

A Computational Study on the Kinetics of 2-Pyridylacetic acid Pyrolysis in the Gas Phase

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Abstract

In this project a theoretical study was carried out on the reaction mechanism associated with the pyrolysis of 2-pyridylacetic acid (2PAA) in the gas phase in which, methylpyridine and carbon dioxide were the products. The previous experimental kinetic data had shown that the pyrolysis process is homogeneous, unimolecular and proceeds through a concerted mechanism. Theoretical studies at the B3LYP level using the 6-31G* basis set confirmed an asynchronous concerted mechanism for this reaction. Computed kinetic and activation parameters are in good agreement with the experimental one.

Keywords: 2-Pyridylacetic acid; Gas phase kinetic; Asynchronous mechanism; Pyrolysis; Unimolecular reaction

Introduction

Recent studies on the gas phase pyrolysis reactions of 2-substituted chloro, hydroxyl, alkoxy, phenoxy and acetoxy carboxylic acids [1-2] show that the acidic H of the COOH group assists as the leaving group for the elimination. Through these reactions the unstable α -lacton has been formed. The α -lactone decomposes rapidly, yielding carbon monoxide and the corresponding carbonyl compound.

If an amino or nitrogen derivative is considered as a leaving group L in organic compounds, it will be difficult for the pyrolysis reaction to proceed through the mentioned pathway. Therefore gas phase pyrolysis for some kinds of amino acids which undergo a different mechanism.

Some reports on the pyrolysis of amino acids and their sodium salts explain that the experimental techniques are inadequate to determine all of the products and these processes occurred in different manner [3]. Also, the experimental and theoretical studies on the several amino acids confirmed that the corresponding zwitterions compounds can not be produced in the gas phase [4].

In view of the scarce information on the gas phase pyrolysis of amino acids including the theoretical and mechanistic consideration, a theoretical study aimed at investigation of 2-pyridylacetic acid pyrolysis in the gas phase.

Computational details

The structures corresponding to the reactant, intermediate, transition state and the products for the pyrolysis reaction were optimized, using the Gaussian 98 computational package with the DFT method as implemented in the computational program.

Since, in addition to the results of our previous studies [5-10], Lee and co-workers have previously reported that the B3LYP hybrid functional gives structures and vibrational frequencies in less time rather than other theoretical methods which are in good agreement with the coupled-cluster theory [11], the optimized geometries of the stationary points on the potential energy surface (PES) were obtained using the Becke's three parameter hybrid exchanges functional with the correlation functional of Lee, Yang and Parr (B3LYP) level of the theory with the 6-31 G* basis set.

The synchronous transit-guided quasi-Newton (STQN) method as implemented by Schlegel et. al was used to locate the TS.

Vibrational frequencies for the points along the reaction paths were determined to provide an estimation of the zero point vibrational energies (ZPVE).

Activation parameters were calculated in the temperature range of the pyrolysis reaction at the B3LYP level of the theory with the different basis sets. Activation energy, E_a , and the Arrhenious factor were computed using the equations (1) and (2), respectively. These equations have been derived from the transition state theory :

$$E_a = \Delta H^\ddagger(T) + RT \quad (1)$$

$$A = (eK_B T/h) \exp (\Delta S^\ddagger(T)/ R) \quad (2)$$

Thermodynamic parameters for the global reaction were calculated at 298.15 K. Also charge changes on the atoms for the reactant, TS, intermediate and methyl pyridine were determined using the natural bond orbital (NBO) analysis.

Results and discussion

Three possible mechanisms can be suggested for the pyrolysis of 2PAA in the gas phase. The first one may be started by the homogeneous cleavage of C4-C5 bond according to Scheme 1, follows by a step-wise radical mechanism. The second possibility is the proceeding through a zwitterionic state in Scheme 2 and the third is direct unimolecular splitting through a concerted mechanism.

C4-C5 bond breaking is the rate determining step in the first mechanism. The C4-C5 bond dissociation energy would be the activation energy of the reaction from the energy point of view.

After full geometry optimization of the probable radicals, their energies were calculated with the UB3LYP level of the theory using a variety of different basis sets. Including the different polarization and diffusion effects. It is obvious from the table 1 that the calculated activation energies are much greater than the experimental one ($E_a=152.74 \text{ kJmol}^{-1}$), therefore the step-wise mechanism is unacceptable.

According to the experimental value for activation entropy, the zwitterionic mechanism can not be reasonable. These conclusions led us to the last mechanism and concerted mechanism was fully investigated.

The concerted pathway involves a two-step mechanism. The first step which is initiated with the H1-N2 bond formation and C4-C5 bond cleavage is a concerted process in which an cyclic intermediate and carbon dioxide are formed via a six- membered cyclic TS (TS1) according to figure 1, where the hydrogen atom of the OH of the carboxyl group migrates to the nitrogen atom of the pyridine ring. The second step is a rapid process in which the aromaticity of the ring is conserved by the hydrogen atom transfer through a four-membered cyclic TS (TS2). Carbon dioxide and methyl pyridine (Prod1) are the major products of the first and second step, respectively.

During the pyrolysis process, when the reactant is transformed to the TS1, H1-N2, C5-O6 and C3-C4 bond lengths decrease, whereas H1-O6, N2-C3 and C4-C5 bond lengths increase. Table 2 shows the geometric parameters for the reactant, TS and intermediate according to atom numbering on figure 1. The comparison between the H1-N2 and C4-C5 bond lengths at the TS1 with the same one in the reactant indicates that the H1-N2 bond formation occurs faster than C4-C5 bond cleavage. Accordingly the new bond formation happens by a slightly asynchronous nature for the concerted mechanism. In table 2 we can notice that the C-C bond lengths of the ring change from the reactant to the products which confirm that the ring aromaticity fluctuates through the reaction.

Charge distribution on the reactant and the TS1 was calculated using the NBO analysis. It can be concluded from table 3 that a large positive charge develops on H1 atom, while N2 atom supports the electronic excess in the reactant. The negative character of N2 atom allows it to attract the positive character of H1 atom at the TS1, which confirms the cyclic TS1. On the other hand the electron density increases for H1 atom and decreases for C5 atom (positive character of C5 and negative one for H1 atom) at the TS1 showing that the new bond formation of H1-N2 is faster than C4-C5 bond cleavage which confirms an asynchronous nature for the concerted mechanism.

High magnitudes of the imaginary vibrational frequencies for the TS1 ($>1000 \text{ icm}^{-1}$ in all of the theoretical levels) indicate that this point is associated with the light atom movement of H1 at the TS1.

Dipole moment changes through the pyrolysis reaction justify the greater polarity of the reactant relative to the TS1. Considering the decrease of dipole moments through the reaction, one can confirm that charge symmetry decreases for the TS1 in comparison to the reactant. This could be another reason for the concerted nature of the reaction mechanism.

Calculated kinetic and thermodynamic parameters for the pyrolysis reaction at 561 and 298 K respectively, are reported in table 4. It can be concluded from table 4 that the improving basis sets from 6-31G* to 6-311+G** has only insignificant effect to the calculated barrier height and exothermicity of the reaction. In addition to this, calculated kinetic parameters are smaller than the experimental values which is another certificate for the underestimation of the energy when the B3LYP method is applied in the energy calculations [5-10]. A comparison of the calculated and experimental kinetic values demonstrates a good agreement especially at the B3LYP/6-31+G** level of the theory.

Energetics of the reactant, transition states, intermediate and products shows that the global pyrolysis process is spontaneous.

Free energy profile for the pyrolysis process of 2PAA is presented in figure 2. At first sight, it appears clearly that the second step of the concerted pathway is kinetically more favorable than the first step and hence, the first step is the rate determining step of the global process. Activation energy for the second step of only 67.5 kJmol^{-1}

Conclusion

Computational studies on the kinetics and mechanism of 2-pyridylacetic acid pyrolysis in the gas phase showed:

- a. The concerted mechanism is preferred to other pathways.

- b. Driving force for the pyrolysis reaction is the initial migration of H1 atom with the extension of C4-C5 bond.
- c. Computational and experimental results are in good agreement, describing an asynchronous six-center concerted mechanism.

Table 1. Calculated energies (-Hartree) using the UB3LYP method (Py=C5H4N)

Basis set	COOH	Py-CH ₂ COO	Py-CH ₂	2PAA	CO ₂	bE [‡] (kJmol ⁻¹)
6-31G*	189.0878	475.4909	286.9289	476.1729	188.5809	410.08
6-31+G*	189.1005	475.5118	286.9419	476.1945	188.5903	399.52
6-31+G**	189.1062	475.5208	286.9511	476.2091	188.5904	398.48
6-311G*	189.1447	475.6038	286.9902	476.2873	188.6408	400.24
6-311+G*	189.1518	475.6153	286.9953	476.2983	188.6466	397.11
6-311+G**	189.1586	475.6249	287.0054	476.3147	188.6466	395.60

Table 2. Optimized geometric parameters (bond lengths in angstrom, angles in degree) for the reactants (2PAA), intermediate (Int) and transition state (TS1) using the 3LYP/6-31G* method in the gas phase

Parameter	2PAA	TS1	Int
H1-C2	1.80	1.26	1.01
N2-C3	1.34	1.38	1.40
C3-C4	1.51	1.38	1.35
C4-C5	1.54	1.80	----
C5-O6	1.33	1.30	----
C5-O7	1.20	1.19	----
N2-C8	1.33	1.36	1.40
C8-C9	1.39	1.36	1.34
C9-C10	1.39	1.42	1.43
C10-C11	1.39	1.37	1.35
C11-C3	1.39	1.43	1.45
H1-O6-C5	41.66	106.15	----
C4-C5-O6	116.03	110.04	----
N2-C3-C4	116.57	118.92	121.17
N2-C3-C4-C5	45.65	56.06	----

Table 3. Calculated NBO charges for the reactant (2PAA), TS, intermediate (Int) and Methyl pyridine (Prod1) in the gas phase using the B3LYP/6-31G* method.

Atom	2PAA	TS1	Int	Prod1
H1	0.51	0.48	0.42	0.24
N2	-0.52	-0.54	-0.58	-0.46
C3	0.23	0.24	0.12	0.22
C4	-0.61	-0.63	-0.57	-0.70
C5	0.83	0.87	----	----
O6	-0.72	-0.72	----	----
O7	-0.58	-0.58	----	----
C8	0.05	0.05	0.03	0.05
C9	-0.28	-0.29	-0.35	-0.29
C10	-0.18	-0.18	-0.22	-0.20
C11	-0.26	-0.25	-0.24	-0.27

Table 4. Calculated gas phase relative energies (in kJmol⁻¹, E=Total energy, H= Enthalpy, G= Gibbs free energy) for the structures involved in the pyrolysis reaction at the B3LYP level

Structure	Basis set	bE	bH	bG
2PAA	6-31G*	0.0	0.0	0.0
Int+CO ₂	6-31G*	70.9	66.2	-23.5
Prod1+ CO ₂	6-31G*	-46.0	-48.5	-97.8
TS2	6-31G*	131.5	129.0	46.3
	6-31G*	141.8	137.2	139.5
	6-31+G*	141.4	136.7	139.1
	6-31+G**	142.1	137.4	139.7
TS1	6-311G*	139.2	134.5	135.9
	6-311+G*	138.1	133.5	134.9
	6-311+G**	140.8	136.2	137.8

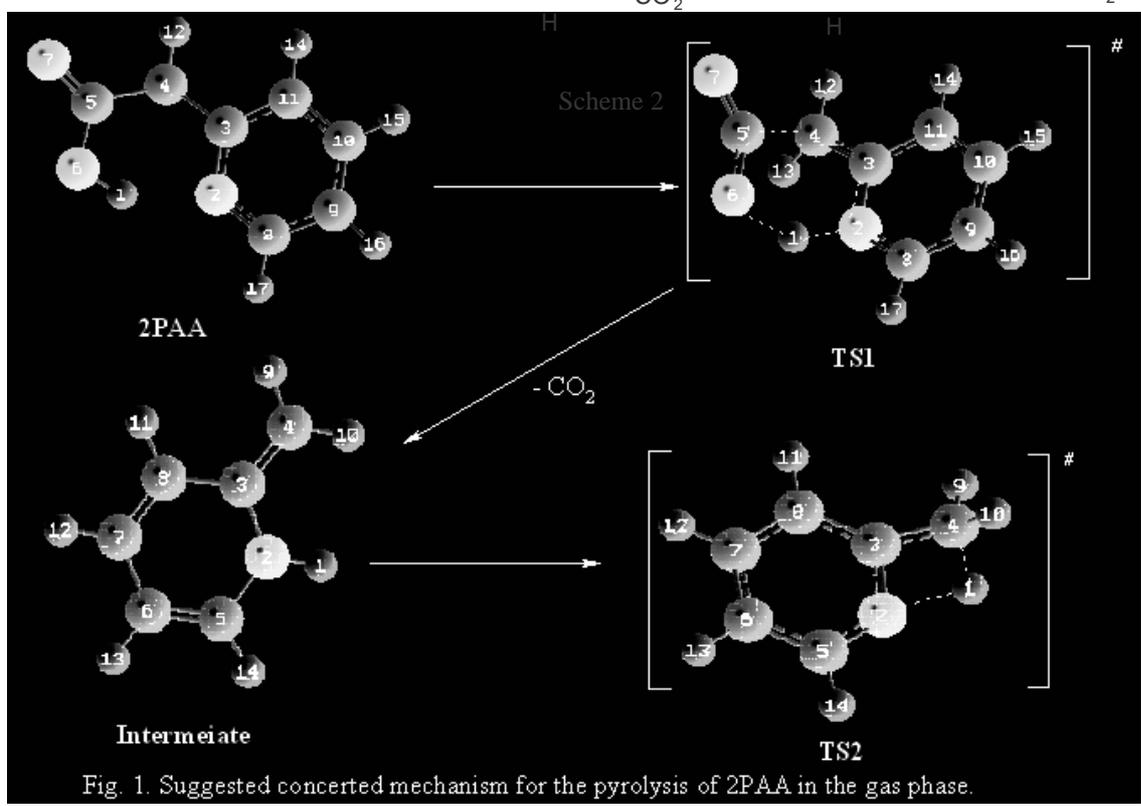
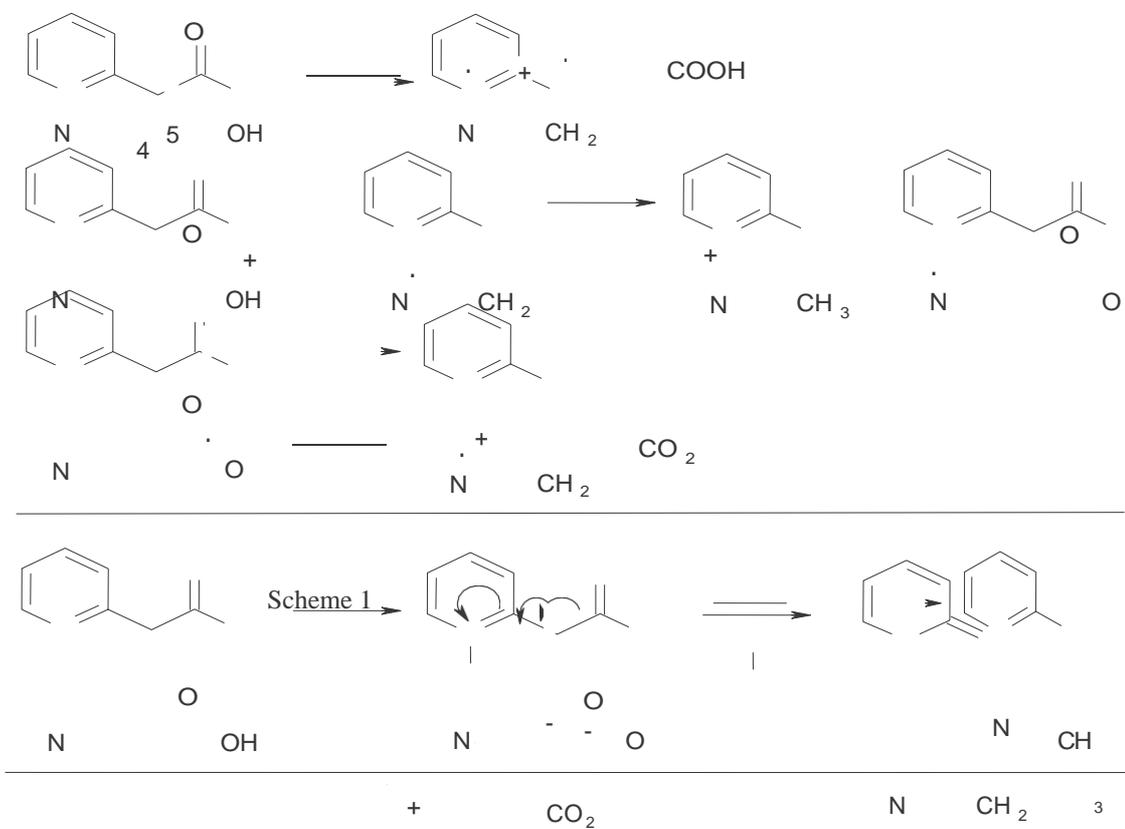


Fig. 1. Suggested concerted mechanism for the pyrolysis of 2PAA in the gas phase.

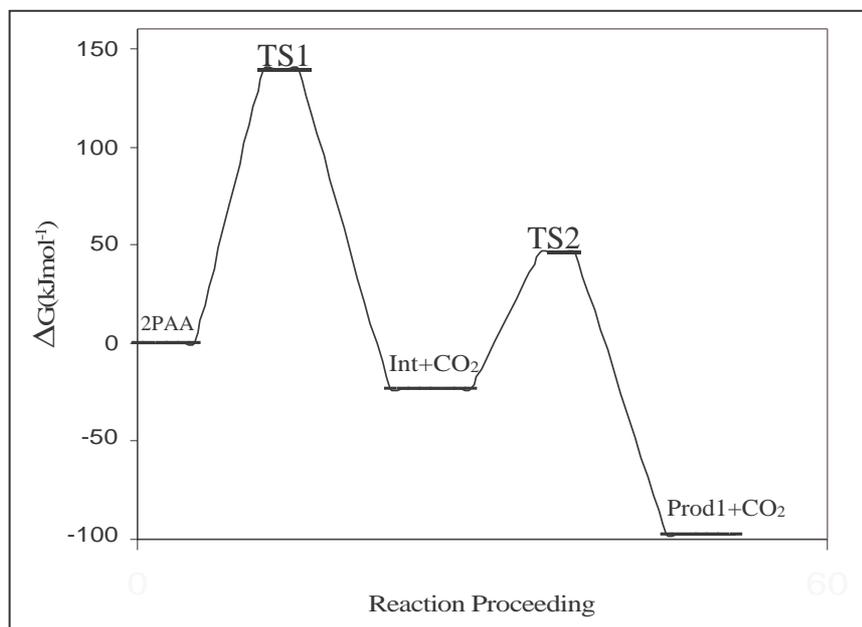


Figure 2. Free energy profile, evaluated at the B3LYP/6-31G* level for the pyrolysis reaction of 2PAA in the gas phase.

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