Journal of Molecular Structure 1049 (2013) 149–156

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Aromatic aldehyde-catalyzed gas-phase decarboxylation of amino acid anion via imine intermediate: An experimental and theoretical study

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HIGHLIGHTS

- Using MS/MS and DFT to study decarboxylation of amino acid anion catalyzed by aromatic aldehyde.
- Decarboxylation of α-amino acid anion is determined by direct dissociation of adjacent C—C bond.
- Dissociation of C—C bond is promoted by conjugation between α-carbon, C=N bond and benzene ring.
- Decarboxylation of non-α-amino acid anion proceeds via a S_N2-like transition state.
- Dissociation of C—C bond and attacking of carbanion to C=N bond or benzene occur synchronously.

ARTICLE INFO

Article history:
Received 16 January 2013
Received in revised form 15 June 2013
Accepted 17 June 2013
Available online 24 June 2013

Keywords:
Tandem mass spectrometry
Density functional theory
Amino acid
Decarboxylation reaction
Aromatic aldehyde catalysis

ABSTRACT

It is generally appreciated that carbonyl compound can promote the decarboxylation of the amino acid. In this paper, we have performed the experimental and theoretical investigation into the gas-phase decarboxylation of the amino acid anion catalyzed by the aromatic aldehyde via the imine intermediate on the basis of the tandem mass spectrometry (MS/MS) technique and density functional theory (DFT) calculation. The results show that the aromatic aldehyde can achieve a remarkable catalytic effect. Moreover, the catalytic mechanism varies according to the type of amino acid: (i) The decarboxylation of α-amino acid anion is determined by the direct dissociation of the C—C bond adjacent to the carboxylate, for the resulting carbanion can be well stabilized by the conjugation between α-carbon, C=N bond and benzene ring. (ii) The decarboxylation of non-α-amino acid anion proceeds via a S_N2-like transition state, in which the dissociation of the C—C bond adjacent to the carboxylate and attacking of the resulting carbanion to the C=N bond or benzene ring take place at the same time. Specifically, for β-alanine, the resulting carbanion preferentially attacks the benzene ring leading to the benzene anion, because attacking the C=N bond in the decarboxylation can produce the unstable three or four-membered ring anion. For the other non-α-amino acid anion, the C=N bond preferentially participates in the decarboxylation, which leads to the pediocratic nitrogen anion.

1. Introduction

Decarboxylation is a chemical reaction that releases carbon dioxide. Specifically, the loss of a carboxyl group is normally described as the direct conversion of its conjugate base, a carboxylate, to carbon dioxide and a carbanion, followed by protonation of the carbanion. Due to their importance, the reactions of this kind have received a great deal of attention in chemistry and biochemistry [1–9].

Amino acids play central roles both as building blocks of proteins and as intermediates in metabolism. Decarboxylation of the amino acids is one of the effective methods for obtaining a number of important amino compounds which are versatile substances in the synthesis of biologically active compounds [10–14]. Therefore, the investigation into the decarboxylation of the amino acids seems to be of great significance. Early research mainly focuses on the radical-induced decarboxylation of amino acids [15–17]. It is evident that this process is important for biological systems considering many well-established enzymatic or metabolic pathways of radical generation "in vivo". Chemically, decarboxylation appears to be initiated by oxidative attack. Recently, carbonyl-induced decarboxylation of amino acids has attracted a lot of interest. Wolfenden's group has reported the ability of acetone to promote the decarboxylation of 2-aminomalonate [18]. Of various methods available, the decarboxylation of tryptophan in the presence of ketone catalyst is the simplest way to the synthesis of tryptamine, which is a very important starting material in the synthesis of various indole alkaloids [13].

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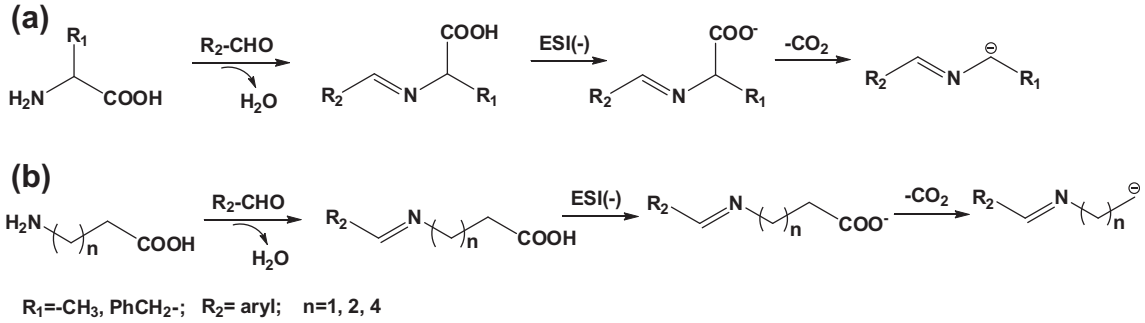
http://dx.doi.org/10.1016/j.molstruc.2013.06.046



Scheme 1. Decarboxylation of the α-amino acid and non-α-amino acid anions catalyzed by the aromatic aldehyde.

Certain progress has been made in the carbonyl-catalyzed decarboxylation of amino acids, however, to the best of our knowledge, most of the investigations concentrate in the liquid reactions. The rate of the decarboxylation is determined by the catalyst and pH value of the solution. However, the carbonyl-catalyzed decarboxylation of amino acids in the gas phase has received considerably less attention. This makes us decide to explore the gas-phase decarboxylation reactions of the amino acids with the assistance of aromatic aldehyde from both experimental and computational perspective, as is shown in Scheme 1. α-Amino acids, such as L-alanine L-phenylalanine and etc, and non-α-amino acids, such as β-alanine, γ-aminobutyric acid and ε-aminocaproic acid, have been selected as the object of study. Herein, two items should be emphasized. First, as this work focuses on the gas-phase decarboxylation of amino acid anion via imine intermediate, only aromatic aldehyde has been selected as the catalyst. The reason is that the use of aliphatic aldehyde probably leads to the problem of obtaining additional intermediates (enamines) which would complicate the mechanistic study of the reactions involved. Secondly, the tandem mass spectrometry in the negative ion mode has been used to study the decarboxylation of the amino acid anion.

It is well known that the C=N bond widely exists in the organocatalyses [19–21], because the formation of the C=N bond can effectively increase the electrophilicity of the corresponding carbonyl. In this paper, the influence that the C=N bond and benzene ring exert on the dissociation of the C—C bond adjacent to the carboxylate and the nature of the decarboxylation will be explored by tandem mass spectrometry technique and DFT calculations.

2. Experimental

2.1. Material

L-alanine, L-phenylalanine, β-alanine, γ-aminobutyric acid, ε-aminocaproic acid, benzaldehyde, cinnamaldehyde, 4-methoxybenzaldehyde and 4-(dimethylamino)-benzaldehyde were obtained from the Sigma-Aldrich Company. These chemical reagents with >95% purity have been used without further purification.

2.2. Mass spectrometry

The mass spectral data were acquired on a LCQ ion trap mass spectrometer from ThermoFinnigan (San Jose, CA, USA) equipped with an electrospray ionization (ESI) interface operated in the negative ion mode. ESI of a CH_3CN/H_2O (3:1) solution containing amino acid (about 500 μM) and a stoichiometric amount of aldehyde was carried out at a flow rate of 15 μL/min into the ESI source. The operation parameters are listed as follows: spray tip potential ~3000 V; capillary voltage: ~20 V; capillary temperature: ~240 °C; Sheath gas flow rate: 9.28 L/min; Tube lens: 55 V. In the MS/MS experiments, the carboxylate anions have been isolated monoisotopically in the ion trap and collisionally activated by the same collision energies. Helium (99.99%) was used as the trapping and collision gas.

2.3. Computational methods

All structures were computed on the basis of the hybrid density functional theory (M06-2X) [22] and the 6-31+G(d, p) basis set which were implemented in Gaussian 09 program package [23]. All the gas phase minima and transition structures (here also referred to as transition states) were characterized by frequency analysis. Frequency calculations identify minimum structures with all real frequencies, while transition states with only one imaginary frequency. Zero point energy (ZPE) corrections were applied at the same level [24]. To confirm the transition states connecting the designated intermediates, intrinsic reaction coordinate (IRC) calculations were carried out. Furthermore, to obtain more reliable energetic data, higher-level single-point energy calculations were performed at M06-2X/6-311++G(3df, 2p) level by using the M06-2X/6-31+G(d, p) optimized geometries.

3. Results and discussion

Several typical amino acids have been selected as the objects of the investigation. Thereinto, L-alanine and L-phenylalanine represent α-amino acids, while non-α-amino acids contain β-alanine, γ-aminobutyric acid and ε-aminocaproic acid. The examination of the direct decarboxylation of these amino acid anions without any catalyst has been performed first. The deprotonated amino acids can be prepared by electrospray ionization of a 3:1 (v/v) acetonitrile/water solution containing these amino acids in the negative ion mode. Then the collision-induced dissociation (CID) experiments of these carboxylate anions will provide the information on the decarboxylation in the gas phase. It is found that the direct decarboxylation of these amino acid anions is hard to take place. In order to avoid the case that the collision energy is not sufficient to strike the C—C bond to lose CO_2, collision energy scanning within the range of possibilities has been performed; however, the fragment ion due to the loss of CO_2 has never been found. As the decarboxylation of the carboxylate belongs to S_E1 reaction [25–27] (see Eqs. (1) and (2)), the rate-determining step is the dissociation of the adjacent C—C bond, which leads to the carbanion and CO_2. Thus, it is difficult for amino acid anion to lose CO_2, maybe because the producing carbanion is very unstable.

$$R{-}X \overset{slow}{\rightarrow} R^- + X^+ \quad (1)$$
$$S_E1$$

$$R^- + Y^+ \overset{fast}{\rightarrow} R{-}Y \quad (2)$$

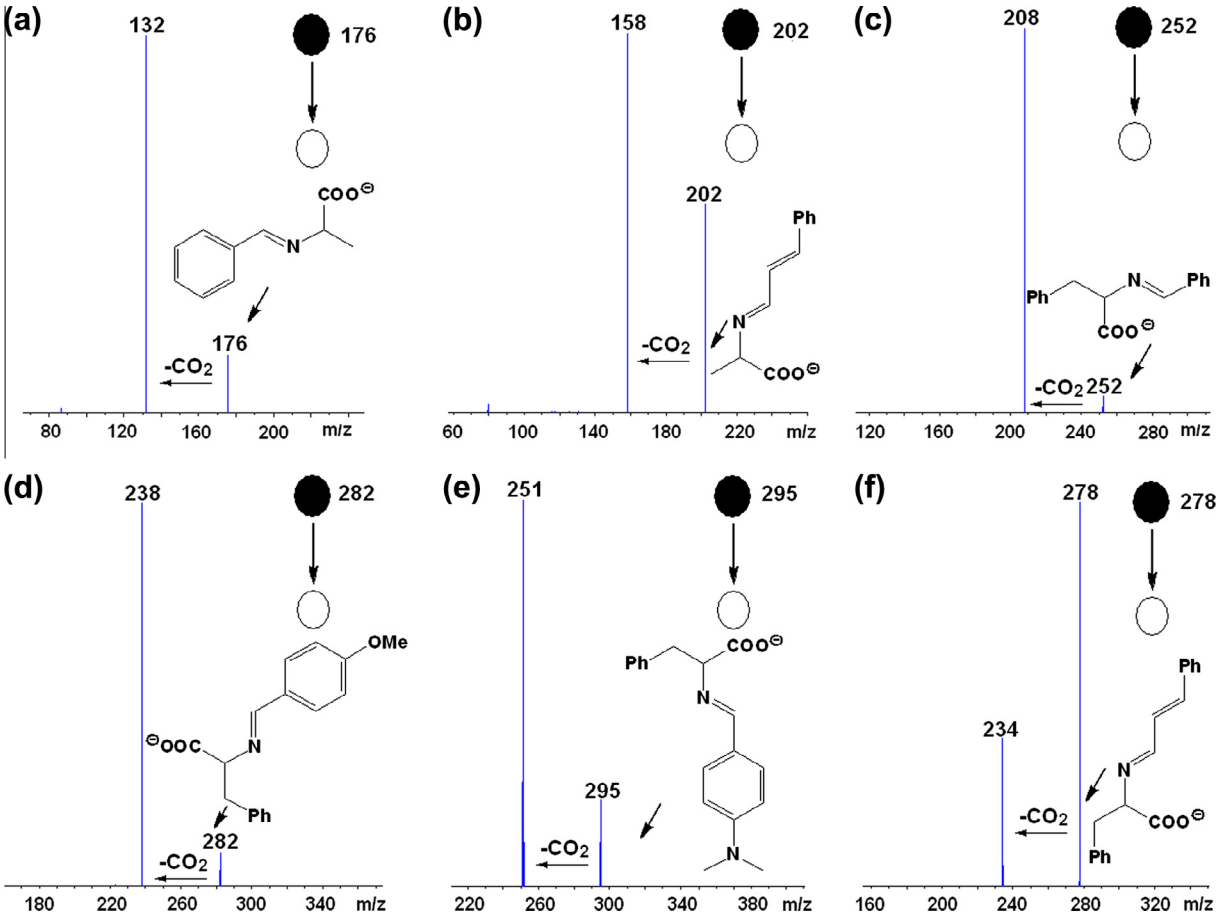


Fig. 1. MS/MS spectra of the carboxylate anions (from α-amino acids) with imine structures.

The next section focuses on the influence that the aromatic aldehyde exerts on the decarboxylation via the C=N bond. The carboxylate anion with imine structure (see Scheme 1a) can be prepared by electrospray ionization of a 3:1 (v/v) acetonitrile/water solution containing the amino acid and a stoichiometric amount of aromatic aldehyde in the negative ion mode. Then the collision-induced dissociation (CID) experiment of this carboxylate anion with the same collision energy as that of the amino acid anion will provide the information on the decarboxylation catalyzed by the aldehyde in the gas phase, as is shown in Fig. 1. Different from that of the amino acid anions, the decarboxylation of the carboxylate anions with imine stuctures seems very easy and the MS/MS spectra are very concise, for basically no other fragment ions have been found except the one due to the loss of CO_2. For L-alanine, benzaldehyde and cinnamaldehyde have been tested and MS/MS spectra of the corresponding carboxylate anions with imine functional groups are depicted in Fig. 1a and b. The corresponding fragment ions due to the loss of CO_2 at *m/z* 132 and 158 are all observed, which means that aromatic aldehyde can effectively promote the decarboxylation of the α-amino acid anions.

Analogously, for L-phenylalanine, the MS/MS spectra of the corresponding carboxylate anions with imine groups are shown in Fig. 1c, d, e and f, respectively. Herein, benzaldehyde, 4-methoxybenzaldehyde, 4-(dimethylamino)benzaldehyde and cinnamaldehyde have been tried. The corresponding fragment ions due to the loss of CO_2 at *m/z* 208, 238, 251 and 234 are all found. Compared with the direct decarboxylation of L-alanine and L-phenylalanine anions, it is evident that the aromatic aldehyde can promote the decarboxylation of these α-amino acid anions. The reason might be that the conjugation system is formed between α-carbon, C=N bond and benzene ring, which can stabilize the resulting carbanion due to the loss of CO_2.

According to the description above, it is easy for the α-amino acid anion to lose CO_2 with the assistance of the aromatic aldehyde. Then, we wonder whether the similar situation happens to the non-α-amino acid anion. The decarboxylation of β-alanine anion with imine structure (see Scheme 1b) has been investigated first, in which the C=N bond is at the β-position. The MS/MS spectrum of the corresponding carboxylate anion with imine group (from benzaldehyde) is shown in Fig. 2a. The corresponding fragment ion due to the loss of CO_2 at *m/z* 132 is observed, which indicates that the aromatic aldehyde can also effectively promote the decarboxylation of β-alanine anion. Analogously, the decarboxylation of the γ-aminobutyric acid and ε-aminocaproic acid anions catalyzed by benzaldehyde was tested with MS/MS method, as are shown in Fig. 2b and c, respectively. The corresponding fragment ions due to the loss of CO_2 at *m/z* 146 and 174 are all observed. It is deduced that the aromatic aldehyde can also achieve a good catalytic effect on the decarboxylation of the non-α-amino acid anion.

To further understand the mechanism of the decarboxylation catalyzed by the aromatic aldehyde, theoretical calculations have been performed. The electronic structure method of choice has been density functional theory (DFT), in particular, the M06-2X hybrid functional. Recently, Brill' group has presented a DFT study of the decarboxylation of the amino acid [28], which indicates that DFT is well fitting for the investigation into the decarboxylation. The next section will focus on the mechanistic study on the decarboxylation of amino acid anion catalyzed by the aromatic aldehyde via the C=N bond.

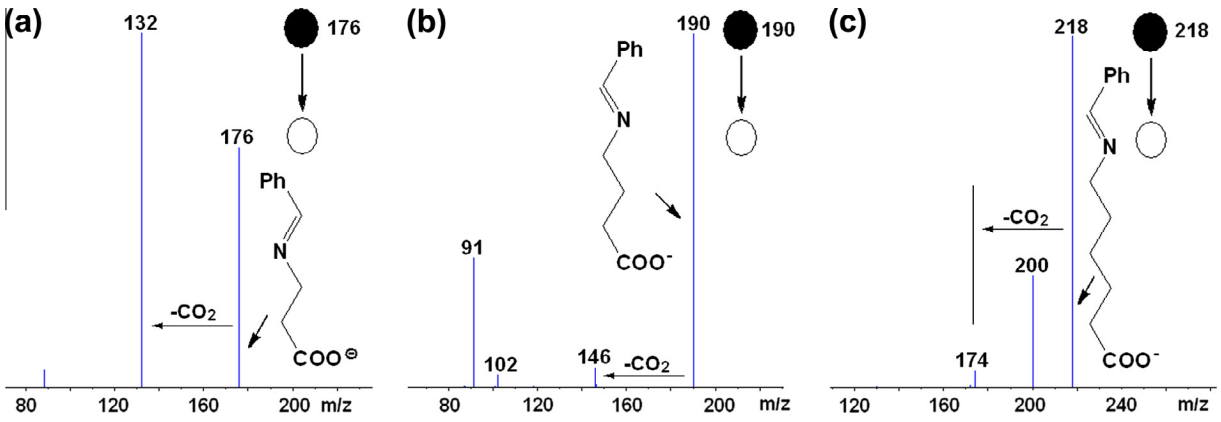
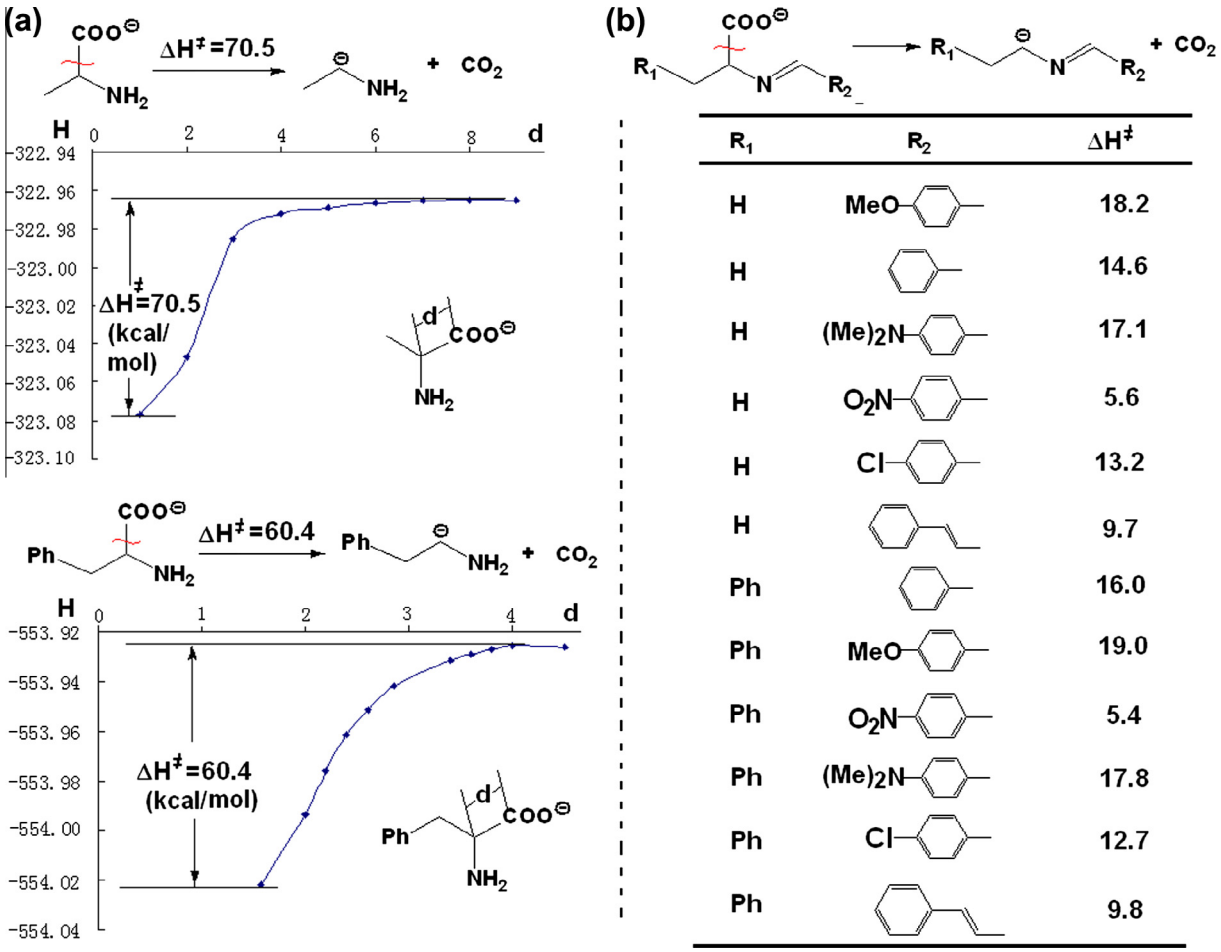


Fig. 2. MS/MS spectra of the carboxylate anions (from non-α-amino acids) with imine structures.



R_1	R_2	$\Delta H^{\ddagger}$
H	MeO	18.2
H		14.6
H	$(Me)_2N$	17.1
H	O_2N	5.6
H	Cl	13.2
H		9.7
Ph		16.0
Ph	MeO	19.0
Ph	O_2N	5.4
Ph	$(Me)_2N$	17.8
Ph	Cl	12.7
Ph		9.8

Fig. 3. (a) The barrier for the decarboxylation of the L-alanine and L-phenylalanine anions; (b) The activation enthalpies for the decarboxylation of the L-alanine and L-phenylalanine anions catalyzed by various of aldehydes (kcal/mol) (Å).

For the α-amino acid anion, the rate-determining step in the decarboxylation is the dissociation of the adjacent C—C bond (see Scheme 1a). Thus, uncatalyzed L-alanine and L-phenylalanine anions were examined first. Unfortunately, the transition states for the corresponding C—C bond dissociation in these α-amino acid anions cannot be located. However, we can also study the decarboxylation in kinetics by using restricted structural optimization. In more specific terms, according to restricting the length of the C—C bond, we can calculate the corresponding barriers for the loss of CO_2, as is shown in Fig. 3a. The barriers for the loss of CO_2 from the L-alanine and L-phenylalanine anions are as high as 70.5 and 60.4 kcal/mol, respectively, which are consistent with the MS/MS experiments. When the amino group in the α-amino acid reacts with different types of aldehydes to give the imines, the transition states for the corresponding C—C bond dissociations in these α-amino acid anions with the imine groups were investigated. Fortunately, the transition state for the decarboxylation catalyzed by the aromatic aldehyde can easily be located and the corresponding

activation enthalpies are depicted in Fig. 3b. For L-alanine (R_1 = H), the activation enthalpy for decarboxylation decreases by at least 52.3 kcal/mol. On the other hand, for L-phenylalanine (R_1 = Ph), the corresponding activation enthalpy also decreases by at least 41.4 kcal/mol.

In addition, the effect of the substituent in the *p*-position of the benzene ring has been taken into account. The substituents contain —$N(CH_3)_2$, —OCH_3, —H, —NO_2 and —Cl. For the L-alanine, the plotting of the activation enthalpies versus the Hammet constants [29–31] σ_p for each substituent is given in Fig. 4a and poor

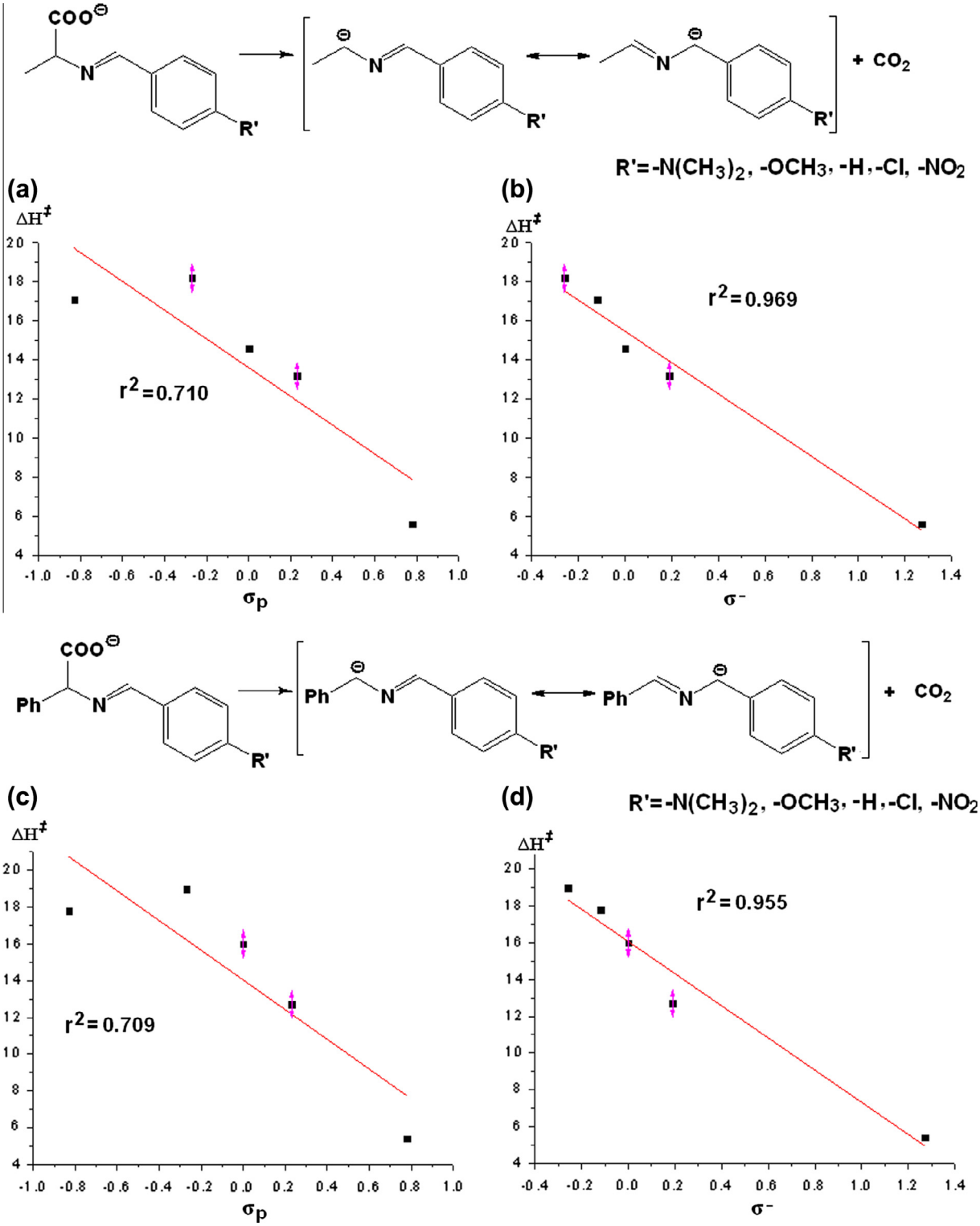


Fig. 4. (a) The plotting of the activation enthalpies versus σ_p for the decarboxylation of L-alanine catalyzed by the aromatic aldehydes; (b) The plotting of the activation enthalpies versus σ^- for the decarboxylation of L-alanine catalyzed by the aromatic aldehydes; (c) The plotting of the activation enthalpies versus σ_p for the decarboxylation of L-phenylalanine catalyzed by the aromatic aldehydes; (d) The plotting of the activation enthalpies versus σ^- for the decarboxylation of L-phenylalanine catalyzed by the aromatic aldehydes.

correlation coefficient (r^2 = 0.710) is obtained. However, when σ_p is replaced by substituent conatant σ^-, good correlation coefficient (r^2 = 0.969) has been obtained, as is shown in Fig. 4b. It can be deduced that there exists a direct resonance interaction between substituent and the anionic reaction center. In other words, in the transition states or the decarboxylation products, the carbon adjacent to the phenyl bears parts of negative charge, which is from the resonance. Simialr condition happens to the decarboxylation of L-phenylalanine catalyzed by the aromatic aldehydes. Fig. 4c shows the plotting of the activation enthalpies versus the Hammet constants σ_p and the corresponding correlation coefficient (r^2) is only 0.709, while that of the activation enthalpies versus the substituent constants σ^- shows good correlation coefficient (r^2 = 0.955). Furthermore, in Fig. 4a–d, the slopes are all negative, which suggests that the electron-withdrawing group can promote the decarboxylation, while the electron-donating group has the opposite effect. The reason might be that electron-withdrawing group increases the stability of the carbanion.

According to the analyses above, for the decarboxylation of α-amino acid anion catalyzed by the aromatic aldehyde, the producing carbanion can be well stabilized by the conjugation between α-carbon, C=N bond and benzene ring. In other words, the negative charge can be dispersed via the resulting π-system. On the other hand, for the non-α-amino acid anion, as there exists no conjugation between α-carbon, C=N bond and benzene ring, we wonder how the aromatic aldehyde catalyzes the decarboxylation. During the process of searching for the transition states for the decarboxylations, it is found that the C=N bond or benzene ring participate in the decarboxylation. The decarboxylation proceeds via a S_N2-like transition state (see Eq. (3)), in which the dissociation of the C—C bond adjacent to the carboxylate and attacking of the resulting carbanion to the C=N bond or benzene ring take place at the same time, as is shown in Scheme 2. The corresponding optimized structures of the transition states are depicted in Fig. 5. With β-alanine for example (Scheme 2a), when the dissociation of the C_4—C_5 bond takes place, it is found that C_5 anion can also attack the C=N bond or benzene ring. Specifically, four pathways are assumed, namely Pathway **i** (N-attack), **ii** (C_1-attack), **iii** (C_2-attack) and **iv** (C_3-attack). The corresponding activation enthalpies are 55.1, 70.7, 55.2 and 53.9 kcal/mol, respectively. Obviously Pathway **iv** is the most favorable and the product is the benzene anion. In other words, the benzene ring is involved in the decarboxylation.

$$R{-}X + Nu^- \rightarrow [Nu^- \cdots R \cdots X] \rightarrow RNu + X^- \quad S_N2$$

Analogously, for γ-aminobutyric acid or ε-aminocaproic acid, four pathways have also been assumed (Scheme 2b and c). DFT calculations show that the most favorable pathways are Pathways

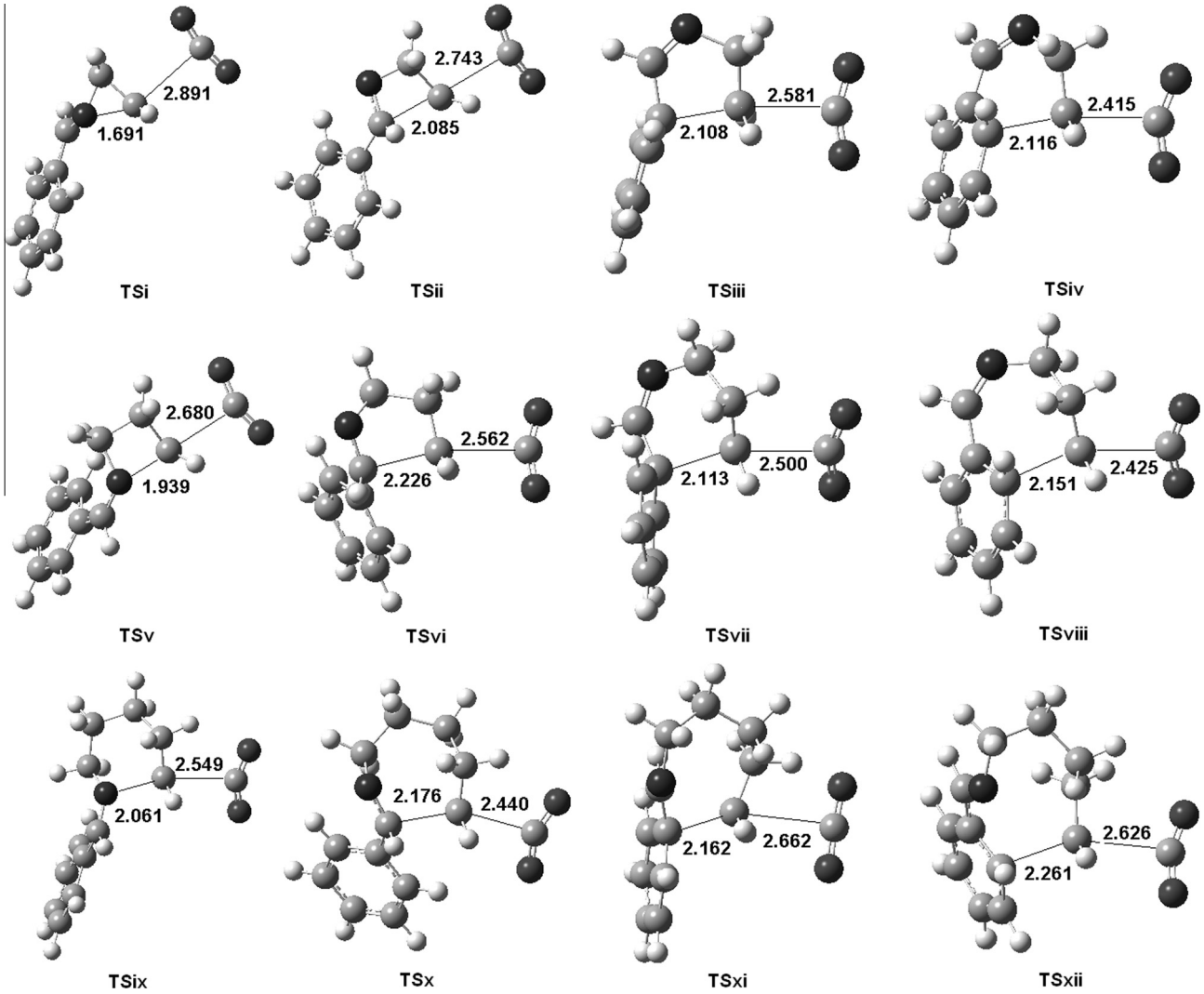
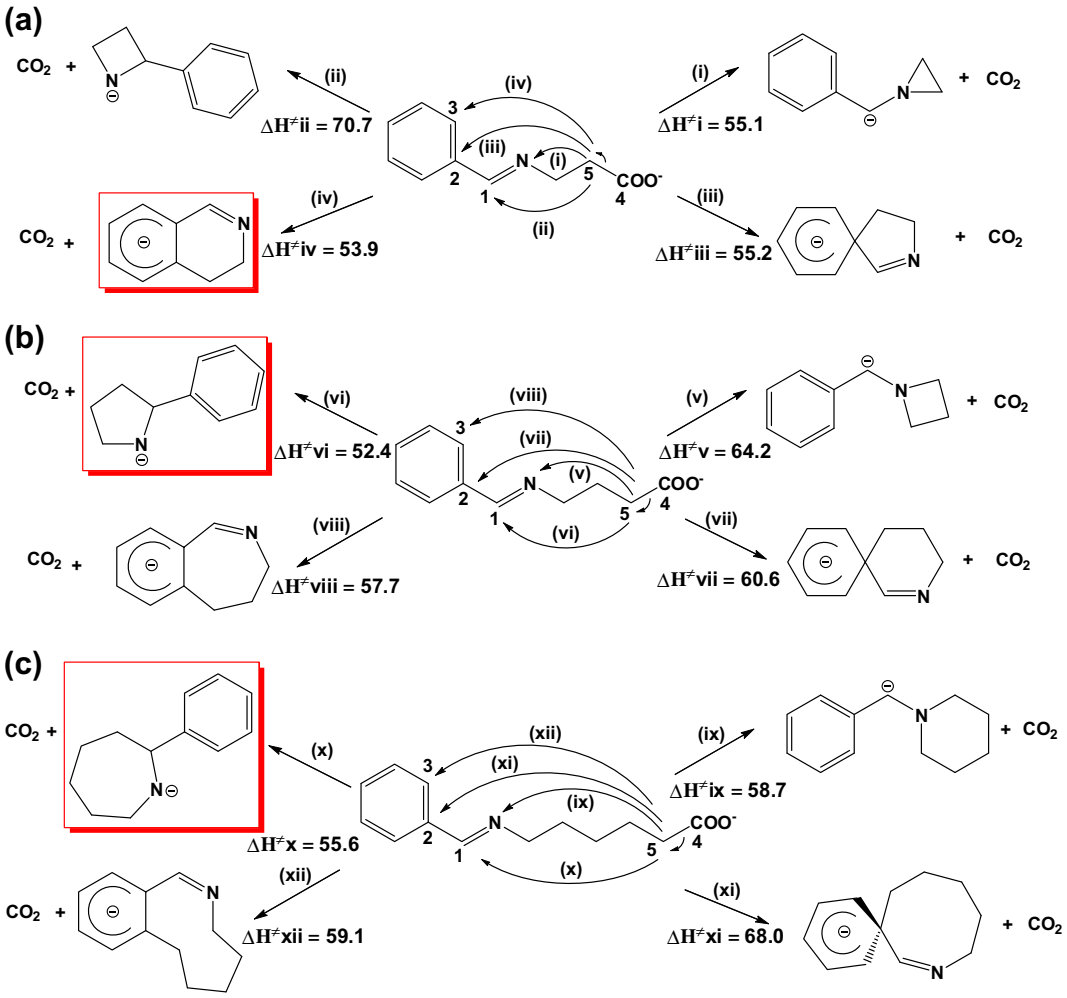


Fig. 5. Optimized structures of the transition states for the decarboxylations of the non-α-amino acid anions catalyzed by the benzaldehyde (Å).



Scheme 2. Proposed pathways for the decarboxylations of the non-α-amino acids catalyzed by the benzaldehyde. (a) β-alanine; (b) γ-aminobutyric acid; (c) ε-aminocaproic acid (kcal/mol).

vi (for γ-aminobutyric acid) and **x** (for ε-aminocaproic acid), respectively. Different from β-alanine, in Pathways vi and **x**, the C=N bond participates in the decarboxylation and the corresponding products are both nitrogen anions. According to the DFT calculations, two items can be concluded: (a) Except β-alanine, for the decarboxylation of the other non-α-amino acid anion catalyzed by the aromatic aldehyde, the carbanion due to the dissociation of the C—C bond adjacent to the carboxylate attacks the C=N bond to produce pediocratic cyclic nitrogen anion, which can promote the decarboxylation. (b) For β-alanine, in Pathways i or **ii**, attacking the C=N bond leads to the unstable three- or four-membered ring product. Thus, the benzene ring participates in the decarboxylation to form pediocratic benzene anion.

4. Conclusions

On the basis of the tandem mass spectrometry (MS/MS) technique and DFT calculations, the present paper has carried out the experimental and theoretical investigation into the decarboxylation of the amino acid anion catalyzed by the aromatic aldehyde. The following conclusions can be made from our results:

1. Whether for α-amino acid or non-α-amino acid anion, both MS/MS experiments and DFT calculations show that the aromatic aldehyde can effectively promote its decarboxylation.
2. The decarboxylation of α-amino acid anion is determined by the direct dissociation of the C—C bond adjacent to the carboxylate. The catalytic mechanism of the aromatic aldehyde is that the producing carbanion can be well stabilized by the conjugation between α-carbon, C=N bond and benzene ring, for the negative charge can be dispersed via the resulting π-system.
3. The decarboxylation of non-α-amino acid anion proceeds via a S_N2-like transition state, in which the dissociation of the C—C bond adjacent to the carboxylate and attack of the resulting carbanion to the C=N bond or benzene ring take place at the same time. Specifically, for β-alanine, the resulting carbanion preferentially attacks the benzene ring leading to the benzene anion, because attacking the C=N bond in the decarboxylation can produce the unstable three or four-membered ring anion. For the other non-α-amino acid anion, the C=N bond preferentially participates in the decarboxylation, which leads to the pediocratic nitrogen anion.

Acknowledgement

The author gratefully acknowledges financial support from the start-up costs to introduce research personnel of Zhejiang Gongshang University (1110XJ2010044, 1110XJ2110044).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2013.06.046.

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