

Experimental Kinetics of 2-Pyridylacetic acid Pyrolysis

M. Izadyar

Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

[Izadyar @um.ac.ir](mailto:Izadyar@um.ac.ir)

Keywords: 2-Pyridylacetic acid; Asynchronous concerted mechanism; Homogeneous.

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, the reaction proceeding will be changed. In view of the scarce information on the gas phase pyrolysis of amino acids including mechanistic consideration, an experimental study aimed at investigation of 2-pyridylacetic acid pyrolysis in the gas phase (Fig.1).

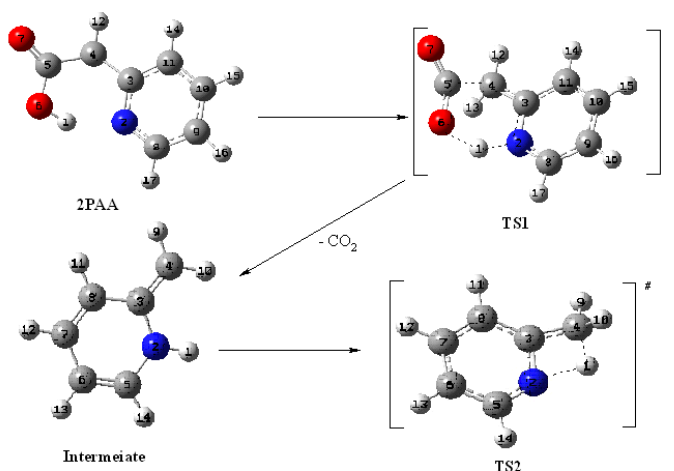


Fig. 1. Suggested concerted mechanism for the pyrolysis of 2PAA in the gas phase.



Experimental

2-pyridylacetic acid hydrochloride was purchased from Aldrich. The hydrochloride was converted to free acids by treatment with fresh Ag_2CO_3 , filtration of the resultant AgCl precipitate, precipitation of dissolved Ag with H_2S and evaporation to dryness. The pyrolysis experiments were performed in a static system over 10 half-lives in the presence of the free radical scavenger (cyclohexene). 2-Pyridyl acetic acid (2PAA) was dissolved in glacial acetic acid and injected directly into the reaction vessel ($\sim 20\mu\text{L}$), using a microsyringe. The reaction mixture was injected into the GC instrument equipped with a thermal conductivity detector (TCD) in each kinetic run.

Gaseous mixture at the definite interval times by a gas-tight syringe (PS, A-2) was injected into the GC capillary column (HP-5, 30 m* 0.32 mm i.d.). The experimental techniques have been described elsewhere [3-5].

Results and discussion

According to scheme 3, pyrolysis reaction of 2PAA demands $P_f/P_0=2.0$, where P_f and P_0 are the final to initial pressures, respectively. The average experimental P_f/P_0 value at five different temperatures between 541.2-583.4 K and 10 half-lives is 1.87.

The homogeneity of this process was studied using the vessels with a surface-to-volume ratio of 3.0 and 6.0 times greater than the unpacked vessel. The effect of different proportions of cyclohexene indicate that the reaction is molecular and not free radical in nature.

The first-order rate coefficients for the reaction calculated from $k = (2.303/t) \log [P_0 / (2P_0 - P_t)]$ were found to be independent of the initial pressure. The average k value is estimated within $\pm 5\%$ standard deviation. A good straight line up to 82% decomposition was achieved by means of plotting the $\log (2P_0 - P_t)$ vs. time t . A least square fit of the rate coefficients in the form of the Arrhenius equation produced the following relationship;

$$\log k = (10.90 \pm 0.32) - (152.74 \pm 2.02 \text{ kJmol}^{-1})(2.303RT)^{-1}$$

Activation parameter values for 2PAA are listed in table 1. Activation energy for the pyrolysis reaction of 2PAA is nearly small relative to similar amino acids such as picolinic acid. This small difference may be attributed to the facile formation of six-center TS for 2PAA rather than five-member TS for picolinic acid. The concerted nature of the reaction could be confirmed by negative values for the activation entropy, too.

Table 1

Experimental kinetic and activation parameters for the pyrolysis reaction in the gas phase

E_a (kJmol ⁻¹)	log A	ΔH^\ddagger (kJmol ⁻¹)	ΔG^\ddagger (kJmol ⁻¹)	$-\Delta S^\ddagger$ (Jmol ⁻¹ K ⁻¹)
152.74	10.90	148.07	176.06	49.82

References:

- [1] V.S. Safont, V. Moliner, J. Anders, L.R. Domingo, J. Phys. Chem. 101 (1997) 1659.
- [2] L.R. Domingo, J. Anders, V. Moliner, V.S. Safont, J. Am. Chem. Soc. 119 (1997) 6415.
- [3] M.R. Gholami, M. Izadyar, J. Phys. Org. Chem. 16 (2003)153.
- [4] M.R. Gholami, M. Izadyar, Chem. Phys. 301 (2004) 45.
- [5] M. Izadyar, N. Zamani, M.R. Gholami, Chem. Phys. 330(2006) 394.