The Elimination Kinetics and Mechanisms of Ethyl piperidine-3-carboxylate, Ethyl 1-methylpiperidine-3-carboxylate, and Ethyl 3-(piperidin-1-yl)propionate in the Gas Phase

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ABSTRACT: The gas-phase elimination kinetics of the above-mentioned compounds were determined in a static reaction system over the temperature range of 369–450.3° C and pressure range of 29–103.5 Torr. The reactions are homogeneous, unimolecular, and obey a first-order rate law. The rate coefficients are given by the following Arrhenius expressions: ethyl 3-(piperidin-1-yl) propionate, $\log k_1(s^{-1}) = (12.79 \pm 0.16) - (199.7 \pm 2.0)$ kJ mol^{-1} $(2.303\ RT)^{-1}$; ethyl 1-methylpiperidine-3-carboxylate, $\log k_1(s^{-1}) = (13.07 \pm 0.12)$–$(212.8 \pm 1.6)$ kJ mol^{-1} $(2.303\ RT)^{-1}$; ethyl piperidine-3-carboxylate, $\log k_1(s^{-1}) = (13.12 \pm 0.13) - (210.4 \pm 1.7)$ kJ mol^{-1} $(2.303\ RT)^{-1}$; and 3-piperidine carboxylic acid, $\log k_1(s^{-1}) = (14.24 \pm 0.17) - (234.4 \pm 2.2)$ kJ mol^{-1} $(2.303\ RT)^{-1}$. The first step of decomposition of these esters is the formation of the corresponding carboxylic acids and ethylene through a concerted six-membered cyclic transition

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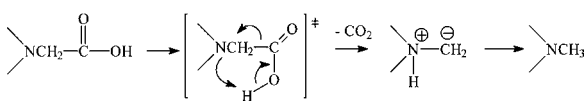
state type of mechanism. The intermediate β-amino acids decarboxylate as the α-amino acids but in terms of a semipolar six-membered cyclic transition state mechanism. © 2005 Wiley Periodicals, Inc. Int J Chem Kinet 38: 106–114, 2006

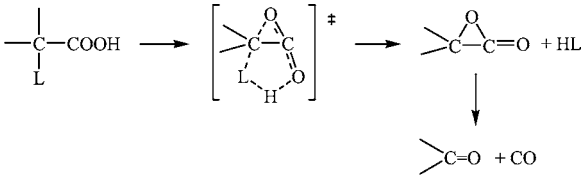
INTRODUCTION

Solid α-amino acids of low molecular weight are difficult to determine their elimination kinetics in the gas phase. These compounds on heating sinter or decompose into vitreous materials, and unfortunately are insoluble in most of the organic solvents. Their high solubility in water, forming zwitterion species, limits their examination as neutral molecules in the gas phase. However, recent investigations have described the homogeneous, unimolecular gas phase pyrolysis of *N*,*N*-dimethylglycine [1], picolinic acid [2], and *N*-phenylglycine [3]. These molecules as 2-substituted amino carboxylic acids undergo decarboxylation as depicted in reaction (1).



(1)

The mechanism of reaction (1) shows to be different from the already reported mechanisms of both experimentally and theoretically gas phase elimination of several types of 2-substituted carboxylic acids. The latter substrates undergo decarbonylation [4–10] as described in reaction (2)

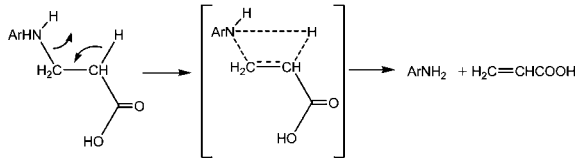


L = Leaving Group: Cl, Br, OH, OR, OPh, OAc.

(2)

The elimination kinetics of *N*,*N*-dimethylglycine [1], picolinic acid [2], and *N*-phenylglycine [3] have been found to be very reactive molecules in the gas phase. The fact that neutral α-amino acids decompose rapidly in the gas phase is supported by the experimental results on the elimination kinetics of the above-mentioned compounds when compared as intermediate products of their corresponding ethyl ester pyrolysis [1–3]. According to these results, it appears that the elimination kinetics of neutral amino acids in the gas phase is feasible.

A few years ago, the gas-phase thermal decomposition of 2-(*N*-phenylamino)propanoic acid [11] was believed to decarbonylate through a five-membered cyclic transition state type of mechanism similar to reaction (2). This result differs from the decarboxylation process of the α-amino acids described in reaction (1). In addition to this work, the pyrolysis products of 2-(*N*-arylamino)propanoic acids [12] were reported to be $ArNH_2$, CH_3CHO, and CO, which led to rationalize reaction pathway (2). In this work [12], the pyrolysis products of 3-(*N*-arylamino)propanoic acids were identified as $ArNH_2$ and acrylic acid. Further, both the experimental results and the theoretical calculations using an ab initio SCF method led to propose a mechanism of a four-membered cyclic transition state as shown in reaction (3).



(3)

A recent work on the gas phase elimination kinetics of ethyl esters of pipecolinic and *N*-methylpipecolinic acids [13] showed as the first step of decomposition the formation of the corresponding carboxylic acids and ethylene. The acid intermediate with the N atom at the α-position of the carboxylic acid, an amino acid derivative, undergoes a very rapid decarboxylation process as depicted in reaction (1). Apparently, this work appears to support the fact that neutral α-amino acids decompose through a five-membered cyclic transition state to give mainly the corresponding substituted amine and CO_2 gas; the present work is aimed at examining a homogeneous, unimolecular, gas phase elimination of some low molecular weight β-amino acids. Unfortunately, low molecular weight β-amino acids are also solid, decompose on heating, and are insoluble in most of the organic solvents. Notwithstanding these limitations, it is intended to determine the kinetic and thermodynamic parameters of the gas phase elimination of β-amino acids intermediates through a consecutive reaction from the corresponding ester decomposition. Further, this work attempts to examine the extent to which the nitrogen atom may affect the elimination process at the β-position of the carboxylic acid intermediates. Therefore, the present investigation was addressed at determining the elimination kinetics of ethyl 3-(piperidin-1-yl) propionate, ethyl 1-methylpiperidine-3-carboxylate, ethyl piperidine-3-carboxylate, and if possible their acids intermediates.

EXPERIMENTAL

The substrates ethyl 3-(piperidin-1-yl) propionate (Aldrich), ethyl 1-methylpiperidine-3-carboxylate (Aldrich), and ethyl piperidine-3-carboxylate (Aldrich) were distilled until 98.6% purity (GC-MS: Saturn 2000, Varian, with a DB-5MS capillary column 30 m $\times$ 0.53 mm. i.d., 0.53 μm film thickness). The pure samples of β-(1-piperidyl)propanoic acid (Aldrich), 3-piperidine carboxylic acid (Aldrich), and 1-methyl-3-piperidine carboxylic acid (by treating ethyl 1-methyl-3-piperidine carboxylate with NaOH and then HCl) could not be examined in the gas phase because they are solid, decompose on heating, and are insoluble in most of the inert organic solvents. The quantitative chromatographic analysis of ethylene was determined by using a gas chromatograph HP 5710A with a Porapak Q (80–100 mesh). The identifications of the products piperidine and *N*-methylpiperidine and *N*-ethylpiperidine were made by comparing with true authentic samples bought from Aldrich and in a GC-MS (Saturn 2000, Varian with a DB-5MS capillary column 30 m $\times$ 0.25 mm. i.d., 0.25 μm).

Kinetics

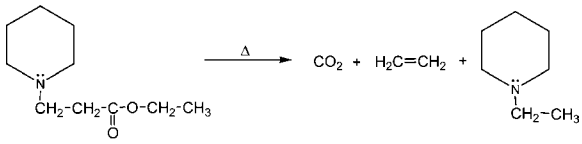
The kinetic determinations were performed in a static reaction system as described before [14–16]. At each temperature, 6–9 runs are carried out in our experiments. The rate coefficients for the ethyl ester decomposition were calculated from the pressure increase manometrically and/or by formation of ethylene product. The temperature was maintained within $\pm 0.2^{\circ}$C through control with a Shinko DIC-PS 23TR resistance thermometer and was measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was observed along the reaction vessel. The starting materials were all injected directly into the reaction vessel with a syringe through a silicone rubber septum. The amount of substrate used for each reaction was $\sim$0.05–0.1 mL.

RESULTS AND DISCUSSION

Authentic samples of β-(1-piperidyl)propanoic acid (Aldrich), 3-piperidine carboxylic acid (Aldrich), and 1-methyl-3-piperidine carboxylic acid (from heating ethyl 1-methyl-3-piperidine carboxylate with NaOH and then HCl) were difficult to examine in the gas phase. These solid materials were found to be insoluble in most of the organic solvents limiting their studies on the static reaction system. However, these compounds as intermediates from pyrolysis of the corresponding ethyl ester may through consecutive reaction give kinetic and mechanistic information during the process of elimination.

Ethyl 3-(Piperidin-1-yl) Propanoate

The elimination products of reaction (4)



(4)

demand a theoretical stoichiometry $P_f/P_0 = 3.0$, where P_f and P_0 are the final and initial pressure, respectively. The average experimental P_f/P_0 at four different temperatures and 10 half-lives is 3.0 (Table I). Further confirmation of stoichiometry (4), up to 60% decomposition, was obtained by comparing the pressure measurements with the quantitative GLC analysis of ethylene formation (Table II).

The reaction was found to be homogeneous since no significant effects on the rates were obtained on using both clean Pyrex and seasoned Pyrex vessels with a surface-to-volume ration of 6.0 relative to the normal clean and seasoned vessels in these experiments (Table III). The effect of different proportions of toluene inhibitor had no effect on the rates (Table IV). No induction period was observed, and the rates were reproducible with a relative standard deviation of not greater that 5% at a given temperature.

The rate coefficients for ethyl 3-(piperidin-1-yl)propionate, calculated from $k_1 = (2.303/t)\ \log [2P_0/(3P_0 - P_t)]$, were found to be independent of the initial pressures (Table V). A plot of log $(3P_0 - P_t)$ against time t gave a good straight line up to 55–60% reaction. The temperature dependence of the rate coefficients and the corresponding Arrhenius equation shown in Table VI, where 90% confidence limits from a least-squares procedure, are given.

Ethyl 1-Methylpiperidine-3-carboxylate

The product formation in the molecular elimination of ethyl-1-methylpiperidine-3-carboxylate is *N*-methylpiperidine, ethylene, and carbon dioxide (reaction (5)).

Table I Ratio of Final (P_f) to Initial Pressure (P_0) of the Substrate

Compound	Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	Aver.
Ethyl 3-(piperidin-1-yl)propionate	389.0	42	125	3.0	3.0
	400.0	53	161	3.0	
	408.8	58	174	3.0	
	420.0	59	177	3.0	
Ethyl 1-methylpiperidine-3-carboxylate	420.1	51	132	2.6	2.8
	430.2	48	134	2.8	
	420.0	67	196	2.9	
	450.5	37	109	2.9	
Ethyl piperidine-3-carboxylate	391.3	111	199	1.8	2.4
	400.9	83	196	2.4	
	410.3	63	156	2.5	
	420.4	89	230	2.6	
	430.9	55	153	2.8	

Table II Stoichiometry of the Reaction

Compound	Temperatures (°C)	Parameter	Values				
Ethyl 3-(piperidin-1-yl) propionate	389.5	Time (min)	3	6	8	10	12
		Reaction (%) (pressure)	14.1	32.2	41.9	49.0	57.1
		Ethylene (%) (GLC)	13.8	30.7	39.3	44.6	54.9
Ethyl 1-methylpiperidine-3-carboxylate	421.3	Time (min)	5	10	15	20	
		Reaction (%) (pressure)	29.3	48.0	62.8	69.6	
		Ethylene (%) (GLC)	28.4	49.8	61.9	70.9	
Ethyl piperidine-3-carboxylate	391.8	Time (min)	15	20	25	30	
		Reaction (%) (pressure)	28.9	36.8	49.2	52.9	
		Ethylene (%) (GLC)	24.2	29.9	33.5	39.9	
		Piperidine (%) (GLC)	5.6	8.4	12	11	
		Sum	29.8	38.3	45.5	49.8	

Table III Homogeneity of the Elimination Reactions

Compound	S/V (cm^{-1})[a]	$\times 10^4 k_1$ (s^{-1})[b]	$\times 10^4 k_1$ (s^{-1})[c]
Ethyl 3-(piperidin-1-yl)propionate at 399.0°C	1	19.37 (±0.1)	19.10 (±0.1)
	6	19.32 (±0.1)	19.13 (±0.0)
Ethyl 1-methylpiperidine-3-carboxylate at 430.3°C	1	18.85 (±0.2)	18.22 (±0.1)
	6	19.02 (±0.2)	18.54 (±0.1)
Ethyl piperidine-3-carboxylate at 410.0°C[d]	1	13.79 (±0.3)	11.49 (±0.1)
	6	14.33 (±0.2)	11.82(±0.1)
3-Piperidine carboxylic acid at 430.5°C[e]	1	10.32 (±0.4)	7.52 (±0.2)
	6	11.06 (±0.5)	7.68 (±0.2)

[a] S = surface area; V = volume.
[b] Clean Pyrex vessel.
[c] Vessel seasoned with allyl bromide.
[d] k-values from the GLC analysis of ethylene.
[e] k-values from the GLC analysis of piperidine.

Table IV Effect of Free Radical Inhibitor Toluene on Rates

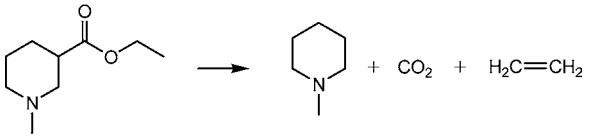
Substrate	Temperature (°C)	P_s (Torr)	P_i (Torr)	P_i/P_s	$\times 10^4 k_1$ (s^{-1})
Ethyl 3-(piperidin-1-yl)propionate	400.4	55.5	–	–	19.30
		51.0	108.5	2.1	19.60
		60.0	182.0	3.0	19.40
		38.5	170.5	4.4	19.50
		41.5	219.0	5.3	19.30
Ethyl 1-methylpiperidine-3-carboxylate	450.4	50.0	–	–	51.23
		54.0	97.0	1.8	51.41
		37.0	70.0	1.9	51.05
		41.5	97.5	2.3	51.41
Ethyl piperidine-3-carboxylate[a]	401.3	89.0	–	–	6.87
		116	73.5	0.6	6.72
		92.0	73.5	0.8	6.92
		83.0	73.0	1.0	6.29
3-Piperidine carboxylic acid[b]	401.5	13.0	–	–	1.33
		41.0	49.5	1.2	1.29
		14.5	45.5	3.1	1.31
		15.0	60.0	4.5	1.28

P_s = Pressure substrate; P_i = pressure inhibitor.
[a]GLC analysis of ethylene.
[b]GLC analysis of piperidine.

Table V Invariability of the Rate Coefficients with Initial Pressure

Compound	Temperature (°C)	Parameters	Value				
Ethyl 3-(piperidin-1-yl)propionate	400.4	P_0 (Torr)	45.0	48.5	53.0	65.5	82.5
		$10^4 k_1$ (s^{-1})	19.4	19.3	19.3	19.4	19.2
Ethyl 1-methylpiperidine-3-carboxylate	430.2	P_0 (Torr)	29.0	35.5	48.0	55.0	
		$\times 10^4 k_1$ (s^{-1})	18.2	18.2	18.5	18.2	
Ethyl piperidine-3-carboxylate[a]	391.8	P_0 (Torr)	53.5	61.5	92.0	104	
		$\times 10^4 k_1$ (s^{-1})	3.92	3.62	3.82	3.95	
3-Piperidine carboxylic acid[b]	420.8	P_0 (Torr)	13.0	24.5	33.0	44.0	
		$\times 10^4 k_1$ (s^{-1})	4.21	4.21	4.19	4.20	

[a]k-values from the GLC analysis of ethylene.
[b]k-values from the GLC analysis of piperidine.



(5)

The theoretical stoichiometry (5) requires a long reaction times $P_f/P_0 = 3.0$. The average experimental results for P_f/P_0 at four different temperatures and 10 half-lives is 2.8 (Table I). To stoichiometry of reaction (5), up to 70% decomposition was satisfactorily verified by comparing the pressure increase with the quantitative GLC analysis of the ethylene product (Table II). Traces of unknown products were detected. The elimination reaction of this substrate can be said to

Table VI The Variation of the Rate Coefficients with Temperatures

Substrate	Parameter	Value					
Ethyl 3-(piperidin-1-yl) propionate	Temperature (°C)	369.0	379.4	389.0	400.0	410.0	421.0
	$\times 10^4 k_1$ (s^{-1})	3.57	6.31	11.3	19.4	33.9	59.2
	Rate equation $\log k_1$ (s^{-1}) = $(12.79 \pm 0.16) - (199.7 \pm 2.0)$ kJ mol^{-1} $(2.303\ RT)^{-1}$						
Ethyl 1-methylpiperidine-3-carboxylate	Temperature (°C)	410.5	420.4	430.3	440.3	450.3	
	$\times 10^4 k_1$ (s^{-1})	6.53	11.0	18.3	30.6	51.3	
	Rate equation $\log k_1$ (s^{-}) = $(13.07 \pm 0.12) - (212.8 \pm 1.6)$ kJ mol^{-1} $(2.303\ RT)^{-1}$						
Ethyl piperidine-3-carboxylate[a]	Temperature (°C)	391.8	401.6	411.3	420.9	430.9	
	$\times 10^4 k_1$ (s^{-1})	3.95	6.70	11.4	19.4	32.4	
	Rate equation $\log k_1$ (s^{-1}) = $(13.12 \pm 0.13) - (210.4 \pm 1.7)$ kJ mol^{-1} $(2.303\ RT)^{-1}$						
3-Piperidine carboxylic acid[b]	Temperature (°C)	391.8	401.6	411.3	420.9	430.9	
	$\times 10^4 k_1$ (s^{-1})	0.72	1.30	2.34	4.21	7.58	
	Rate equation $\log k_1$ (s^{-1}) = $(14.24 \pm 0.17) - (234.4 \pm 2.2)$ kJ mol^{-1} $(2.303\ RT)^{-1}$						

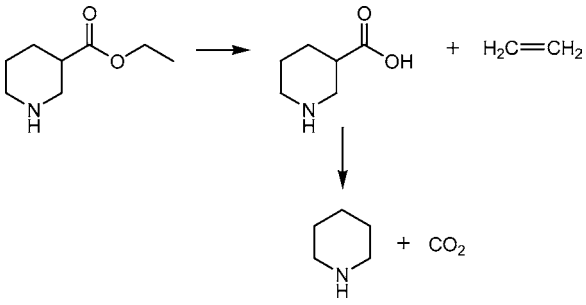
[a] k-values from the GLC analysis of ethylene.
[b] k-values from the GLC analysis of piperidine.

be homogeneous since no significant effect on the rates are obtained when using both clean Pyrex and seasoned Pyrex vessels with a surface-to-volume ratio of 6.0 relative to greater the normal vessel, which is equal to 1.0 (Table III). Toluene as a free radical suppressor had no effect on rates (Table IV), and no induction period was observed. The k values were reproducible with a relative standard deviation not greater than 5% at a given temperature.

The rate coefficients for elimination, calculated from $k_1 = (2.303/t) \log [2P_0/(3P_0 - P_t)]$, are invariable to initial pressures (Table V), and the first-order plot of $\log (3P_0 - P_t)$ against time t gave a good straight line up to 70% decomposition. The variation of the rate coefficients with temperature and the corresponding Arrhenius equation is described in Table VI (90% confidence coefficients from a least-squares procedure).

Ethyl Piperidine-3-carboxylate

The products of the gas phase elimination of ethyl piperidine-3-carboxylate are described in reaction (6):



(6)

The experimental ratio of P_f/P_0 from 1.8 to 2.8 with an average of 2.4 described in Table I implies a consecutive reaction. To check stoichiometry (6), up to 50% decomposition, was possible by comparing the percentage decomposition of the substrate from pressure measurements with those obtained from the summation of the gas chromatographic (GLC) analyses of piperidine and ethylene formation (Table II). The effect of the surface area on the rate of elimination was carried out in a vessel packed with small cylindrical glass balls, with a surface-to-volume ratio of 6.0 relative to that of the normal unpacked vessel, which is equal to 1 (Table III). The rate of elimination of this substrate was unaffected in seasoned packed and unpacked vessels. However, clean packed and unpacked Pyrex vessels showed some heterogeneous effect on the rate coefficients. The effect of the addition of different proportions of the free radical inhibitor toluene is shown in Table IV. The rate coefficients are reproducible with a standard deviation not greater than 5% at a given temperature.

The rate coefficients, in seasoned vessels, were found to be independent of the initial pressure (Table V), and the first-order rate was calculated from the quantitative analyses of product formation. For ethylene formation: $k = -1/t \ln (P_0 - P_{\text{ethylene}})/P_0$, and for piperidine formation: $k = -1/t \ln (P_{3\text{pca}} - P_{\text{piperidine}})/P_{3\text{pca}}$ (where 3pca is 3-piperidine carboxylic acid). The variation of the rate coefficients with temperature and the corresponding Arrhenius parameters is given in Table VI, where 90% confidence limits from a least-squares procedure are given.

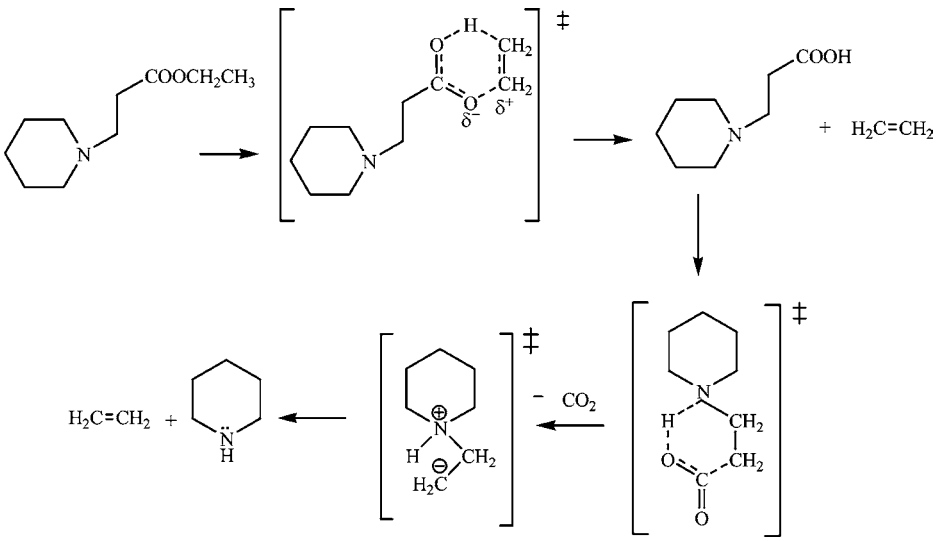
Table VII Kinetic and Thermodynamic Parameters at 400°C

Compound	$\times 10^4$ k_1 (s^{-1})	E_a (kJ mol^{-1})	log A (s^{-1})	$\Delta S^{\neq}$ (J $mol\ K^{-1}$)	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
Ethyl 3-(piperidin-1-yl) propionate	19.5	199.7 ± 2.0	12.79 ± 0.16	-15.2	194.1	204.3
Ethyl 1-methyl -piperidine-3-carboxylate	3.38	212.8 ± 1.6	13.07 ± 0.12	-9.81	205.2	211.8
Ethyl piperidine-3-carboxylate	6.16	210.4 ± 1.7	13.12 ± 0.13	-8.85	204.8	210.8
3-Piperidine carboxylic acid	1.11	234.4 ± 2.2	14.24 ± 0.17	12.6	228.8	220.3

Similarly, even if the amino substituent is at the β-position of a carboxylic acid, i.e. β-amino acid, was also not a leaving substituent. However, β-(*N*-arylamino)propanoic acids reported to give $ArNH_2$ and acrylic acid [12] (reaction (3)) differ from the product formation of the β-amino carboxylic acid intermediates of the corresponding ethyl ester examined in the present work. These types of β-amino acids also decarboxylate by the same mechanism of α-amino acids. In spite of the N atom is within a cyclic system and of an energy required for a favorable conformation, these β-N-substituted carboxylic acids do not show the piperidyl to be a leaving group.

According to product formations and the kinetic and thermodynamic parameters, the mechanisms of these eliminations may be considered as described in (7), (8), and (9):

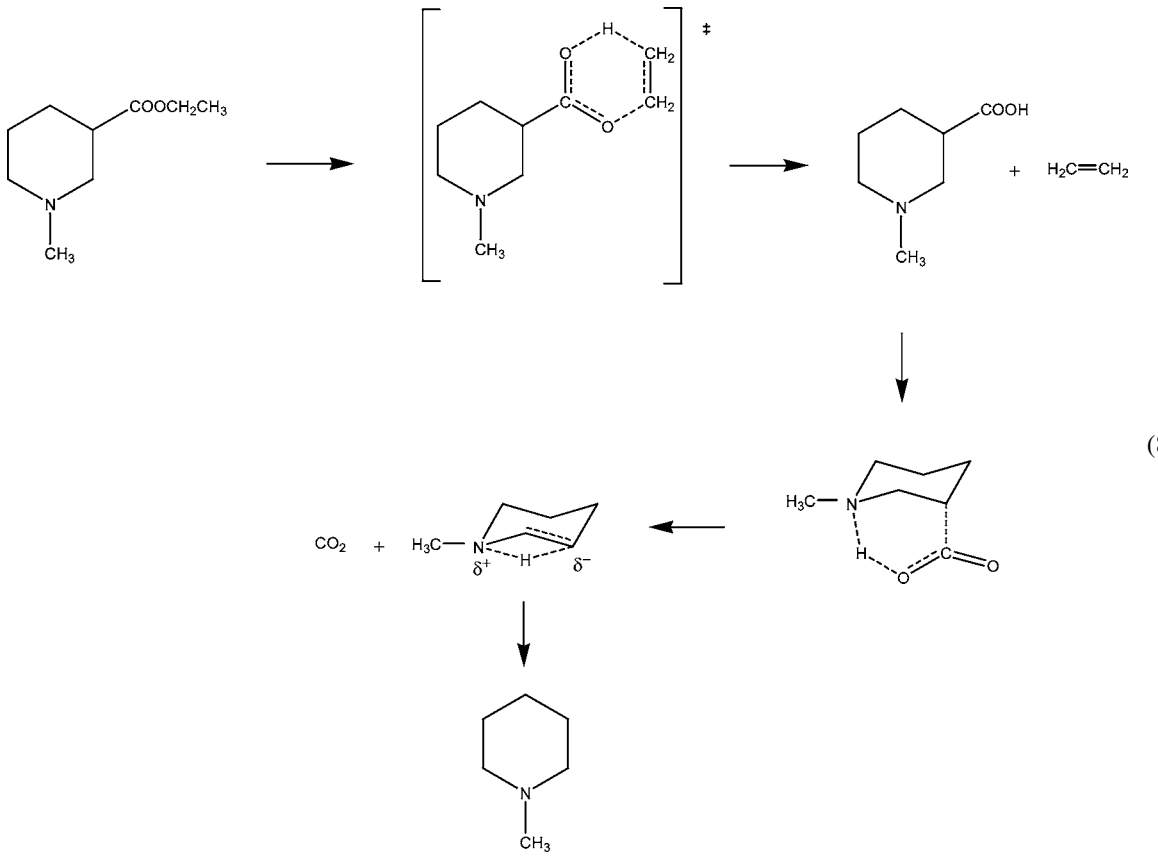
For the ethyl 3-(piperidin-1-yl) propionate:



(7)

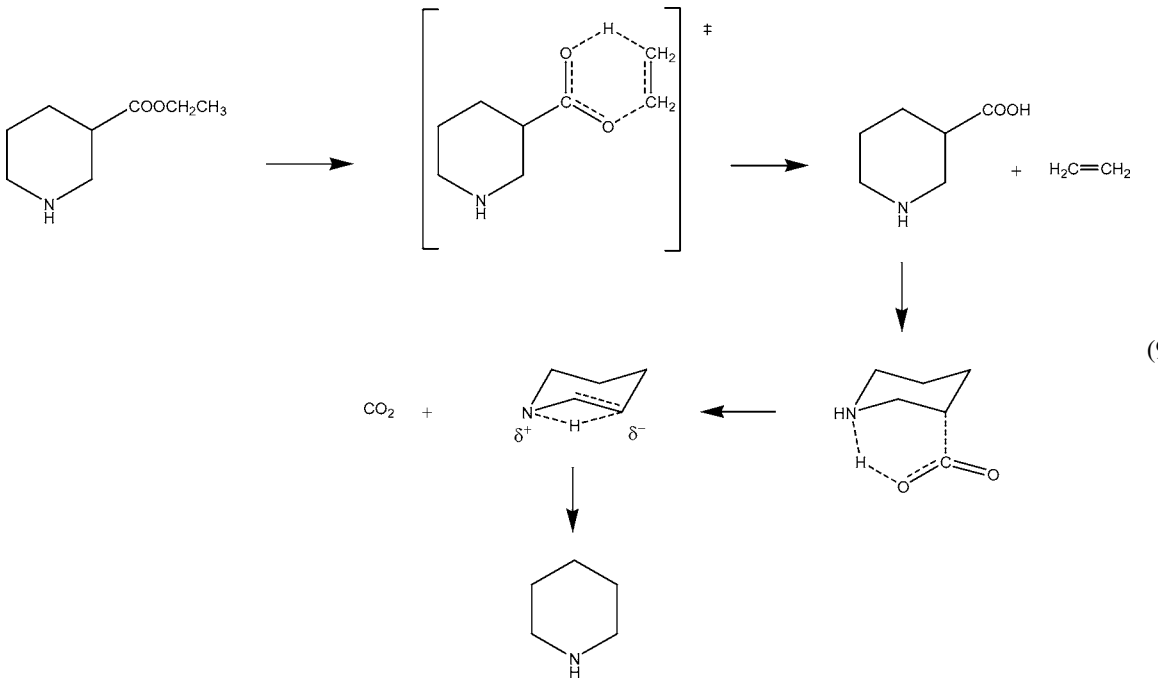
The acid intermediates of ethyl 1-methylpiperidine-3-carboxylate (reaction (8)) and ethyl piperidine-3-carboxylate (reaction (9)) are assumed to proceed through a six-membered cyclic transition state where the chair conformation appears to favor the elimination reaction. In the case of ethyl piperidine-3-carboxylate (reaction (9)), and the corresponding β-amino acid, i.e. 3-piperidine carboxylic acid, it was possible to examine the kinetic and thermodynamic parameters as reported in Table VII. However, 1-methylpiperidine carboxylic acid, intermediate of the corresponding ethyl ester (reaction (8)), was difficult for a complete kinetic study. Apparently, under the reaction conditions, this β-amino acid decarboxylates rapidly making difficult any possible measurements of kinetic data. The rapid decomposition of the unstable intermediate 1-methylpiperidine carboxylic acid may be due to an increase in the nucleophilicity of the N atom by the electronic transmission of the CH_3 group. Such an increase in the nucleophilicity of the N atom may become more polarized when approaching the acidic H of the COOH group, thus causing a lowering in the energy. Consequently, a rapid elimination, i.e. decarboxylation, may be obtained.

For ethyl 1-methylpiperidine-3-carboxylate:



(8)

For ethyl piperidine-3-carboxylate:



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