***Ab Initio* Dynamics of Thermal Unimolecular Decomposition of Furan:**

A Combined Deterministic and Stochastic Master Equation Model

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Graphical abstract

Abstract

The detailed reaction mechanism for the thermal unimolecular decomposition of furan was comprehensively investigated in a wide range of temperatures (800-2000 K) and pressures (0.001-100 atm). The main reaction pathways were explored using different composite electronic structure methods including W1U, CBS-QB3, CBS-APNO, G3, G3B3 and G4. The temperature- and pressure-dependent dynamic behaviors of the furan pyrolysis (including time-dependent species profiles and rate coefficients) were characterized using the integrated *deterministic* and *stochastic* Master Equation/Rice–Ramsperger–Kassel–Marcus (ME/RRKM) models. These calculations embodied the hindered internal rotation (HIR) and quantum tunneling corrections. Using both atomization and isodesmic approaches, the calculated value for the standard heat of formation (ΔH_f^{298K}) of furan was found to be -8.4 kcal/mol which is in good agreement with literature values. Besides the C-H simple bond fission channels, it is found that the pyrolysis mechanism involves hydrogen atom transfer reactions yielding α -carbene and β -carbene as intermediates which eventually decompose and/or isomerize producing three final products, viz. $C_2H_2 + CH_2CO$ (**P1**), $CH_3CCH + CO$ (**P2**), and $CH_2CCH + HCO$ (**P3**). While the pathways **P1** and **P2** appear to be the primary products of furan decomposition at temperatures higher than 1300 K, the channels **P3**, **P4** and **P5** are found to be insignificant. Our calculations reveal that the unimolecular decomposition of furan mainly occurs *via* β -carbene with a contribution of 85 – 91% between 1600 K and 2000 K and at 1 atm pressure which agrees well with the findings of Urness and co-workers' recent measurements (*J. Chem. Phys.*, 2013, **139**, 124305). The calculated values of the rate coefficients, $k(T, P)$, and the thermodynamic properties of the species involved are found to be in good agreement with the experimental results. Therefore, the new data reported in this work are highly recommended for the future modeling and simulation of furan-related

combustion applications. The performance of the considered electronic structure methods for kinetic purposes was also discussed.

Keywords: biofuel, furan pyrolysis, rate constants, RRKM/ME, stochastic, and deterministic.

Introduction

Over the past decades, there are overwhelmingly concerns towards the depletion of oil reserves and global warming due to increasing production of CO₂ burning fossil fuels. To mitigate these challenges, numerous studies and research projects were carried out seeking the renewable energy resources that can replace the conventional fossil fuels and meet the future energy demands in an economically, environmentally and socially sustainable manner^{1,2}. Biofuels, including alcohols, esters, ethers, aldehydes and furans are potential renewable fuels that can be blended with the conventional fossil fuels for transportational usage in many countries.³⁻⁶ Specifically, furan and its derivatives^{7,8} are considered as potential biofuels with several advantages over the first-generation biofuels^{9,10} as they can be produced from lignocellulose obtained from non-food raw materials such as woods, crop residues or even municipal wastes.^{9,11,12} For example, the 2,5-dimethylfuran (2,5-DMF) has an energy density of 29.3 MJ/L¹⁰ that is comparable to a typical gasoline (31.9 MJ/L)¹⁰, and also it has a higher octane value¹³ which offers an excellent platform as a potential biofuel or as a fuel additive for its application in the internal combustion engines.^{14,15} Furan and its derivatives appear as important reaction intermediates during the burning of biomass and fossil fuels.¹⁶⁻¹⁸ Also, furan is one of the major degradation products formed during the thermal pyrolysis of leaf and wood¹⁹ as well as an important part of tobacco smoke.²⁰ Therefore, understanding of the detailed kinetic behaviors of furan - the smallest member in the furanic biofuels - is the key to efficiently assess the applicability of furan and its derivatives as alternative fuels in the practical combustion devices.

The gas-phase thermal reactions of furan were studied by several groups both experimentally^{18,21-32} and theoretically.³³⁻³⁶ In a recent single pulse shock tube study, Guarneri *et al.*³⁷ assessed the efficiency of furan as a model oxygenated reburn fuel for the reduction of NO,

and found that NO removal by furan is as effective as propene. A little while ago, Grela *et al.*²² investigated the unimolecular reactions of furan and methylated furans in a heatable flow reactor at very low pressures $\sim 10^{-3}$ torr using an online mass spectrometer to analyze the products. They found that these furans decompose between 1050 K and 1270 K by unimolecular ring breakdown process releasing CO either exclusively in case of furan and 2-methylfuran (2-MF) or as the main reaction channel for 2,5-DMF. In 1988, Bruinsma *et al.*²⁴ pyrolyzed a series of cyclic compounds including furan and its derivatives in a coiled tube flow reactor to investigate their thermal stability. They postulated that the breakage of the C-O bond in furan is the most probable pathway resembling diphenyl ether in light of the low thermal stability. They provided an Arrhenius equation, $k(T) = 10^{12.9} \times \exp(-65789 \text{ cal mol}^{-1}/RT) \text{ s}^{-1}$ to quantify the thermal stability of furan over the temperature range of 960–1085 K. Lifshitz *et al.*^{23,38,39} investigated the thermal decomposition of furan, 2-MF and 2,5-DMF using a shock tube over the temperature range of 1050–1460 K and pressure of 1.5–3.0 atm. They measured the final products using the gas chromatography coupled to a mass spectrometer and proposed a chemical kinetic model based on their results. They found that the reactivity of furans increases with increasing of alkylation to the furan ring, i.e., 2,5-DMF > 2-MF > Furan. This reactivity trend of furans is found to be consistent with the previous works^{22,24}. Organ *et al.*¹⁸ conducted similar experiments on furan by utilizing the single pulse shock tube technique to extend the temperature range over 1100 K and 1700 K and pressure of ~ 20 atm. They detected CO, C₃H₄ (propyne), C₂H₂ and CH₂CO directly which enabled them to extract the mechanistic information of the initial steps in furan pyrolysis. Similar to Lifshitz *et al.*²³ they proposed that the pyrolysis of furan occurs by the homolytic C-O bond scission forming a biradical.

Later in 1998, Fulle *et al.*²⁵ conducted shock tubes experiments by combining the Laser-Schlieren (LS) and Time-of-Flight Mass Spectrometry (TOF-MS) detection techniques over the temperature range of 1300–3000 K and at pressures 100 - 600 Torr. These experiments allowed the authors to confirm the two dominant molecular channels, namely $\text{C}_2\text{H}_2 + \text{CH}_2\text{CO}$ and $\text{C}_3\text{H}_4 + \text{CO}$ for furan decomposition. Their total high pressure limiting rate coefficients for furan decomposition can be given by $k^\infty(T) = 10^{15.3} \times \exp(-78748 \text{ cal mol}^{-1}/RT) \text{ s}^{-1}$. In 2009, Vasiliou *et al.*²⁸ investigated furan decomposition using a high-temperature Silicon Carbide (SiC) tubular reactor coupled to a photoionization mass spectrometer as well as an infrared spectrophotometer. They pointed out the importance of two reaction pathways in furan pyrolysis generating the products: (CO + propyne) and ($\text{C}_2\text{H}_2 + \text{CH}_2\text{CO}$). Additionally, they observed propargyl radicals (C_3H_3) being produced at higher temperatures ($1550 \pm 100 \text{ K}$). Recently, Tian *et al.*³⁶ developed a detailed kinetic model based on their experimental and kinetic investigations of premixed laminar furan/oxygen/argon flames using Molecular Beam Mass Spectrometry (MBMS) with synchrotron-based tunable VUV photoionization. Their model predictions were in reasonable agreement with their experimental results. Also, their mechanism was successfully validated against the species time histories of Fulle *et al.*²⁵ work on furan pyrolysis. Recently, Weber *et al.*³² studied the pyrolysis reactions of furan, 2-MF and 2,5-DMF in shock-tube experiments behind reflected shock waves over the temperature of 1200 – 1900 K and pressures between 0.7 and 1.6 atm. Above 1600 K, the authors found that the original kinetic mechanism proposed by Liu *et al.*²⁹ severely underpredicted their experimentally measured H-atom concentration-time profiles. The authors refined the rate parameters for sensitive reactions profiles to build a modified kinetic model for furan pyrolysis which was capable of describing their experimental results better and pin down the reaction channel for the source of H atoms. The authors concluded that the decomposition of furan

proceeds via a ring-opening process to form formyl allene (CH_2CCHCHO) which decomposes mostly to produce C_3H_4 (propyne) + CO and that C_3H_4 is the major source of H atoms.

As discussed above, there are numerous experimental studies rendering to understand the initial steps in the pyrolysis of furan. Yet, there were only four theoretical calculations and/or simulations.³³⁻³⁶ Liu *et al.*^{33,34} explored the potential energy surface of furan decomposition at the QCISD(T)/6-311++G**// B3LYP/6-31G** level of theory. Their calculations targeted to map out the reaction mechanism and compute the thermochemistry of all reaction channels pertinent to furan decomposition. However, they did not proceed for kinetic analysis to rationalize the relative importance of various channels. Sendt *et al.*³⁵ computed the potential energy surface at CASSCF, CASPT2 and G2(MP2) levels of theory. The rate coefficients and the thermochemistry of some key channels were reported, however, the computations for the pressure dependence of the rate coefficients were not carried out. The authors developed a detailed kinetic model and validated against the experimental data of Organ *et al.*¹⁸ on furan pyrolysis. However, their kinetic model was neither intended to present the combustion chemistry of alkylated furan²⁹ nor extensively used to validate furan data.³⁰ Recently, a modified kinetic model was developed by Wei *et al.*³⁰ by refining the chemical kinetic mechanism of Tian *et al.*³⁶ which performed remarkably in predicting their ignition delay times as well as furan decomposition data. These data were obtained behind the reflected shock waves over the temperature range of 1320-1880 K, pressures of 1.2-10.4 atm for the mixtures of equivalence ratio ranging from 0.5 to 2.0. More recently, Urness *et al.*³¹ applied silicon carbide microtubular reactor to measure the branching ratios of the main products in the thermal pyrolysis of furan over the temperature range of 1200-1600 K and pressures of 100-300 Torr. Their experiments supported a preference of 80-90% of furan decomposition to occur via

the β -carbene. Despite several studies, there still remains a considerable room for a detailed investigation of the reaction kinetics of the thermal decomposition of furan.

In this work, we propose the reaction energetics on the singlet Potential Energy Surfaces (PES) of furan decomposition. We found that the reaction progresses with an H atom migration to form carbene intermediates which eventually lead to CO + propyne and C₂H₂ + CH₂CO as dominant products. A similar revelation was also made by Liu *et al.*^{27,28}, which dismisses numerous earlier hypotheses^{18,22,23} of the furan decomposition pathways occurring via biradical formation. In the current work, we used a novel approach by combining fundamental chemistry and reaction rate theory simulation to fully characterize the kinetic behavior of furan. This sort of detailed kinetic study is scarce in the literature and can be considered as part of a continuing effort to fully comprehend the combustion chemistry of furan over a wide range of thermodynamic conditions ($T = 800\text{--}2000$ K and $P = 0.001\text{--}100$ atm). To shed light into the title reaction, we adapted a similar methodology as described in our previous study.⁴⁰ We employed high-level *ab initio* calculations using various composite methods to characterize the energetics of the reaction. The information on the reaction energetics was then utilized to rationalize the role of various channels by calculating their pressure and temperature dependence of the rate coefficients using the combined deterministic^{41,42} and stochastic^{43,44} statistical rate models. We believe that this work will provide a complete integrated picture on furan pyrolysis in a wide range of conditions as demanded by Tian *et al.*³⁶ in a recent study.

Computational Method

Geometries of reactants, products, reaction intermediates and transition states (TSs) were calculated using B3LYP/cc-pVTZ+d level of theory.⁴⁵⁻⁴⁷ Vibrational frequencies were calculated to ensure the minimum and transition state structures, and a scaling factor of 0.985⁴⁸ was used to

calculate the Zero-Point Energy (ZPE) which was then incorporated to correct the thermochemical properties. Firstly, the energetics of the reaction were computed using the less accurate composite methods such as CBS-QB3⁴⁹, CBS-APNO⁵⁰, G3⁵¹, G3B3⁵² and G4⁵³ levels of theory. Secondly, we further applied Martin's W1U composite method⁵⁴⁻⁵⁶, which is an approximation to the CCSD(T) with the infinite-basis-set limit, to verify the accuracy of electronic energy results,. A recent theoretical work of Szőri *et al.*⁵⁷ showed that the W1U method can be considered as one of the most accurate composite methods⁵⁸ with the absolute mean deviation of 0.5 kcal/mol. For all transition states, Intrinsic Reaction Coordinate (IRC)^{59,60} calculations were carried out at the B3LYP/cc-pVTZ+d level of theory to confirm the identity of corresponding reactants and products in the PES. All calculations were performed using the Gaussian 09 quantum chemistry package.⁶¹

The standard enthalpy of formation for all species has been determined by the atomization energy method⁶² (see ref. ⁶³ for details). The entropies and heat capacities of the molecules were estimated using statistical thermodynamics.⁶⁴ Kinetic analyses including both the deterministic^{41,42} and stochastic^{43,44} approaches within the framework of the Master Equation/Rice–Ramsperger–Kassel–Marcus (ME/RRKM) were carried out using the Multi-Species Multi-Channels (MSMC) program.⁶⁵ The performance of the MSMC engine was recently improved by the enhancements of stochastic profiles simulation and rate constant extraction. Quantum tunneling effect was accounted for each elementary steps using the Eckart⁶⁶ correction. Instead of harmonic oscillator approximation, the low-frequency vibrational modes were treated as hindered internal rotors (HIR) to obtain accurate partition functions. Here, the hindrance potentials, $V(\theta)$, as a function of torsional angle, θ , along the single bonds (i.e., C–C, cf. Supplementary Figure S4) were explicitly obtained at the B3LYP/6-311G(2d,d,p) level of theory via relaxed surface scans with the step size of 10° for the dihedral angles of corresponding

rotations. The HIR parameters were determined with the use of MSMC-GUI^{67,68}, the details of

which can be found in our previous work.⁶⁹ The reaction path degeneracy⁷⁰, $L^\ddagger = \frac{m^\ddagger}{m} \times \frac{\sigma_{\text{external}}}{\sigma_{\text{external}}^\ddagger}$

(where $m^\ddagger$ and m are the number of optical isomers of transition state and reactant(s); $\sigma_{\text{external}}^\ddagger$ and σ_{external} are the external rotation symmetry numbers of the transition state and reactant(s), respectively), was included in the calculations of the rate coefficients.

For reactions having no intrinsic energy barriers, Inverse Laplace Transform (ILT) approach⁷¹ was employed to obtain the microcanonical rate constants, $k(E)$. For the calculations of $k(E)$, the density of states (DOS) of the reacting species and the empirical Arrhenius parameters (A_∞ and $E_\infty \approx E_0$) of the high pressure limiting rate coefficients are required. Finally, $k(E)$ near the reaction threshold can be obtained by using the equation: $k(E) = A_\infty \frac{\rho(E-E_0)}{\rho(E)}$, where $\rho(E)$ is the density of states of the dissociating species and E_0 is the critical energy that equals the enthalpy of reaction at 0 K. The energy-transfer process was computed on the basis of the exponential-down model with $\langle \Delta E_{\text{down}} \rangle = 260.0 \times \left(\frac{T}{298} \right)^{0.8} \text{ cm}^{-1}$ for Ar as the bath gas.^{72,73} The Lennard-Jones (L-J) parameters $\varepsilon/k_B = 114.2 \text{ K}$ and $\sigma = 3.47 \text{ \AA}$ were used for argon⁷⁴ while $\varepsilon/k_B = 357 \text{ K}$ and $\sigma = 5.18 \text{ \AA}$ were used for furan and its isomers.³⁶ The Beyer–Swinehart algorithm⁷⁵ was used for harmonic oscillator vibrational modes to compute the density and the sum of states which were then convoluted with hindered rotational modes externally using Fast Fourier Transform (FFT) method.⁷⁶ By default, the energy bin size of 1 cm^{-1} is used for the DOS calculations. Finally, the temperature- and pressure-dependent rate coefficients, $k(T, P)$, of furan decomposition were

computed over 800 – 2000 K and 0.001–100 atm using 5×10^8 trials to minimize stochastic uncertainties of minor reaction pathways.

Results and Discussion

Potential Energy Surface

Two independent theoretical studies revealed that the mechanism of furan pyrolysis proceeds via two separate pathways involving a pair of carbenes.^{34,35} Since the barrier height for the formation of carbene intermediates was reported to be lower than that for the biradical formation,^{28,29} we explored the potential energy surface (PES) of furan unimolecular reactions via carbene intermediates only. To capture an integrated picture of PES, the breaking of the C-H bond of furan to form 2-furyl or 3-furyl radical and H atom were also considered. (cf. Figure S1 in supplementary information (SI) file)

All optimized geometries of reactants, products, intermediates and transition states pertinent to furan pyrolysis were presented in Figure S2 of SI file and compared to the available literature data. Generally, the calculated bond lengths and angles are found to be consistent with the literature data with maximum errors of ~ 0.1 Å and 5° for the bond lengths and bond angles, respectively. In particular, the geometries of furan obtained at the B3LYP/cc-pVTZ+d level in this study are very close to previous literature values⁷⁷ which implies that B3LYP/cc-pVTZ+d level of theory is appropriate for geometry optimizations of this system. The harmonic vibrational frequencies were also listed in Table S1 of SI, showing a slight variation as compared to the literature values. For instance, mean absolute percentage deviations are 1.9, 2.4, 2.8, 3.0, 4.6 and 4.9 for CO, furan, CH₂CO, CH₃CCH, HCO radical and C₂H₂, respectively.

Figure 1: ZPE-corrected relative energies at 0 K in the potential energy surface for the unimolecular decomposition of furan. The numbers, computed at W1U level of theory, denote the energies in kcal/mole relative to furan. Dashed lines represent the channels with no intrinsic barriers.

The possible reaction pathways in the PES of furan decomposition was depicted in Figure 1. For clarity, Figure 1 provides only the energy obtained from W1U calculations as one of the composite methods applied.⁵⁸ It is seen that the decomposition of furan proceeds via two routes. Both pathways involve H-migration to form two carbene intermediates^{34,35} (**INT1** and **INT2**) which can eventually dissociate to form the final products: $\text{C}_2\text{H}_2 + \text{CH}_2\text{CO}$ (**P1**), $\text{CH}_3\text{CCH} + \text{CO}$ (**P2**) and $\text{H}_2\text{CCCH} + \text{HCO}$ radicals (**P3**), respectively. Note that before forming the final products **P2** and **P3**, **INT2** can undergo C-O bond fission by overcoming a subtle barrier of about 0.6 kcal/mol via **TS4** to produce a stable intermediate **INT3** (buta-2,3-dienal). In contrast, α -carbene (**INT1**) directly leads to $\text{C}_2\text{H}_2 + \text{CH}_2\text{CO}$ (**P1**) via **TS2** by overcoming an energy barrier of 29.8 kcal/mol. We note here that **INT3** was not considered by Tian *et al.*³⁶, and its appearance in the PES of furan is expected to play a key role in the reaction kinetics of furan. Apart from the two molecular reaction channels proceeding via carbenes, furan can also dissociate via simple C-H

bond fission leading into 2-furyal + H (**P4**) and 3-furyal + H (**P5**). However, these channels are highly endothermic ($\Delta_{\text{rxn}}H^\circ_{0\text{ K}} \approx 118.5$ kcal/mol). This indicates that the C-H bonds in furan are much stronger than that of benzene (112.1 kcal/mol)³⁵; therefore, **P4** and **P5** may be kinetically insignificant during the pyrolysis reaction of furan below 2000 K. Nonetheless, our kinetic analysis considered these bond fission channels for a thorough understanding of furan pyrolysis.

Additionally, we constructed the PES of furan pyrolysis by employing various composite methods (CBS-QB3, CBS-APNO, G3, G3B3 and G4). This allowed us to evaluate the accuracy of various composite methods with respect to W1U method. Table 1 compares the results from various composite methods along with the literature data. As can be seen, the performance of various levels of theory is excellent as compared to the W1U method. For instance, mean absolute percentage deviations (MAD) are 0.7, 1.0, 2.1, 2.2, and 1.7 between W1U and CBS-QB3, CBS-APNO, G3, G3B3 and G4, respectively. Nevertheless, the W1U results show a larger deviation as compared to CASPT2/cc-pVTZ values reported by Sendt *et al.*³⁵ (i.e., the MAD between W1U and CASPT2/cc-pVTZ is 8.7%) but still agrees well with G2(MP2) numbers (i.e., the MAD is 3.4%). The differences might have stemmed from a systematic error pertinent to the electronic states of electron pairs (e.g., the singlet-triplet splitting in methylene is over-estimated by ~2.9 kcal/mol).⁷⁸

Surprisingly, our CBS-QB3 results are different from those calculated by Tian *et al.*³⁶ at the same level of theory (e.g, large differences of ~1.9, 1.4 and 1.3 kcal/mol were found for INT3, TS5 and P1, respectively). Other methods (e.g., W1U, CBS-APNO, G3, G3B3 and G4) or even the reference calculations³⁵ (CASPT2/cc-pVTZ and G2(MP2)) are strongly in favor of our CBS-QB3 calculations. Despite, Tian *et al.*³⁶ claimed that their activation energies are in a good agreement with those obtained by Sendt *et al.*³⁵ at the G2B2 and CASS-SCF level of theory. As

uncertainties in the relative positions of the species in the PES can induce large errors in the kinetic part, it is very important to validate and/or confirm the reliability of the PES. We emphasize that the good agreement among the six ab initio methods employed in this study (i.e., W1U, CBS-QB3, CBS-APNO, G3, G3B3, and G4) confirms the reliability of the PES displayed in Figure 1.

Table 1: Zero-point energy corrected relative energies (in kcal·mol⁻¹) of all species involved at different levels of theory at 0 K. The numbers are relative to furan energy. See Figure 1 for the species notations.

Species	This work						Reference		
	W1U	CBS-QB3	CBS-APNO	G3	G3B3	G4	CASPT2/cc-pVTZ ³⁵	G2MP2 ³⁵	CBS-QB3 ³⁶
INT1	55.9	56.2	56.4	55.5	55.4	55.4	63.1	54.7	-
INT2	59.8	59.9	60.0	59.1	58.8	59.3	66.7	58.6	-
INT3	25.0	24.7	25.4	23.5	23.4	24.0	31.1	26.7	22.8
TS1	66.3	66.9	66.2	66.6	66.5	66.2	66.9	64.5	-
TS2	85.7	84.3	84.6	84.3	83.6	84.1	84.1	82.7	83.6
TS3	70.2	70.5	70.0	70.0	70.0	70.0	68.8	69.1	70.4
TS4	60.4	60.3	59.9	58.9	59.2	60.0	63.1	58.6	-
TS5	68.9	67.8	67.1	66.7	67.5	67.6	66.7	65.7	66.4
P1	49.7	50.1	50.8	48.4	47.8	48.8	53.8	49.2	48.8
P2	24.5	24.7	24.8	23.4	23.0	22.9	30.8	22.5	23.9
P3	99.8	100.2	99.8	98.4	98.2	98.2	98.9	101.3	-
P4	118.4	118.8	119.3	119.8	118.9	117.7	N/A	N/A	-
P5	118.5	119.1	119.5	119.8	118.9	117.8	N/A	N/A	-
MAD^[a] (%)		0.73	1.00	2.06	2.18	1.67	8.74	3.37	-

^[a] Mean Absolute Deviation (MAD) (%) of various levels of theory as compared to W1U method.

Thermochemical Properties

To ensure the accuracy of our calculations, the calculated thermodynamic properties ($\Delta_f H^\circ$, S° and C_p° at 298 K) of all species involved in the system obtained using various methods (W1U, CBS-QB3, CBS-APNO, G3, G3B3 and G4) were presented in Table S2 and compared to the available literature data for some species (e.g., furan, C_2H_2 , CH_2CO , CH_3CCH , CO, HCO, H_2CCH , H, 2-furyl, 3-furyl and **INT3**). The comparison shows that our calculations are in good agreement with the literature values within the uncertainties (e.g., the maximum differences between ours and ATcT numbers are less than 0.8 kcal/mol, 0.2 cal/mol/K and 0.3 cal/mol/K for $\Delta_f H^\circ$, S° and C_p° at 298 K, respectively). As can be seen in Table 2, the average value of $\Delta_f H^\circ$ at 298 K of furan derived from the *atomization*⁶² (-8.1 kcal/mol) and *isodesmic*⁷⁹ (-8.6 ± 0.1 kcal/mol) approaches of this work are in accordance with the experimental values (-8.6 ± 0.2 kcal/mol)^{77,78} and theoretical values^{36,80-84} within the ‘chemical accuracy’⁸⁵ of ~1 kcal/mol. The W1U calculated bond dissociation energy ($BDE_{298\text{ K}}$) of $C-H_\alpha$ and $C-H_\beta$ are very close to each other, e.g., 119.8 and 119.9 kcal/mol, respectively, which is 7 kcal/mol higher than that of benzene.⁸⁶ Our BDE values show excellent agreement with the experimental value reported by Kristen *et al.*⁸⁷ (119.8 kcal/mol). Again, these discussions led us to conclude that W1U is the correct choice of ab initio method to accurately obtain the kinetic behavior of furan pyrolysis.

Table 2: Comparison between calculated and literature standard enthalpies of formation for furan.

Methodology	Level of theory	$\Delta_f H^\circ_{298}$ (kcal/mol)
Atomization scheme ^a	W1U	-9.4
	CBS-QB3	-7.6
	CBS-APNO	-9.0
	G3	-7.2
	G3B3	-7.5
	G4	-7.6
	Average	-8.1

<p>Isodesmic scheme^{a, b}</p> <p>(cyclopentadiene) (dimethyl ether) → (furan) (propane)</p>	W1U	-8.6 ± 0.1
	CBS-QB3	-8.5 ± 0.1
	CBS-APNO	-9.3 ± 0.1
	G3	-8.7 ± 0.1
	G3B3	-8.3 ± 0.1
	G4	-8.3 ± 0.1
	Average	(-8.6 ± 0.1)
Literature data	Computational	-7.5 ⁸⁰ (-7.7 ± 0.5) ⁸¹ -8.2 ^{82,83} -8.3 ³⁶ (-8.3 ± 0.7) ⁸⁴
	Experimental	(-8.3 ± 0.2)^{88,89}

^a This work using atomization scheme; ^b This work using isodesmic reaction framework with the heat of formation ($\Delta_f H^\circ$ at 298 K) from the experimental data: cyclopentadiene = 31.9 kcal/mol⁹⁰; dimethyl ether = (-44.0 ± 0.1) kcal/mol⁹¹ and propane = (-25.0 ± 0.1) kcal/mol⁹².

Kinetic Analysis

The high-pressure limit rate constants, $k^\infty(T)$, for all elementary reactions were calculated employing W1U PES and using the Conventional Transition State Theory (CTST) with explicit corrections of tunneling and hindered internal rotations. The calculated values of $k^\infty(T)$ were fitted to the modified three parameters Arrhenius expression, and the resulting parameters were listed in Table 3 for the temperature range of 800 – 2000 K. Unfortunately, the literature data for the elementary steps of furan pyrolysis reactions are scarce. Tian *et al.*³⁶ and Sendt *et al.*³⁵ reported the rate coefficients for the step **INT3** → CH₃C≡CH + CO (**P2**). For the elementary step, **INT3** → **P2**, their data are compared with ours in the Arrhenius plot displayed in Figure 2. As can be seen, our rate coefficients computed using W1U energetics agree reasonably well with those obtained by Tian *et al.*³⁶ and Sendt *et al.*³⁵ with MAD about 60.2% and 53.8%, respectively. Interestingly, the corrections for HIR and quantum tunneling was found to have a slight effect on the computed values of the rate coefficients. For instance, HIR treatment led to an increase of the rate coefficients

by ~1.5 times from 800 to 2000 K; and tunneling has a minimal effect on the rate coefficients (~1.2 times increase between 250 K and to 2000 K).

Table 3: Arrhenius parameters for the high-pressure limiting rate coefficients, $k^\infty(T)$, for the elementary steps involved in the unimolecular decomposition of furan obtained in this work using W1U method for 800-2000 K.

No.	Reaction	$k(T) = A \times T^n \times \exp(-E_a/RT)$		
		$A^{[a]}$	n	E_a/R
1	Furan $\rightarrow$ INT1 (reverse reaction)	2.7×10^{12}	0.50	33360.0
		2.3×10^{12}	0.26	5045.0
2	INT1 $\rightarrow$ P1 (reverse reaction)	3.0×10^{14}	0.23	16280.0
		1.4×10^{21}	2.56	16880.0
3	Furan $\rightarrow$ INT2 (reverse reaction)	3.2×10^{12}	0.46	35280.0
		1.7×10^{12}	0.28	4968.0
4	INT2 $\rightarrow$ INT3 (reverse reaction)	1.0×10^{13}	0.02	515.4
		2.5×10^{12}	-0.24	17240.0
5	INT3 $\rightarrow$ P2 (reverse reaction)	3.0×10^{12}	0.31	21940.0
		3.1×10^{23}	3.05	20770.0
6	INT3 $\rightarrow$ P3 ^[b]	7.9×10^{14}	0.00	35164.7
7	P4 $\rightarrow$ Furan ^[c]	1.7×10^{-10}	0.00	0.0
8	P5 $\rightarrow$ Furan ^[c]	1.7×10^{-10}	0.00	0.0

^[a] Units of [s⁻¹] for first-order reactions and [cm³ molecule⁻¹ s⁻¹] for second-order reactions. ^{[b],[c]} Taken from the works of Sendt *et al.*³¹ and Tian *et al.*³², respectively, for the barrierless channels.

Figure 2: Arrhenius plots for the high-pressure limiting rate coefficients, $k^\infty(T)$, of the elementary reaction, **INT3** $\rightarrow$ **P2**, comparing our data (“pw” denotes “present work”) with Tian *et al.*³⁶ and Sendt *et al.*³⁵.

The mole fraction time-histories were computed using both the deterministic and the stochastic ME/RRKM models on the full PES shown in Figure 1. Both models were independently adapted within the framework of rigorous ME/RRKM to compliment each other and to capture the important chemistry and physics with certainty of such complicated chemical system. Figure 3 depicts the normalized time-resolved species profiles for the title reaction (furan $\rightarrow$ products) at a representative condition of 1500 K and 1 atm. Additional time-resolved concentration profiles for other conditions can be found in the supplementary information (see Figure S5 and S6). As seen in Figure 3, the species time profiles derived from the two kinetic models are indistinguishably revealing **P2** as the primary product of furan decomposition contributing ca. 91.6% of the total product formed. **P1** contributes only about 8.2%, whereas **P3**, **P4** & **P5** are negligible (less than

0.2%) under the conditions considered here. Our observations are in line with the results of a recent shock tube study by Weber *et al.* who also reached to a similar conclusion stating that **P2** is the major channel of furan decomposition with a negligible contribution coming from **P3**. Weber *et al.* did not observe any H atoms forming below 1500 K which led them to conclude that the reaction leading to channel **P3** is not occurring and that the origin of H atoms in their experiments must be from the thermal decomposition of propyne. However, it is probably noteworthy to mention that their experiments are blind to discriminate between the channels P1 and P2 to confirm the origin of H atoms.

Figure 3: Time-resolved species profiles (in logarithmic scale) for the unimolecular decomposition of furan at 1500 K and 1 atm obtained using both the deterministic and the stochastic (with 5×10^8 trials) approaches.

Further reliability check of our computations is nicely illustrated in Figure 4. Here, the calculated time-resolved mole fraction of furan is compared with that of previous experimental²⁵ and theoretical³⁶ studies at 1533 K and 198 Torr (Ne was used as a bath gas). Clearly, our computational results simulate excellently the experimental data from Fulle *et al.*²⁵ for furan decay as compared to the performance of the computational results of Tian and co-workers³⁶, who used a simplified PES (cf. Figure S2). Our calculated values can be found in Table S5 of supplementary information. Until this point, we are already confident about the reliability of our reported values of the rate coefficients over the specified range temperatures and pressures.

Figure 4: Mole fraction time-histories of furan pyrolysis for $T = 1533$ K, $p = 198$ Torr (Ne as bath gas): symbols are the experimental results from Fulle *et al.*²⁵; solid and dashed lines are theoretical predictions from the present work (black), Tian *et al.*³⁶ (violet) and Fulle *et al.*²⁵ (red).

The reliability check continues by performing an eigenpair analysis of the deterministic rate model. As seen in Figure 5, a remarkable mixing in the eigenvalue spectrum is discernible.

Here, the difference between the fastest Chemically Significant Eigenvalues (CSEs) and the slowest internal energy relaxation eigenvalues (IEREs) is less than one order of magnitude which is true for all temperatures and a pressure of 1 atm (cf. Figure 6). As a result, the phenomenological rate constants, $k(T, p)$ derived by using the CSE approach may be unreliable. In such a case, an improved approach, the GMPE method,⁹³ should be the correct choice instead. Alternatively, the stochastic model can also be a good choice but it requires a statistically sufficient number of trials (e.g., 5×10^8 as used in this work).

Figure 5: Eigenvalue spectra as a function of temperature for furan $\rightarrow$ products at 1 atm. Only the eigenvalues of the smallest magnitude are presented: solid and dashed lines represent chemically significant eigenvalues (CSEs) and internal energy relaxation eigenvalues (IEREs) modes, respectively. For these computations, full PES as described in Figure 1 was used.

The phenomenological rate constants, $k(T, p)$ of the furan $\rightarrow$ products as a function of temperature and pressure are depicted in Figure 6. As can be seen, the pressure stabilization of **INT3** becomes a favorite channel at high pressures and low temperatures. The dominance of **INT3** remains intact up to even 1600 K for a pressure of 100 atm. The collisional stabilization of the intermediates **INT1** & **INT2** is not considered due to the shallow nature of their wells. **P2** is highly favorable at high temperatures and low pressures (see Figure 6). As seen in Figure 6d, the formation of **P1** and **P2** becomes competitive even for $p = 1$ atm with the stabilization step of **INT3** at temperatures higher than 1300 K. In Figure 7, the temperature and pressure dependence of the rate coefficients, $k(T, p)$, for various channels are plotted. The reaction, furan $\rightarrow$ C₂H₂ + CH₂CO (**P1**), exhibits highly pressure dependence over 800 – 2000 K (cf. Figure 7a). However, furan $\rightarrow$ CH₃CCH + CO (**P2**) channel shows more complicated $k(T, p)$ behaviour as illustrated in Figure 7b. Interestingly, **P2** shows an anomaly by displaying a negative pressure-dependence below 1000 K. However, this reaction flips to display an usual trend of $k(T, P)$ at higher temperatures. The higher selectivity of **P2** at low pressures may be attributed to ‘well-skipping’⁹⁴ phenomenon. In a particular scenario like this one, the “energized” reaction may proceed via more than one transition state without requiring it to stabilize in an intermediate well(s)⁹⁵ because of the inefficient stabilization at lower pressure regime. As for the channel **P1**, ‘well-skipping’ is highly unlikely because the intermediate **INT1** lies in a very shallow well (e.g., only ~ 10.4 kcal/mol lower than **TS1**, cf. Figure 1), and its pressure stabilization is unachievable even at extremely high pressures. Therefore, the existence of **INT1** is kinetically irrelevant in the PES of furan pyrolysis.

Figure 6: Arrhenius plots for the rate coefficients of the reaction (furan $\rightarrow$ products) at indicated pressures. Only the most important reaction pathways are shown here.

Figure 7: Arrhenius plots for the calculated values of the rate coefficients, $k(T, P)$, for the reactions: furan $\rightarrow$ **P1** (a); furan $\rightarrow$ **P2** (b); furan $\rightarrow$ **INT3** (c) and furan $\rightarrow$ products (d) at indicated pressures. The calculations were carried out using the full PES described in Figure 1. Only the most important reaction pathways are shown here.

Pressure-dependent behaviors of the two channels, furan $\rightarrow$ **P1** and furan $\rightarrow$ **P2**, at different temperatures from 800 to 2000 K were plotted in Figure 8. The modified Arrhenius parameters obtained by fitting of the rate constants for the main channels, furan $\rightarrow$ **INT3**, furan $\rightarrow$ **P1**, furan $\rightarrow$ **P2** and overall reaction, furan $\rightarrow$ products, were also compiled in Table S3 of supplementary information. Again, Figure 8(b) further justifies that **P2** displays a more complicated effect of pressure on the calculated rate coefficients of **P2** than **P1** owing to the ‘well-skipping’⁹⁴ phenomena of **P2** (i.e., **P2** is formed directly from the reactant). **P1** exhibits a usual positive pressure-dependence over the considered temperature range of 800-2000 K with a clear fall-off

region (cf. Figure 8a). In contrast, **P2** shows an anomaly in the pressure dependence by displaying both the positive and negative effects of pressure at high and low temperatures, respectively).

Figure 8: Calculated values of the rate coefficients, $k(T, p)$, for the reactions: furan $\rightarrow$ **P1** (a) and furan $\rightarrow$ **P2** (b) at indicated temperatures. The calculations were carried out using the full PES described in Figure 1.

In Figure 9, our theoretical predictions for the total rate coefficients of the reaction (furan $\rightarrow$ products) are compared with the literature values reported in previous measurements or calculations. Such comparisons are also made in Figure S7 of the supplementary information for the major channels leading to **P1** & **P2**. In general, our calculated values of the rate coefficients agree reasonably well with that of previously reported experimental^{18,23-25} and theoretical^{35,36} data (cf. Figure 10b-e) within the uncertainties. Apart from the measurement of Grela *et al.*²², which underestimates our theoretical values by a factor of ~ 3 (cf. Figure 9a) at a very low pressure of 1.3×10^{-4} atm, our kinetic model predicts the remaining literature values excellently. The discrepancy of Grela *et al.*²² can also be observed with the models developed by Sendt *et al.*³⁵ and Tian *et al.*³⁶ At high-pressures, the values for the rate coefficients given by Tian *et al.*³⁶ are higher than the experimental values from Fulle *et al.*²⁵ but our calculations are in better agreement. For example, we predict $k_{\infty}(T = 1500 \text{ K})$ to be $6.2 \times 10^3 \text{ s}^{-1}$ which agrees excellently with the

experimental value of Fulle *et al.*²⁵ ($k_{\infty}(T = 1500 \text{ K}) = 6.7 \times 10^3 \text{ s}^{-1}$); whereas the values provided by Tian *et al.*³⁶ ($14.1 \times 10^3 \text{ s}^{-1}$) and Sendt *et al.*³⁵ ($4.6 \times 10^3 \text{ s}^{-1}$) are little far off (cf. Figure 10e). Having said that, our computed values of the rate coefficients find excellent agreement with the latest experimental data of Fulle *et al.*²⁵ on furan pyrolysis. Therefore, we believe that our theoretical models using both deterministic and stochastic approaches to describing the detailed kinetic behaviors of the furan pyrolysis are more reliable compared to earlier theoretical studies.

Figure 9: Arrhenius plots showing the comparison between calculated and literature rate coefficients of furan $\rightarrow$ products at the specified conditions. The experimental data are taken from the work of Grela *et al.* (Grela 1985)²²; Lifshitz *et al.* (Lifshitz 1986)²³; Bruinsma *et al.* (Bruinsma 1988)²⁴; Organ *et al.* (Organ 1991)¹⁸; Fulle *et al.* (Fulle 1998)²⁵, and the calculated data are taken from the work of Sendt *et al.* (Sendt 2000)³⁵ and Tian *et al.* (Tian 2011)³⁶. Our calculations were carried out using the full PES described in Figure 1.

The values of the rate coefficients obtained at W1U level of theory are further compared with that obtained from other composite methods such as CBS-QB3, CBS-APNO, G3, G3B3 and G4. The results are as displayed in Figures 10 and 11. Clearly, all the composite methods performed very well in predicting the rate coefficients of furan pyrolysis (see Figure 10). As seen in Figure 11, even the less expensive composite methods such as CBS-QB3, CBS-APNO, G3, G3B3 and G4 are capable of predicting reliable kinetic picture for the furan pyrolysis. Even in the worst-case scenario, the largest MAD was found to be less than 25%. Noteworthy, CBS-QB3 and G4 appear to perform better than the others with less than 15% of MAD. This information may be very useful for the future calculations involving similar systems, such as 2-MF and 2,5-DMF pyrolysis where W1U is probably limited or costly due to their size constrain up to 6 and 7 heavy atoms. In such systems, CBS-QB3 or G4 can be the choice of inexpensive ab initio methods for reliable kinetic pictures. Here, we further note that CBS-QB3 has been the choice for the investigation of the reaction mechanism of the pyrolysis of 2-MF⁹⁶ and 2,5-DMF⁹⁷ recently.

Figure 10: Arrhenius plot comparing $k(T, p = 1 \text{ atm})$ for furan $\rightarrow$ products obtained at different electronic structure methods (i.e., W1U, CBS-APNO, CBS-QB3, G3, G3B3 and G4).

Figure 11: Relative absolute deviations of the rate coefficients for furan $\rightarrow$ products obtained at CBS-APNO, CBS-QB3, G3, G3B3 and G4 methods as compared to that of W1U method over 800 – 2000 K and 1 atm.

Branching Ratios

Figure 12 presents the temperature dependence of the branching ratio for furan $\rightarrow$ products, at 1 atm (see Figure S8 for the results of other conditions). As can be seen, furan is mainly consumed to produce **INT3** at $T \leq 1300$ K (e.g., 95.4 and 50.4% at 800 and 1300 K, respectively). The formation of **INT1** & **INT2** can be ignored as discussed above. At $T \geq 1300$ K, **P2** becomes increasingly important and remains a major channel contributing over 80% at temperatures above 1600 K. This channel reaches a maximum of 90.8% at 1800 K before gradually decreasing due to the increasing contribution of **P1** at high temperatures (e.g., 2.9% and at 1300 K and 11.0% at 2000 K). Yet, **P2** remains as the dominating channel at high temperatures. Our calculation reveals that furan decomposes mainly via the β -carbene channel accounting ca. 85–91% over 1600K–2000 K and at a pressure of 1 atm. This is in excellent accord with the measurement of Urness *et al.*³¹ who reported that 80–90% of furan pyrolysis occurs via the β -carbene channel. The calculated branching ratio of β -carbene channel in this work is also consistent with that of Sendt *et al.*³⁵ (~ 80% at 1600 K) but it is higher than the estimated values of Tian *et al.*³⁶ ~ 50% and Wei *et al.*³⁰ ~ 60% at 1600 K. Because **P3**, **P4** & **P5** (not shown in Figure 10) are energetically high, they are found to be insignificant with the combined contribution of less than 0.1% even at 2000 K and 1 atm. At $T \geq 1550$ K, Vasiliou *et al.*²⁸ suggested that furan can produce $C_3H_3 + HCO$ radicals (**P3**) but we neglected this channel in our kinetic analysis due to the fact that the calculated ratio of $[C_3H_3 \text{ radical}]/[CH_3CCH]$ is about 0.05%. Tian *et al.*³⁶ and Sendt *et al.*³⁵ found a similar ratio of ~ 1.8% and 0.01%, respectively for 1600 K and 1atm. The mechanism for the formation of

propargyl (C_3H_3) radicals is proposed to be via formyl allene (**INT3**) $\rightarrow \text{C}_3\text{H}_3 + \text{HCO}$ (**P3**) by Tian *et al.*³⁶ while Sendt *et al.*³⁵ proposed via the formation CH_3CCH (**P2**) $\rightarrow \text{C}_3\text{H}_3 + \text{H}$ pathway. The proposed pathway via CH_3CCH resonates well with the conclusion of recent works by Cheng *et al.* (2017)⁹⁸ and by Weber *et al.*³² who pointed out that C_3H_3 radical is mainly formed from C_3H_4 isomers rather than from furan directly. Moreover, Urness and co-workers³¹ determined the fraction of propargyl (C_3H_3) radical to propyne (CH_3CCH) using a silicon carbide microtubular reactor and found that the $[\text{C}_3\text{H}_3]/[\text{CH}_3\text{CCH}]$ branching ratio (increasing from ~2% at 1500 K to ~10% at 1600 K over the pressure range of 100–300 Torr). However, they also pointed out the problems associated with the uncertainty in the photocurrent measured by the photodiode when analyzing their data at large energy range³¹.

Figure 12: Temperature dependence of the branching ratio of furan $\rightarrow$ products at 1 atm. The calculations were carried out using the full PES provided in Figure 1.

Conclusions

In this work, a detailed theoretical investigation on gas-phase unimolecular decomposition reactions of furan was carried out by employing the combination of the high-level electronic structure calculations such as W1U, CBS-QB3, CBS-APNO, G3, G3B3 and G4) and the rigorous integrated *deterministic* and *stochastic* ME/RRKM rate models which included the corrections for the hindered internal rotation and quantum tunneling effects. We found that the unimolecular decomposition of furan is initiated by a hydrogen atom transfer routed through α -carbene (**INT1**) and β -carbene (**INT2**) intermediates, where **INT1** can only form $\text{C}_2\text{H}_2 + \text{CH}_2\text{CO}$ (**P1**) as final product and the latter can form a stable acyclic intermediate, formyl allene (**INT3**), which further decomposes to produce either $\text{CH}_3\text{CCH} + \text{CO}$ (**P2**) or $\text{CH}_2\text{CCH} + \text{HCO}$ radicals (**P3**). Two direct dissociation channels by breaking C-H bonds of furan to give 2-furyl + H radicals (**P4**) and 3-furyl + H radicals (**P5**) were also taken into account in the *ab initio* molecular calculations. As **P4** and **P5** are energetically high channels, their contribution is expected to be insignificant.

Our detailed kinetic analyses suggest that the pyrolysis of furan mainly proceeds via β -carbene, accounting for 85–91% of the total product formation in the temperature range of 1600–2000 K and at 1 atm, which agrees excellently with Urness *et al.*³¹ report of 80-90% for the branching ratio. At $T \leq 1300$ K and 1 atm, the formation of the **INT3** intermediate is the dominant channel due to pressure stabilization. High temperatures and low pressures favor the formation of bimolecular channels: $\text{C}_2\text{H}_2 + \text{CH}_2\text{CO}$ (**P1**) and $\text{CH}_3\text{CCH} + \text{CO}$ (**P2**). **P3** plays a minor role because of its high endothermic nature. Unlike **P1**, **P2** exhibits a complicated pressure dependence owing to the “well-skipping” phenomenon at low temperatures. Consequently, we observed a negative pressure-dependence for **P2** at temperatures below 1000 K. In short, the temperature- and pressure-dependent data from this work has revealed a detail kinetic picture of furan pyrolysis.

Our calculated numbers including the thermochemical properties of the species involved, the species distribution and the kinetic parameters are found in good agreement with previous experimental studies. Thus, our reported data are recommended for the future kinetic modeling to solve the combustion problems involving furan for the temperature range of 800–2000 K and pressure 0.001–100 atm. Finally, after comparing the results from W1U and the other composite methods (CBS-QB3, CBS-APNO, G3, G3B3 and G4), we conclude that CBS-QB3 and G4 methods can be equally reliable as W1U to investigate the pyrolysis reactions of larger systems such as 2-methylfuran, 2,5-dimethylfuran or other furan-related compounds.

Acknowledgments

Computing resources provided by the Institute for Computational Science and Technology – Ho Chi Minh City, University of Science and International University, VNU-HCM are gratefully acknowledged. This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 104.06-2017.61. We also thank Minh v. Duong (ICST) for helpful discussion on the kinetic calculations.

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Notes

The authors declare no competing financial interest.

Supporting Information Available:

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