, 6-31G** used in the Lim's calculations [11] and the IRC calculations, depicted in Figure S3, were

performed on all TSs to verify our reliable results. The harmonic vibrational frequencies provided in the Table S1 are slightly higher than those available in the literature. For the sake of simplification, Figure 1 also presents the ZPE-corrected energy obtained from W1U calculations as "benchmark accuracy" [41] and those literature data available. The energies computed at W1U match excellently with those of the other methods except for the calculated data of Lim *et al.* [11] who employed a small basis set, namely, 6-31G** as discussed above (cf. Table 1). Our analysis herein suggests the W1U energetic profiles accompanied with the geometry and frequency information from B3LYP/cc-pVTZ+d can be considered as the most accurate data available for detailed kinetic analysis.

Table 1: Relative energies (in kcal/mol) to each reactant of the species involved and the corresponding transition states at different levels of theory at 0 K. The zero-point energy (ZPE) correction was included.

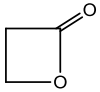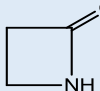| Method	TS1	TS2	TS3	TS4	$C_2H_4 + CO_2$ (**P1**)	$CH_2CO +$ CH_2O (**P2**)	$C_2H_4 +$ HNCO (**P3**)	$CH_2CO +$ CH_2NH (**P4**)
W1U[a]	**40.6**	**55.9**	**51.2**	**53.9**	**-15.5**	**28.0**	**6.3**	**31.7**
CBS-APNO[a]	39.8	55.0	50.5	52.7	-14.7	28.6	6.4	32.3
CBS-QB3[a]	40.6	55.4	51.2	52.9	-15.0	28.1	6.6	32.0
G3[a]	39.6	54.9	50.2	52.3	-16.1	27.7	5.3	31.0
G4[a]	40.4	55.7	50.6	53.0	-16.1	27.5	5.5	30.8
Ref.[b]	38.1	53.7	49.1	64.1	-13.8	27.4	7.1	31.6

[a] This work; [b] from the study of Lim *et al.* [11], calculated at B3LYP/6-31G** level of theory.

The calculated thermodynamic properties including heat of formation (ΔH_f^{298}) and entropy (S^{298}) for the species involved were compared to the literature data, shown in Table 2, in an attempt to evaluate the reliability of our computed numbers. In general, the calculated values are very consistent with the literature data (e.g., the differences are normally less than 0.5 kcal/mol and 1.0 cal/mol-K for ΔH_f^{298} and S^{298}, respectively, when compared to the ATcT data and less than 1.5 kcal/mol and 0.2 cal/mol-K for ΔH_f^{298} and S^{298}, respectively, when compared to the NIST data). Therefore, more confidence has been gained in our calculated data which were derived from a solid framework as presented previously.

As mentioned previously, the variational effects were also investigated for all reaction channels (cf. supplementary Figure S9). In particular, the effects were found not important for all channels (e.g., the mean absolute deviation between k^{TST} and k^{cVTST} is 8.2 and 16.0 % for the important channels via **TS1** and **TS3**, respectively); therefore, no effort was made to include the variational effects in the pressure analysis. Moreover, due to the limitation of the MSMC code,

only the 1-D Eckart model was used to investigate the tunneling effect (cf. supplementary Figure S10) which is shown not so important (i.e., the tunneling factors are small with the maximum value of 2.7 for channel **P1** at 300 K). The use of the simple model instead of the multidimensional tunneling treatments such as small-curvature tunneling (SCT) and large-curvature tunneling (LCT) might introduce some uncertainty to the calculated rate constants and the product branching ratios at temperature lower than 500 K; therefore, the valid temperature range for the calculated rate constants in this study is from 500 to 2000 K.

Table 2: Comparison of calculated thermodynamic properties of selected structures (only species for kinetic analysis) from the title reaction with experimental data (NIST= Webbook NIST, webbook.nist.gov, ATcT = Active Thermochemical Tables [42, 43][a]). Unit: $\Delta H_f^{298\,K}$ in kcal·mol^{-1}, $S^{298\,K}$ in cal·mol^{-1}·K^{-1}.

Species	Method	$\Delta H_f^{298\,K}$	$S^{298\,K}$
β-propiolactone	Ab initio[b]	-68.6	68.4
	NIST	-68.4 [44]	68.4 [45]
β-propiolactam	Ab initio[b]	-24.5	70.2
	NIST	N/A	N/A
TS1	Ab initio[b]	-27.7	71.0
TS2	Ab initio[b]	-12.2	71.4
TS3	Ab initio[b]	27.0	72.7
TS4	Ab initio[b]	29.3	70.1
C$_2$H$_4$ (ethylene)	Ab initio[b]	12.2	52.4
	ATcT[a]	12.6	52.4
	NIST	12.5 [46]	52.4 [46]
CO$_2$ (carbon dioxide)	Ab initio[b]	-94.8	51.2
	ATcT[a]	-94.0	51.1
	NIST	-94.1[46]	51.1[46]
CH$_2$CO (ketene)	Ab initio[b]	-11.4	57.8
	ATcT[a]	-11.6	60.1

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	NIST	(-11.4 ± 0.4) [47]	57.8 [45]
CH$_2$O (formaldehyde)	*Ab initio*[b]	-26.6	52.3
	ATcT[a]	-26.1	52.3
	NIST	-27.7 [46]	52.3 [46]
HNC=O (isocyanic acid)	*Ab initio*[b]	-28.9	57.1
	ATcT[a]	-28.3	56.9
	NIST	-24.3 [46]	56.9 [46]
CH$_2$=NH (methanimine)	*Ab initio*[b]	20.8	54.4
	ATcT[a]	20.2	53.0
	NIST	(16.0 ± 2.0) [48]	N/A

[a] Values collected from Burcat's online database, http://garfield.chem.elte.hu/Burcat/burcat.html (access date: August 2016);

[b] This work at W1U level. ΔH_f was calculated by atomization method.

The pressure- and temperature-dependent analyses were carried out using the potential energy surface and molecular properties calculated at W1U level. In particular, both deterministic [34] and stochastic [49] simulations were independently performed within the ME/RRKM framework, implemented and updated in MSMC code [34], to predict the time-resolved species profiles from which macroscopic rate coefficients were extracted. Representatively, Figure 2 shows the normalized time-resolved profiles for two substances (β-propiolactone and β-propiolactam) and products (C_2H_4 + CO_2 (**P1**), CH_2CO + CH_2O (**P2**) and C_2H_4 + HNCO (**P3**), CH_2CO + CH_2NH (**P4**) from β-propiolactone and β-propiolactam, respectively) at 500 K and 760 torr. It can be seen that the stochastic method even at moderately trial number of ten thousand, is able to predict the profiles which are indistinguishable with those obtained from the deterministic framework (using double precision diagonalization procedure). Details of the stochastic simulations at different conditions were presented in supplementary Figure S4. For β-propiolactone, the calculated time-resolved profiles showed that the only main product channel is C_2H_4 + CO_2 (**P1**) for the whole T&P range (cf. Figure S4 (a-d)). The other product, CH_2CO + CH_2O (**P2**), does not play a role even at high temperature and high pressure

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due to its high barrier (~15 kcal/mol higher than that of P1, cf. Figure 1). On the other hands, β-propiolactam can decompose to both C_2H_4 + HNCO (**P3**, dominant channel) and CH_2CO + CH_2NH (**P4**, minor one). Channel **P3** is more favorable at low temperature and low pressure while channel **P4** shows its role at high temperature (cf Figure S4 (e-h)) with the barrier difference of ~2.7 kcal/mol. The finding is consistent with the previous experimental observation [11].

(a) β-propiolactone → products
(T = 500 K & P = 760 torr)

C$_2$H$_4$ + CO$_2$ (P1)

+ Red   : stochastic (100 trials)
+ Green: stochastic (10000 trials)
+ Black : deterministic (dashed lines)

β-propiolactone

CH$_2$CO + CH$_2$O (P2)

(b) β-propiolactam → products
(T = 500 K & P = 760 torr)

β-propiolactam

C$_2$H$_4$ + HNCO (P3)

+ Red   : stochastic (100 trials)
+ Green: stochastic (10000 trials)
+ Black : deterministic (dashed lines)

CH$_2$CO + CH$_2$NH (P4)
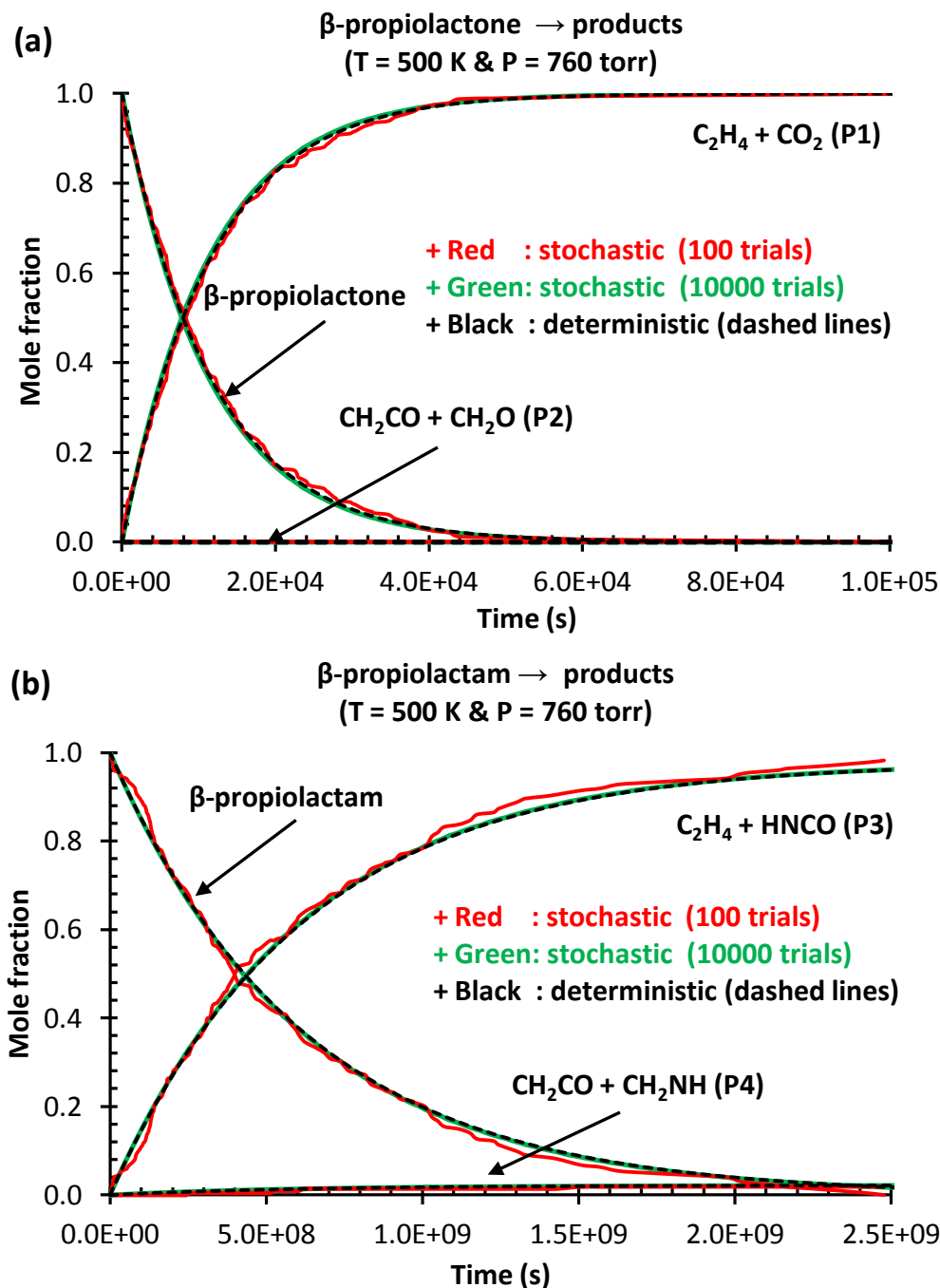
Figure 2: Time-resolved species profiles for the unimolecular decomposition of *β*-propiolactone (**a**) and *β*-propiolactam (**b**) at 500 K and 760 torr using the stochastic (with different numbers of trials of 100 and 10000) and deterministic approaches.

It is noted, however, that our eigenpair analysis showed that a mixing in eigenvalue spectrum, between the fastest chemically significant eigenvalue (CSE) and the slowest internal energy relaxation eigenvalue (IERE), where the difference is less than 1 order of magnitude,

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occurs at around $T \geq 1500$ K with P = 0.001 torr, $T \geq 1800$ K with P = 100 torr and $T \geq 1500$ K with P = 0.001 torr, $T \geq 2000$ K with P = 100 torr for β-propiolactone and β-propiolactam, respectively (c.f. Figure S8), thus the CSE approach cannot be used to derive the phenomenological rate constants for conditions. Alternatively, the stochastic model is the method of choice to obtain reliable results but with a sufficiently large number of trials as discussed previously. In short, we have demonstrated that the two approaches, deterministic and stochastic, were systematically carried out within the solid ME/RRKM framework to complement each other in an endeavor to have more confidence in capturing the correct chemistry/physics of these reactions for any condition of interest.

The calculated temperature- and pressure-dependent rate coefficients $k(T, P)$ were tabulated in Table S2 and plotted in Figures 3 and S5. It was noticed that pressure has a minor effect on these channels (e.g., the fall-off curves are not quite noticeable). The fall-off regions, however, shifted to the high pressure with temperature and these regions become more noticeable at high temperature (e.g., $T > 800$ K), which is the same behavior observed for the thermal decomposition of acetic anhydride [50]. The kinetic and thermodynamic data in the Chemkin format were compiled in the supplementary Tables S2 & S3 in order to facilitate reactor modeling/simulation using this sub-kinetic model. As seen in Figure 4, our calculated rate coefficients, $k(T, P)$, for β-propiolactone $\rightarrow$ C_2H_4 + CO_2 (Rxn. 1), are in very good agreement with the experimental data measured by James and coworkers [12] (James 1969); Frey and coworkers [13] (Frey 1985) and Santioste Bermejo [14] (Santiuste 1987) at different pressures as a function of temperatures (e.g., ratios of the rate values of James [12] and Santioste [14] to the calculated ones are 1.1 and 1.2 at T = 500 K & P = 10 torr and T = 575 K & P = 100 torr, repetively).
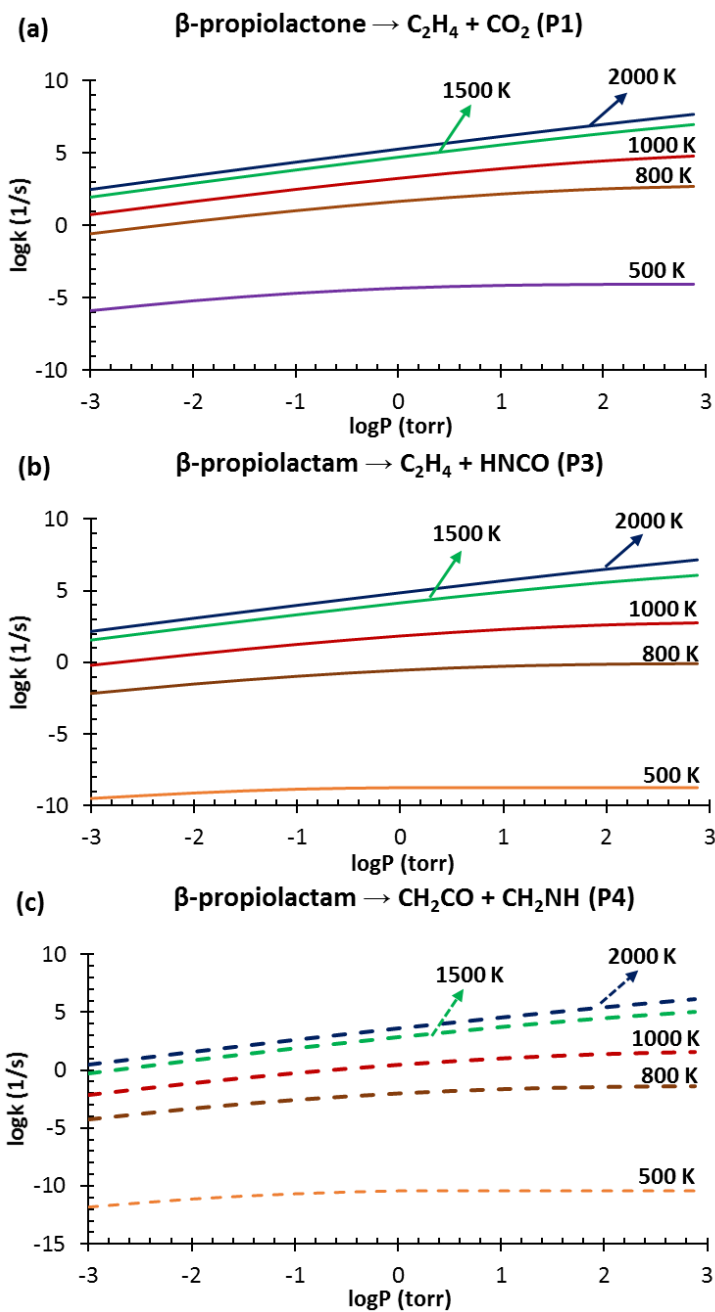
Figure 3: Calculated rate coefficients for the unimolecular decomposition of β-propiolactone (**a**) and β-propiolactam (**b-c**) as a function of pressure at different temperatures (i.e., 500, 800, 1000, 1500 and 2000 K). Only the important reaction pathways are shown here.

β-propiolactone → C₂H₄ + CO₂ (P1)
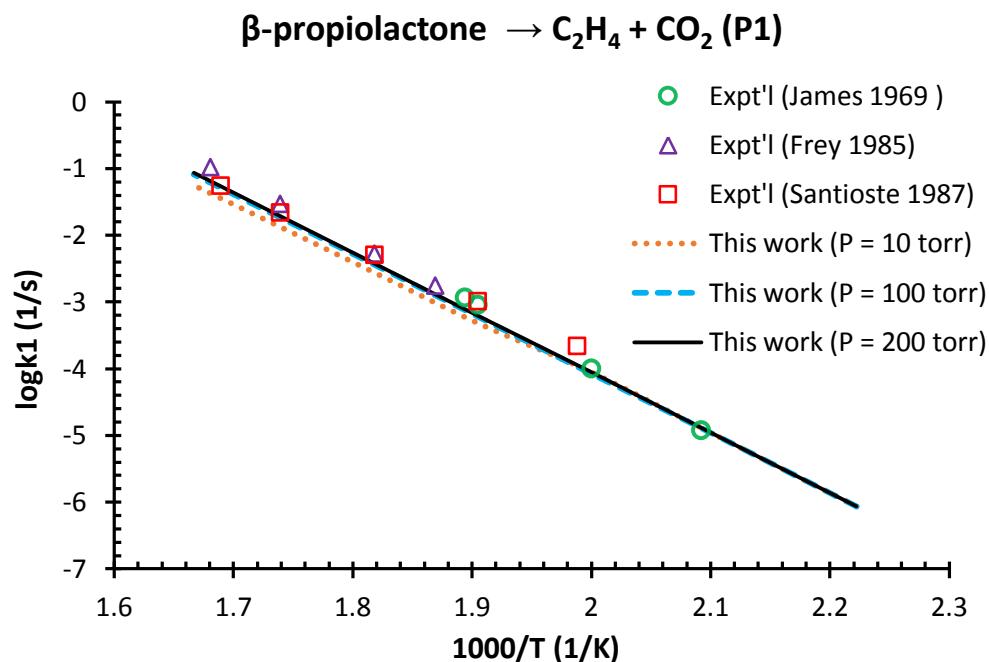
Figure 4: Comparison between calculated and experimental rate coefficients as a function of temperature at different pressures for β-propiolactone $\rightarrow$ C_2H_4 + CO_2 (Rxn. 1). Experimental data are from the work of James and coworkers [12] ("James 1969", P = 3.6 – 15.5 torr); Frey and coworkers [13] ("Frey 1985", P = 0.1 – 6.0 torr) and Santioste Bermejo [14] ("Santiuste 1987", P = 30.0 – 272.3 torr).

The branching ratio of the two decomposition channels from β-propiolactone (**P1**:**P2**) basically remains unchanged with temperature (e.g., ~ 99.9:0.1 and 99.8:0.2 at T = 500 K and T = 2000 K, respectively, for P = 0.001 torr, cf. Figure S6), while that from β-propiolactam (**P3**:**P4**) decreases noticeably with temperature (e.g., ~ 99.3:0.7 and 96.7:3.3 at T = 500 K and T = 2000 K, respectively, for P = 0.001 torr). Note that the high-pressure branching ratios were also plotted in Figure S7. It is found that pressure does not play a role for **P1:P2** ratio but **P3:P4** (e.g., the **P3:P4** ratio is 99.3:0.7 and 97.8:2.2 at P = 0.001 and 100 torr, respectively, for T = 500 K, cf. Figure S6). These observations on the effects of temperature and pressure on the mechanisms are consistent with the detailed PES provided in Figure 1 in which the barrier height

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differences between the two channels for each system is noticeably different as discussed previously. Our calculated results including the branching ratios and the time-resolved species profiles confirm the observation in the previous experiment [11] that these authors only detected $C_2H_4 + CO_2$ (**P1**) and $C_2H_4 + NHCO$ (**P3**); $CH_2CO + CH_2NH$ (**P4**) when decomposed of β-propiolactone and β-propiolactam, respectively.

Conclusions

In this study, the unimolecular decomposition reactions of β-propiolactone and β-propiolactam were investigated using highly accurate composite W1U method and modern deterministic/stochastic RRKM/ME statistical rate models. The results show that β-propiolactone can only form $C_2H_4 + CO_2$ (**P1**) (e.g., accounting for more than 99.9 % at T < 2000 K and P = 100 torr); while β-propiolactam can decompose to $C_2H_4 + HNCO$ (**P3**) as a dominant channel (accounting for more than 97.8 % at T < 500 K and P = 100 torr) and minor product, $CH_2CO + CH_2NH$ (**P4**) (accounting for less than 8.2 % at T < 2000 K and at P = 100 torr). The temperature-pressure dependent rate constant calculations based on the RRKM/ME solutions were found to be in excellent match with limited experimental data, which significantly confirm/verify the experimental observation and the available measurements; thus the calculated rates can be confidently used to describe the evolution of the two systems for the broad range of conditions (T = 500 – 2000 K and P = 0.001 – 760.0 torr).

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References

[1]   G. Wuitschik, M. Rogers-Evans, K. Müller, H. Fischer, B. Wagner, F. Schuler, L. Polonchuk, E.M. Carreira, Angew. Chem., Int. Ed. 118 (2006) 7900.
[2]   T. Bach, K. Kather, O. Krämer, J. Org. Chem. 63 (1998) 1910.
[3]   Y. Dejaegher, N.M. Kuz'menok, A.M. Zvonok, N. De Kimpe, Chem. Rev. 102 (2002) 29.
[4]   E.M. Wright, B.J. Warner, H.E. Foreman, L.R. McCunn, K.N. Urness, J. Phys. Chem. A 119 (2015) 7966.
[5]   X.L. Zheng, H.Y. Sun, C.K. Law, J. Phys. Chem. A 109 (2005) 9044.
[6]   I. Auzmendi-Murua, S. Charaya, J.W. Bozzelli, J. Phys. Chem. A 117 (2013) 378.
[7]   J.W. Bozzelli, A.M. Dean, J. Phys. Chem. 97 (1993) 4427.
[8]   C.A. Taatjes, J. Phys. Chem. A 110 (2006) 4299.
[9]   T.H. McGee, A. Schleifer, J. Phys. Chem. 76 (1972) 963.
[10]   P. Vansteenkiste, V. Van Speybroeck, G. Verniest, N. De Kimpe, M. Waroquier, J. Phys. Chem. A 111 (2007) 2797.
[11]   C.C. Lim, Z.P. Xu, H.H. Huang, C.Y. Mok, W.S. Chin, Chem. Phys. Lett. 325 (2000) 433.
[12]   T.L. James, C.A. Wellington, J. Am. Chem. Soc. 91 (1969) 7743.
[13]   H.M. Frey, I.M. Pidgeon, J. Chem. Soc., Faraday Trans. 1 81 (1985) 1087.
[14]   Y.M. Santioste Bermejo, Afinidad 44 (1987) 424−427.
[15]   A. Moyano, M.A. Pericas, E. Valenti, J. Org. Chem. 54 (1989) 573.
[16]   I. Morao, B. Lecea, A. Arrieta, F.P. Cossío, J. Am. Chem. Soc. 119 (1997) 816.
[17]   V.S. Safont, J. Andrés, L.R. Domingo, Chem. Phys. Lett. 288 (1998) 261.
[18]   X.-F. Ren, M.I. Konaklieva, H. Shi, S. Dickey, D.V. Lim, J. Gonzalez, E. Turos, J. Org. Chem. 63 (1998) 8898.
[19]   K. Mogilaiah, R.B. Rao, K.N. Reddy, Ind. J. Chem. B 38 (1999) 818.

[20]   P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.
[21]   J. Poater, M. Solà, M. Duran, J. Robles, Phys. Chem. Chem. Phys. 4 (2002) 722.
[22]   T.H. Dunning, J. Chem. Phys. 90 (1989) 1007.
[23]   K. Andersson, P.-A.k. Malmqvist, B.r.O. Roos, J. Chem. Phys. 96 (1992) 1218.
[24]   P. Celani, H.-J. Werner, J. Chem. Phys. 112 (2000) 5546.
[25]   H.-J. Werner, Mol. Phys. 89 (2010) 645.
[26]   M. Szori, I.G. Csizmadia, C. Fittschen, B. Viskolcz, J. Phys. Chem. A 113 (2009) 9981.
[27]   C. Gonzalez, H.B. Schlegel, J. Chem. Phys 90 (1989) 2154.
[28]   C. Gonzalez, H.B. Schlegel, J. Phys. Chem 94 (1990) 5523.
[29]   J.A. Montgomery-Jr., M.J. Frisch, J.W. Ochterski, G.A. Petersson, J. Chem. Phys. 110 (1999) 2822.
[30]   J.W. Ochterski, G.A. Petersson, J.A. Montgomery, J. Chem. Phys. 104 (1996) 2598.
[31]   L.A. Curtiss, K. Raghavachari, P.C. Redfern, V. Rassolov, J.A. Pople, J. Chem. Phys. 109 (1998) 7764.
[32]   L.A. Curtiss, P.C. Redfern, K. Raghavachari, J. Chem. Phys. 126 (2007) 084108.
[33]   M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, *et al*, Gaussian 09, Revision A.1. Gaussian, Inc., Wallingford CT, 2009.
[34]   M.v. Duong, H.T. Nguyen, N. Truong, T.N.M. Le, L.K. Huynh, Int. J. Chem. Kinet. 47 (2015) 564.
[35]   T.H.M. Le, S.T. Do, L.K. Huynh, Comput. Theor. Chem. 1100 (2017) 61.
[36]   C. Eckart, Phys. Rev. 35 (1930) 1303.
[37]   T. Tan, X. Yang, Y. Ju, E.A. Carter, J. Phys. Chem. B 120 (2016) 1590.
[38]   B.E. Poling, J.M. Prausnitz, J.P. O'Connel, The Properties of Gases and Liquids, 5th ed., McGraw-Hill Education, New York, Chicago, San Francisco, Athens, London, Madrid, Mexico City, Milan, New Delhi, Singapore, Sydney, Toronto, 2004.
[39]   Z. Tian, T. Yuan, R. Fournet, P.A. Glaude, B. Sirjean, F. Battin-Leclerc, K. Zhang, F. Qi, Combust. Flame 158 (2011) 756.
[40]   D.G. Truhlar, B.C. Garrett, Annu. Rev. Phys. Chem. 35 (1984) 159.
[41]   J.M.L. Martin, G.d. Oliveira, J. Chem. Phys. 111 (1999) 1843.
[42]   B. Ruscic, R.E. Pinzon, G.v. Laszewski, D. Kodeboyina, A. Burcat, D. Leahy, D. Montoya, A.F. Wagner, J. Phys.: Conf. Ser. 16 (2005) 561.
[43]   B. Ruscic, R.E. Pinzon, M.L. Morton, N.K. Srinivasan, M.C. Su, J.W. Sutherland, J.V. Michael, J. Phys. Chem. A 110 (2006) 6592.
[44]   Y.G. Dmitriev, K.Z. Kotovich, V.V. Kochubei, L.O. Mineravina, Vestn. L'vov. Politekhn. Inst. 221 (1988) 34.
[45]   M. Frenkel, K.N. Marsh, R.C. Wilhoit, G.J. Kabo, G.N. Roganov, Thermodynamics of Organic Compounds in the Gas State, Thermodynamics Research Center, College Station, TX, 1994.
[46]   M.W. Chase, Jr, J. Phys. Chem. Ref. Data, Monograph 9 (1998) 1.
[47]   R.L. Nuttall, A.H. Laufer, M.V. Kilday, J. Chem. Thermodyn. 3 (1971) 167.
[48]   R.A.L. Peerboom, S. Ingemann, N.M.M. Nibbering, J.F. Liebman, J. Chem. Soc., Perkin Trans. 2 (1990) 1825.
[49]   D.T. Gillespie, J. Comput. Phys. 22 (1976) 403.

[50]   T.V. Mai, M.V. Duong, H.T. Nguyen, K.C. Lin, L.K. Huynh, J. Phys. Chem. A 121 (2017) 3028.

Graphical abstract
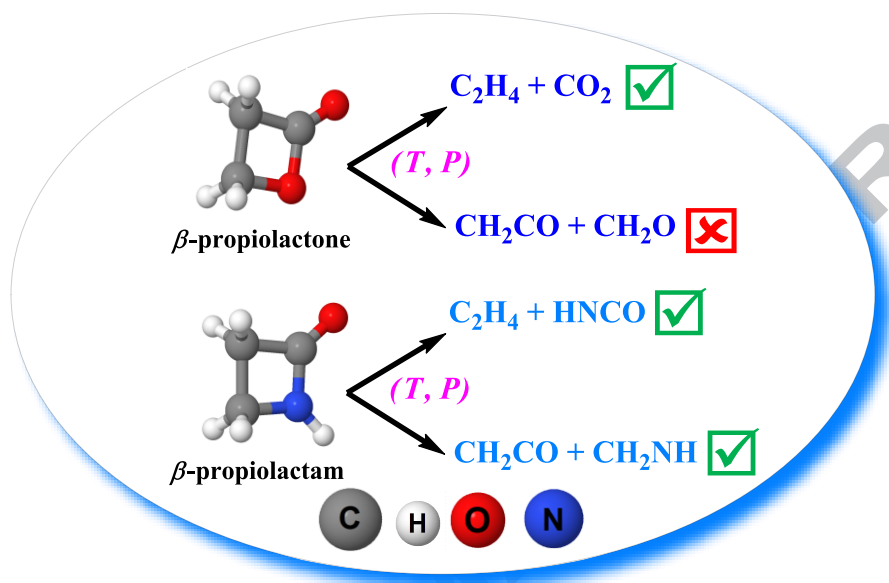
Highlights

- Thermal decomposition mechanisms of β-propiolactone and β-propiolactam were studied with the accurate composite W1U method.

- Time-resolved temperature- and pressure-dependent behaviors of the title reactions were characterized using the integrated *deterministic* and *stochastic* model within the framework of master equation/Rice–Ramsperger–Kassel–Marcus (ME/RRKM).

- Calculated numbers are in excellent agreement with scatter experimental data.

- A detailed kinetic sub-mechanism, consisting of thermodynamic and kinetic data in Chemkin format, was provided for the range of 500–2000 K and 0.001–760 torr.