ELSEVIER

Kinetics and mechanism of thermal gas-phase elimination of β-substituted carboxylic acids

S. A. Al-Awadi, M. R. Abdallah, H. H. Dib, M. R. Ibrahim, N. A. Al-Awadi*
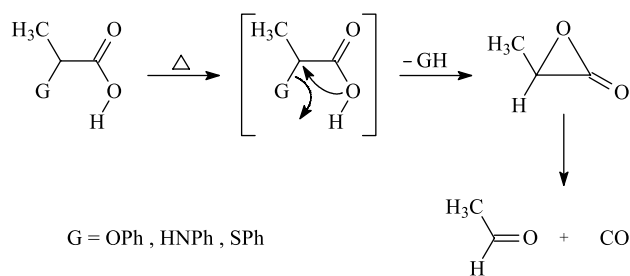and O. M. E. El-Dusouqui

Department of Chemistry, University of Kuwait, PO Box 5969, Safat 13060, Kuwait

Abstract—3-Phenoxypropanoic acid (**1**), 3-(phenylthio)propanoic acid (**2**), and 4-phenylbutanoic acid (**3**) were pyrolysed between 520 and 682 K. Analysis of the pyrolysates showed the elimination products to be acrylic acid and the corresponding arene. Pyrolysis of ethyl 3-phenoxypropanoate (**4**) and its methyl analogue (**5**), ethyl 3-(phenylthio)propanoate (**6**) and its methyl counterpart (**7**), and 3-phenoxypropane nitrile (**8**) were also investigated between 617 and 737 K. The thermal gas-phase elimination kinetics and product analysis are compatible with a thermal retro-Michael reaction pathway involving a four-membered cyclic transition state.
© 2005 Elsevier Ltd. All rights reserved.

1. Introduction

A feasible mechanism for the gas-phase pyrolytic reaction of α-substituted carboxylic acids, namely 2-phenoxypropanoic acid and its phenylthio and phenylamino analogues, has been proposed (Scheme 1).[1] Besides, we have recently, reported on the thermal gas-phase elimination of β-aminoarylpropanoic acid.[2] Product analysis indicates the formation of acrylic acid and substituted aniline. Two acceptable mechanistic pathways were suggested to account for the formation of the reaction products (Scheme 2). To discriminate between the two possibilities, the two alternative reaction pathways were subjected to theoretical calculations using the ab initio SCF method, and the computational results favour the cyclic four-membered transition state (Scheme 2: ii; TS-II). In this study, we report on the thermal gas-phase elimination reaction of eight β-substituted propanoic acids and derivatives (Fig. 1).

2. Results and discussion

2.1. Kinetics and product analysis

The products of pyrolysis were analyzed and spectrometrically characterized. The constituents of the pyrolysates of the β-substituted acids under study (**1–3**, **8**) were established to be the corresponding arene fragments (PhOH, PhSH, PhCH$_3$) together with acrylic acid, and for compound **8** the second pyrolytic product was acrylonitrile. The ethyl and methyl esters (**4–7**) also gave the corresponding arenes (PhOH, PhSH). However, the ethyl esters (**4**, **6**) gave acrylic acid, while the methyl esters (**5**, **7**) produced methyl acrylate.

The kinetic behaviour of each substrate was investigated, and the electronic effects of substituents at the β-carbon of the propanoic acid and its derivatives studied by comparison of the molecular reactivity of substrates **1–8**. These compounds were each well behaved kinetically, and gave reproducible first-order rate constants with strict Arrhenius

Scheme 1. Reaction pathway of gas-phase pyrolysis of α-substituted propanoic acid.

X= NH, O, S, CH$_2$
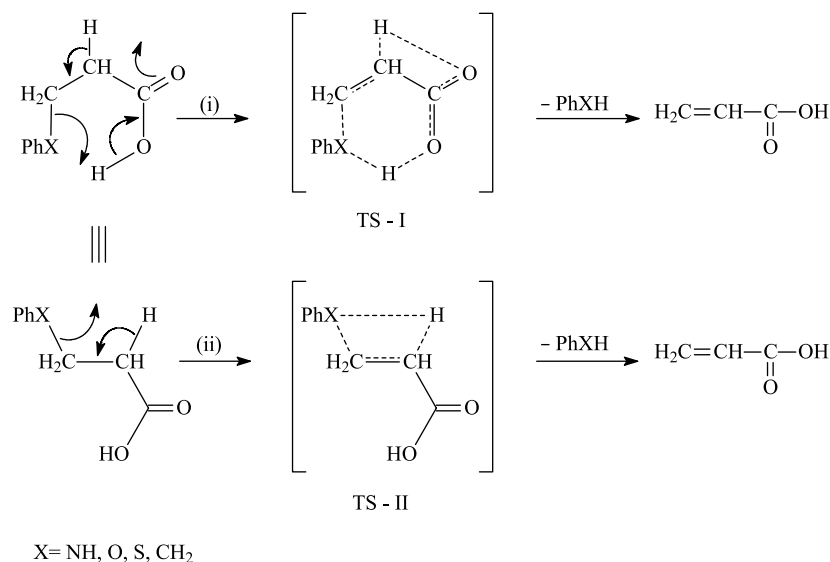
Scheme 2. Gas-phase elimination reaction of β-substituted propanoic acid.

	X	Y	
(**1**)	OPh	COOH	3-Phenoxypropanoic acid
(**2**)	SPh	COOH	3-(Phenylthio)propanoic acid
(**3**)	CH$_2$Ph	COOH	4-Phenylbutanoic acid
(**4**)	OPh	COOEt	Ethyl 3-phenoxypropanoate
(**5**)	OPh	COOMe	Methyl 3-phenoxypropanoate
(**6**)	SPh	COOEt	Ethyl 3-(phenylthio)propanoate
(**7**)	SPh	COOMe	Methyl 3-(phenylthio)propanoate
(**8**)	OPh	CN	3-Phenoxypropane nitrile

Figure 1. β-Substituted propanoic acid and its derivatives.

plot linearity over 90% of the reaction duration. Since, a sixfold change in the amount of substrate per kinetic run indicated no significant change in rate coefficient, these reactions were deemed to be unimolecular first-order processes. The kinetic data are summarized in Table 1, and the kinetic consequences of changing the β-substituent from PhCH$_2$ to PhO, PhS and PhNH, and of changing Y from acid (CO$_2$H) function to CN and ester moieties are recorded in Figure 2.

The elimination pathway of acids **1**–**3** involves the transition state (TS) shown in Figure 2. An identical transition state is proposed for compound **8**. Our earlier theoretical ab initio calculations have argued in favour of the reaction pathway for the thermal gas-phase elimination reaction of acid **9**, which involves a four-membered cyclic TS (Scheme 2, pathway (ii)).[2] We have now extended the theoretical investigation to include the three acids **1**–**3** (see Section

2.2). The results for the four acids displayed in Figure 3 clearly demonstrate that the four-membered transition state (TS-I) is energetically more favourable than TS-II (Scheme 2, pathway (i)). The results also illustrate a dramatic difference between TS-I and TS-II for X=S and CH$_2$ than for X=O and NH. In the transition state of the elimination reaction (TS-I) two σ bonds are being weakened (C–X (bond a) and C–H (bond b) in Fig. 2), while σ and π bonds are being formed. This complex process of bond-breaking and making resulted in an order of molecular reactivities in which acid **3** (X=CH$_2$) is ca. 19–34 times less reactive than the acids in which X=O, S or NH. This finding correlates well with the relative polarity of the (C–X) bond in these substrates. The effect of substituents on C–H bond-breaking (bond b) and π bond formation (C=C bond) is reflected in a rate-reduction factor of ca. 158 when a carboxylic (CO$_2$H) acid moiety (**1**) is replaced by the more electron-withdrawing cyano (CN) group (**8**). A rate-reduction factor of ca. 72 is also observed when the acid group is replaced by methyl ester group (**5**), and a larger (227-fold) decrease in rate is obtained on comparing the reactivities of acid **2** and methyl ester **7**.

The proposed mechanisms of the thermal gas-phase elimination reaction of the ethyl and methyl esters are noteworthy (Scheme 3). The ethyl esters (**4**, **6**) react, respectively, ca. 165 and 173 times slower than the corresponding carboxylic acids (**1**, **2**). However, the products of pyrolysis include acrylic acid and no ethyl acrylate. It is, therefore, suggested that these esters first, eliminate ethene and the acid (PhCH$_2$CH$_2$CO$_2$H) via a cyclic six-membered TS, and the acid then undergoes rapid secondary decomposition via a faster step to give PhXH and acrylic acid as shown for acid pyrolysis. Ethyl acrylate would have been obtained if the four-membered TS was involved in the pyrolysis of the ethyl esters (**4**, **6**). Pyrolysis of the methyl esters (**5**, **7**), on the other hand, produced methyl acrylate and no acrylic acid. These results seem to substantiate a methyl ester reaction pathway involving a

Table 1. Rate coeffecients and Arrhenius parameters of β-substituted carboxylic acids and their derivatives (**1–8**)

No.	T/K	10^4 k/s^{-1}	log A/s^{-1}	E_a/kJ mol^{-1}	k$_{600\ K}$/s^{-1}
1	544.7	1.723	12.21±0.18	166.55±1.91	5.13×10^{-3}
	554.7	3.486			
	564.8	6.427			
	574.9	11.53			
	604.7	67.07			
2	520.2	1.526	8.63±0.62	124.23±6.46	6.59×10^{-3}
	532.5	2.434			
	543.8	5.429			
	555.1	10.93			
	568.8	16.47			
3	615.6	3.416	5.29±0.24	103.48±2.97	1.93×10^{-4}
	629.0	4.944			
	643.2	7.321			
	655.6	10.75			
	668. 5	15.91			
	681.9	25.41			
4	616.6	3.934	8.48±0.23	149.26±2.92	3.10×10^{-5}
	650.0	6.128			
	664.6	8.720			
	679.9	15.28			
	720.2	20.49			
5	633.3	2.243	5.26±0.14	108.06±1.80	7.13×10^{-5}
	654.8	4.544			
	666.0	5.840			
	677.1	8.132			
	687.3	11.13			
	698.3	15.18			
	711.0	21.38			
6	634.8	2.345	9.80±0.47	163.33±5.93	3.80×10^{-5}
	645.1	4.011			
	655.1	5.953			
	665.0	9.05			
	675.1	13.79			
	684.9	22.65			
	694.7	36.16			
7	651.5	2.137	6.05±0.30	121.65±3.98	2.90×10^{-5}
	665.6	3.068			
	679.6	4.590			
	693.6	8.314			
	722.0	17.47			
	736.9	27.53			
8	635.2	2.161	10.65±0.37	173.94±4.60	3.25×10^{-5}
	644.6	3.799			
	655.6	6.376			
	665.8	10.16			
	674.6	14.21			
	685.0	25.63			

cyclic four-membered TS analogous to that shown for the acids [Scheme 2, pathway (ii)].

It is of interest to note that the results of the theoretical ab initio calculations show the gas-phase thermodynamic stabilities of the arene fragments to be in the order: PhNH$_2$ ≫ PhCH$_3$ ∼ PhOH > PhSH. The results appear to correlate with the expected gas-phase acidities of these compounds and the relative proton affinities of their incipient conjugate bases. The thermodynamic stability of the products of gas-phase elimination is an important contributing factor to both molecular reactivity and reaction pathway.[3]

It is worth mentioning here, that ethyl β-hydroxycarb-oxylates were reported to decompose thermally in the gas-phase to a mixture of aldehydes and/or ketones and ethyl acetate (Scheme 4).[4] Small amounts of ethene and carboxylic acid were also detected among the products of

reaction (Scheme 5). This mechanistic pathway was a subject of a theoretical calculation by Natrio and his group.[5] The free energy profile, evaluated at the MP2/3-31 G(d) level of theory, showed clearly that the formation of ethyl acetate and carbonyl compounds is kinetically more favourable than the formation of ethene and carboxylic acid. The theoretical study concluded that the C=O bond breaking and O–H bond forming can be seen as the driving force of the reaction. A safe conclusion from these studies is that thermal gas-phase elimination reactions of ethyl esters of carboxylic acids proceed by a mechanism involving preferred six-membered cyclic transition states.

2.2. Computational studies

The theoretical studies on the gas-phase thermolysis of the three β-substituted propanoic acids (**1–3**) were carried out using ab initio SCF method. The calculations were undertaken to explore the nature of the reaction mechanism
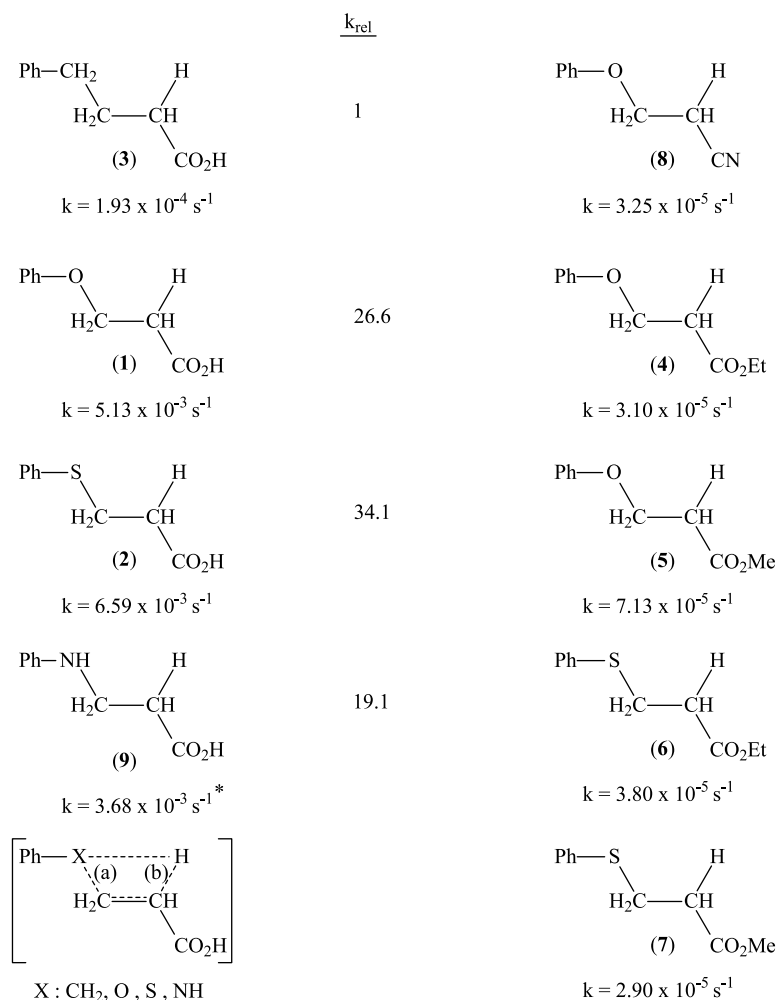
k_{rel}

Ph—CH$_2$ H

H$_2$C——CH

(3)   CO$_2$H   1

k = 1.93 x 10^{-4} s^{-1}

Ph—O   H

H$_2$C——CH

(1)   CO$_2$H   26.6

k = 5.13 x 10^{-3} s^{-1}

Ph—S   H

H$_2$C——CH

(2)   CO$_2$H   34.1

k = 6.59 x 10^{-3} s^{-1}

Ph—NH   H

H$_2$C——CH

(9)   CO$_2$H   19.1

k = 3.68 x 10^{-3} s^{-1} *

$$\left[\begin{array}{c} Ph\!-\!X\text{------}H \\ \text{(a)} \quad \text{(b)} \\ H_2C\!=\!=\!CH \\ CO_2H \end{array} \right]$$

X : CH$_2$, O , S , NH

Ph—O   H

H$_2$C——CH

(8)   CN

k = 3.25 x 10^{-5} s^{-1}

Ph—O   H

H$_2$C——CH

(4)   CO$_2$Et

k = 3.10 x 10^{-5} s^{-1}

Ph—O   H

H$_2$C——CH

(5)   CO$_2$Me

k = 7.13 x 10^{-5} s^{-1}

Ph—S   H

H$_2$C——CH

(6)   CO$_2$Et

k = 3.80 x 10^{-5} s^{-1}

Ph—S   H

H$_2$C——CH

(7)   CO$_2$Me

k = 2.90 x 10^{-5} s^{-1}

Figure 2. Transition state and relative reactivities at 600 K for the gas-phase pyrolysis of β-substituted propanoic acids (**1–3**, **8**, **9**) and esters (**4–7**). *Ref. [2].

of the unimolecular thermal decomposition of the three acids. Two alternative reaction pathways for the decomposition process have been evaluated. All the calculations have been performed on the TITAN computational package.[6]

The geometric parameters for the reactants, the transition states (TS), and the products of the two reaction pathways were fully optimized at the HF/6-31G* level of theory to obtain the energy profiles corresponding to the three reactions. A scaling factor[7] of 0.9135 for the zero-point vibrational energies has been used. The structures obtained from the optimization calculations are represented in Figure 4.

Table 2 illustrates the main distances of each optimized structure of the three studied reactions. During the thermolytic process, when the reactant is being transformed into TS-II, the X$_1$–C$_2$ and C$_3$–H$_7$ distances increase, whereas the C$_2$–C$_3$ and H$_7$–X$_1$ distances decrease, for X=O, S or CH$_2$.

The electronic energies, zero-point vibrational energies, enthalpies and entropies, evaluated at the HF/6-31G* level of theory for the reactants, transition states and reaction products involved in the two alternative pathways of the three reactions are collated in Table 3. The free energy profiles obtained at the HF/6-31G* level for the decomposition process of the three β-substituted propanoic acids (**1–3**) under study and that of acid (**9**)[2] are presented in Figure 3. The free energy values of the two suggested transition states show that TS-II has an energy barrier lower than TS-I. The calculated activation free energies are 316, 15.21, and 21.07 kJ mol^{-1} for the four-membered ring cyclic transition states (TS-II): X=O, S and CH$_2$, respectively. The corresponding values based on the cyclic six-membered transition state (TS-I) are, 363, 370 and 490 kJ mol^{-1}, respectively. The present and reported results indicate that the cyclic four-membered transition state (TS-II) is more favoured than the alternative cyclic six-membered transition state.[2]

3. Experimental

3.1. General

Melting points were determined on a Shimadzu-Gallenkamp apparatus and are uncorrected. Elemental analysis was by means of a LECO CHNS-932 Elemental Analyzer. NMR spectra were measured using a Bruker DPX 400 MHz
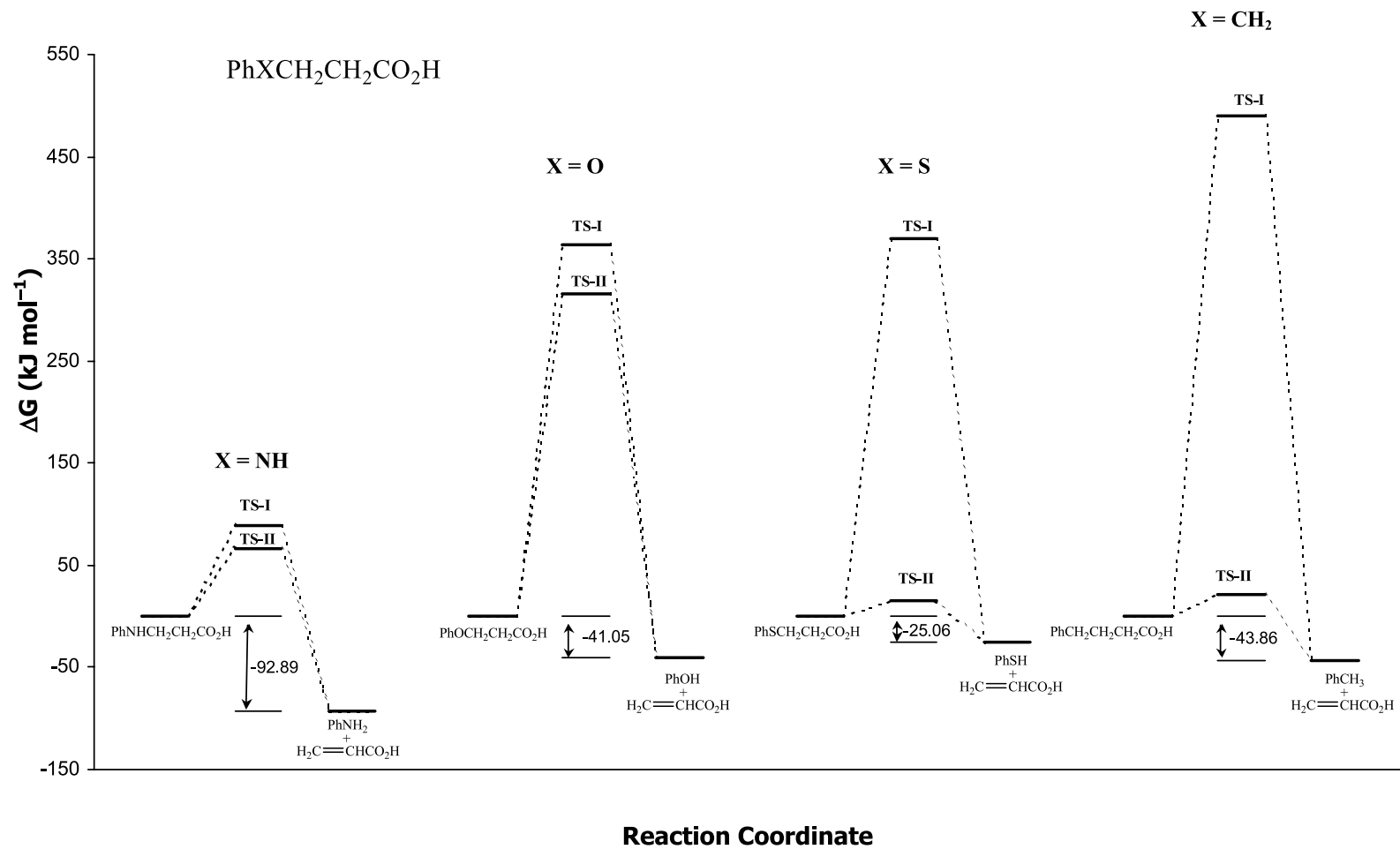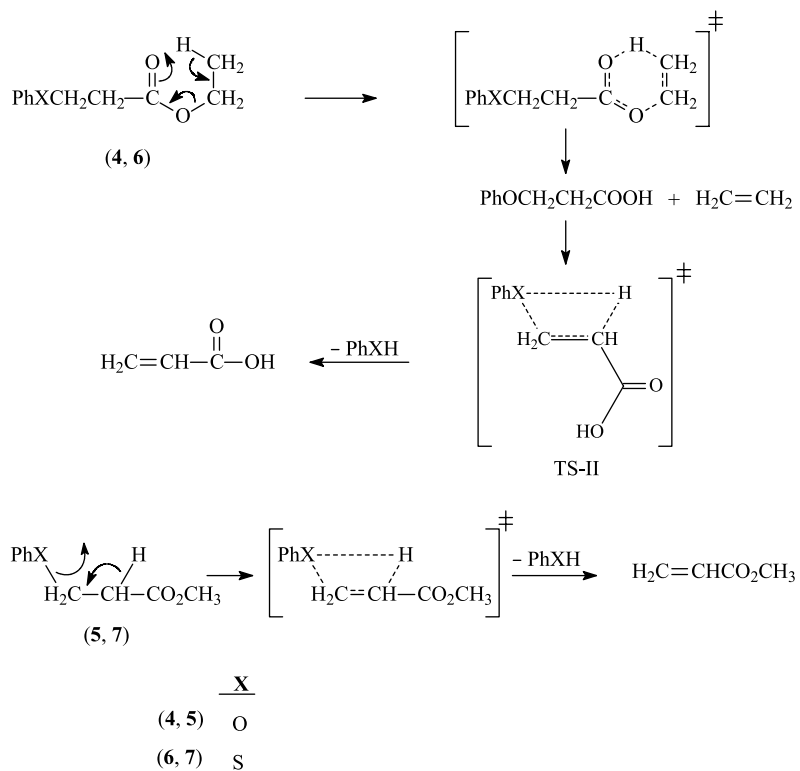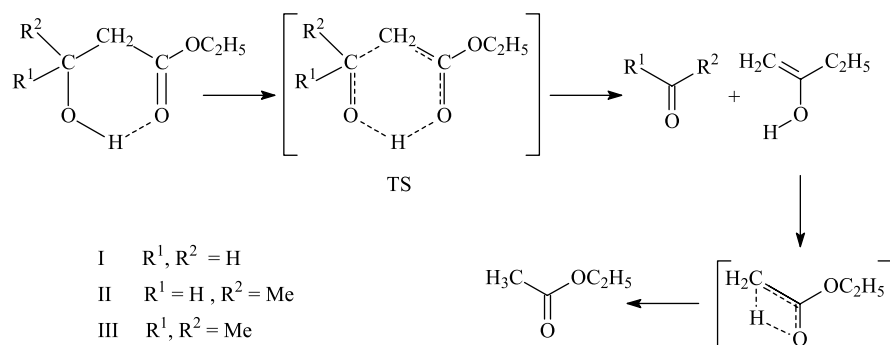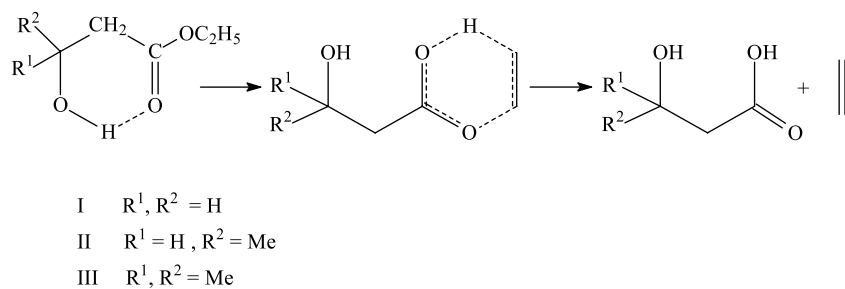
Figure 3. Theoretical ab initio calculations of TS of alternative thermolysis pathways.

Scheme 3. Alternative gas-phase elimination pathway of ethyl and methyl 3-phenoxy- (**4**, **5**) and ethyl and methyl 3-(phenylthio)propanoate (**6**, **7**).

Scheme 4. Mechanism of decomposition of ethyl β-hydroxycarboxylates.[3]

Scheme 5. Side-reaction of decomposition of ethyl β-hydroxycarboxylate.
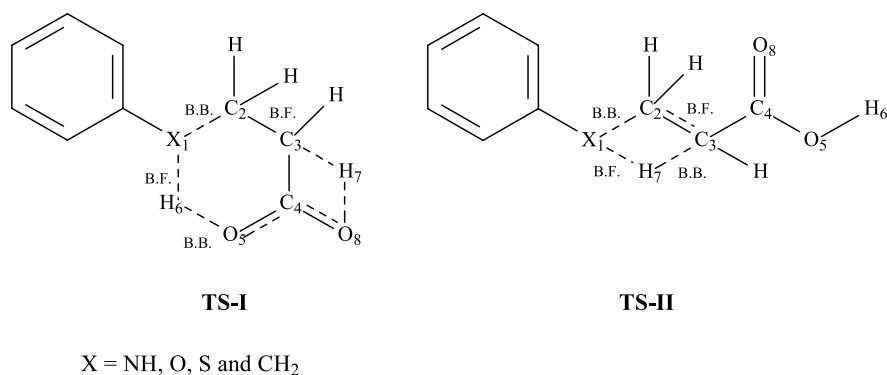
Figure 4. Schematic representation of the optimized structure of TS-I and TS-II.

Table 2. Main distances (Å), in reactants and transition states of the three reactions calculated at the HF/6-31G* level

Species	Distance (Å)			
	X_1–C_2	C_2–C_3	C_3–H_7	H_7–X_1
A: X=O				
Reactant	1.410	1.512	1.087	2.053
TS-I	1.442	1.500	1.528	3.822
TS-II	1.660	1.453	1.537	1.142
B: X=S				
Reactant	1.825	1.526	1.088	3.697
TS-I	1.851	1.505	1.519	4.251
TS-II	1.872	1.500	1.522	2.673
C: X=CH$_2$				
Reactant	1.535	1.526	1.087	2.787
TS-I	1.535	1.507	1.073	2.788
TS-II	1.537	1.505	1.091	2.561

3.2. Synthesis

3.2.1. 3-Phenoxypropanoic acid (1).
A mixture of 3-phenoxypropionitrile (14.6 g, 0.1 mol) and HCl (20 mL, 6 M) was heated under reflux for 3 h. The reaction mixture was cooled and the precipitate was collected and crystallized from benzene/petroleum ether (40:60) as colourless crystals: 13.6 g (85%), mp 95–96 °C (lit.[8] mp 95–96 °C). MS: $m/z=166$ (M$^+$); IR (KBr): 1695 cm^{-1} (CO); ^{1}H NMR (CDCl$_3$): δ 2.88 (t, $J=6.2$ Hz, 2H, CH_2CO), 4.28 (t, $J=6.2$ Hz, 2H, OCH_2), 6.98 (m, 3H, ArH), 7.31 (t, $J=7.8$ Hz, 2H, ArH); ^{13}C NMR (CDCl$_3$): δ 34.9, 63.5, 115.2, 121.7, 130.1, 158.9, 177.4. Anal. Calcd for C$_9$H$_{10}$O$_3$ (166.18): C, 65.06; H, 6.02. Found: C, 65.12; H, 6.03.

Table 3. Total energy, zero-point vibrational energy (ZPE), and thermal correction to enthalpy and entropy, evaluated at HF/6-31G*, for the reactants, transition states and products

Species	Total energy (Hartrees)	ZPE (kcal mol^{-1})	Enthalpy (kcal mol^{-1})	Entropy (cal mol^{-1} K^{-1})
A: X=O				
Reactant	−571.238336	119.638	125.99	103.074
TS-AI	−571.095924	115.878	122.098	101.65
TS-AII	−571.111045	114.853	121.283	103.345
PhOH	−305.557894	70.511	73.764	73.625
B: X=S				
Reactant	−893.895435	117.337	124.177	109.38
TS-CI	−893.751866	113.514	120.154	105.849
TS-CII	−893.892301	117.235	123.63	105.29
PhSH	−628.210176	67.040	70.76	78.57
C: X=CH$_2$				
Reactant	−535.526826	135.393	142.099	106.723
TS-BI	−535.236821	132.783	139.541	106.332
TS-BII	−535.422609	135.448	141.62	102.3
PhCH$_3$	−269.740079	85.944	89.63	79.21
H$_2$C=CHCOOH	−265.653665	45.866	48.866	70.635

superconducting spectrometer, and FT-IR measurements were from a Perkin Elmer 2000 FT-IR system. Mass spectrometric analysis was carried out on a VG-Autospec-Q high performance tri-sector GC/MS/MS, and the instrument for HPLC was an Agilent 1100 series LC/MSD with an API-ES/APCI ionization mode.

4-Phenylbutanoic acid (**3**) is a commercial sample obtained from Merck.

3.2.2. 3-(Phenylthio)propanoic acid (2).
A mixture of ethyl 3-(phenylthio)propanoate (10.5 g, 0.05 mol) and hydrochloric acid (20 mL, 6 M) was heated under reflux for 4 h with vigorous stirring. The reaction mixture was cooled and the precipitate was collected and crystallized from hexane to give white crystals: 7.5 g (82%), mp 59–60 °C (lit.[9] mp 58.5–59.5 °C). MS: $m/z=182$ (M$^+$); IR (KBr): 1695 cm^{-1} (CO); ^{1}H NMR (CDCl$_3$): δ 2.70 (t, $J=7.3$ Hz, 2H, CH_2CO), 3.18 (t, $J=7.3$ Hz, 2H, SCH_2),

7.2–7.4 (m, 5H, ArH), 12.19 (s, 1H, OH); ^{13}C NMR (CDCl$_3$): δ 29.4, 34.7, 127.4, 129.7, 130.9, 135.4, 178.1. Anal. Calcd for C$_9$H$_{10}$SO$_2$ (182.24): C, 59.34; H, 5.49; S, 17.58. Found: C, 59.85; H, 5.58; S, 17.37.

3.2.3. Ethyl 3-phenoxypropanoate (4).

3-Phenoxypropanoic acid (1.66 g, 0.01 mol) was dissolved in 17 mL of absolute ethanol saturated with dry hydrogen chloride. The solution was heated under reflux for 1 h. Normal work up resulted in a colourless oil (lit.[10] bp 170 °C, 40 Torr), yield is 1.74 g (90%). MS: m/z = 194 (M$^+$); ^{1}H NMR (CDCl$_3$): δ 1.30 (t, J = 7.1 Hz, 3H, CH$_2$*CH$_3$*), 2.82 (q, J = 7.1 Hz, 2H, CH$_2$*CH$_2$*CO), 4.22 (q, J = 7.1 Hz, 2H, O*CH$_2$*CH$_3$), 4.26 (q, J = 7.1 Hz, 2H, O*CH$_2$*CH$_2$), 6.95–7.00 (m, 3H, ArH), 7.30–7.32 (m, 2H, ArH); ^{13}C NMR (CDCl$_3$): δ 14.79, 35.25, 61.34, 63.96, 115.24, 121.58, 130.04, 159.09, 171.69. Anal. Calcd for C$_{11}$H$_{14}$O$_3$ (194.23): C, 68.04; H, 7.20. Found; C, 68.10; H, 7.09.

3.2.4. Methyl 3-phenoxypropanoate (5).

3-Phenoxypropanoic acid (1.66 g, 0.01 mol) was dissolved in 15 mL dry methanol saturated with dry hydrogen chloride. The mixture was heated under reflux for 1 h. Normal work up resulted in colourless oil (lit.[11] bp 85 °C, 0.4 Torr), yield is 1.5 g (90%). MS: m/z = 180 (M$^+$·); ^{1}H NMR (CDCl$_3$): δ 2.83 (t, J = 6.4 Hz, 2H, CH$_2$), 3.75 (s, 3H, CH$_3$), 4.27 (t, J = 6.4 Hz, 2H, CH$_2$), 6.92 (d, J = 8.2 Hz, 2H, ArH), 6.98 (t, J = 7.8 Hz, 1H, ArH), 7.30 (t, J = 7.8 Hz, 2H, ArH). Anal. Calcd for C$_{10}$H$_{12}$O$_3$ (180.20): C, 66.65; H, 6.71. Found; C, 66.55; H, 6.63.

3.2.5. Ethyl 3-(phenylthio)propanoate (6).

A mixture of thiophenol (11.2 g, 0.1 mol) and THF (25 mL) and triethyl amine (9 g, 0.1 mol) was cooled at 0 °C, and then ethyl acrylate (10 g, 0.1 mol) was added to the mixture. The mixture was stirred and kept on ice for 2 h and then over night at room temperature. The product was extracted with ether (50 mL), washed with aqueous sodium hydroxide (10 mL, 1 M), dried over sodium sulfate and filtered. After removal of the solvent, the product was subjected to vacuum distillation and a residue was obtained as yellow oil (15 g, 71%), (lit.[12] bp 116–117 °C, 3 Torr). MS: m/z = 210 (M$^+$); IR (KBr): 1734 cm^{-1} (CO); ^{1}H NMR (CDCl$_3$): δ 1.27 (t, J = 7.1 Hz, 3H, CH$_3$), 2.63 (t, J = 7.4 Hz, 2H, CH$_2$), 3.18 (t, J = 7.4 Hz, 2H, CH$_2$), 4.15 (q, J = 7.2 Hz, 2H, CH$_2$), 7.22 (t, J = 6.8 Hz, 1H, ArH), 7.28 (t, J = 7.2 Hz, 2H, ArH), 7.38 (d, J = 7.6 Hz, 2H, ArH); ^{13}C NMR (CDCl$_3$): δ 14.8, 29.6, 35.0, 61.3, 127.1, 129.6, 130.7, 135.8, 172.3. Anal. Calcd for C$_{11}$H$_{14}$O$_2$S (210.29): C, 62.85; H, 6.66; S, 15.23. Found: C, 63.11; H, 6.86; S, 15.38.

3.2.6. Methyl 3-(phenylthio)propanoate (7).

Methyl acrylate (20 g) was added to 17 mL thiophenol containing 0.1 g of concentrated HCl. The mixture was kept cold in an ice bath for 16 h. The product was extracted with ether (50 mL), washed with aqueous sodium hydroxide (10 mL, 1 M), dried over anhydrous sodium sulfate and filtered. After removal of the solvent, the product was distilled under vacuum and the residue obtained was yellow oil (16 g, 60%), (lit.[13] bp 113–116 °C, 2 Torr). MS: m/z = 196 (M$^+$); ^{1}H NMR (CDCl$_3$): δ 2.61 (t, J = 7.4 Hz, 2H, CH$_2$), 3.15 (t, J = 7.4 Hz, 2H, CH$_2$), 3.62 (s, 3H, CH$_3$), 7.18 (t, J = 7.2 Hz, 1H, ArH), 7.27 (t, J = 7.4 Hz, 2H, ArH), 7.34 (d, J = 7.4 Hz, 2H, ArH). Anal. Calcd for C$_{10}$H$_{12}$O$_2$S (196.26): C, 61.20; H, 6.16; S, 16.34. Found: C, 61.12; H, 6.10; S, 16.30.

3.2.7. 3-Phenoxypropionitrile (8).

A mixture of phenol (0.25 mol), acrylonitrile (2–4 mol) and triton B (dimethyl benzyl acetylammonium hydroxide) (2–5 mL) was heated under reflux for 20 h. The reaction mixture was diluted with two volumes of solvent (ether or CHCl$_3$) filtered and washed successively with 5% sodium hydroxide, dilute hydrochloric acid followed by water. The solvent was evaporated and the residue was recrystallized from benzene/petroleum ether (40:60) to yield 3-phenoxypropionitrile (70%), mp 59–60 °C (lit.[14] mp 59–60 °C). MS: m/z = 147 (M$^+$); ^{1}H NMR (CDCl$_3$): δ 2.85 (t, J = 6.2 Hz, 2H, CH$_2$), 4.22 (t, J = 6.2 Hz, 2H, CH$_2$), 6.93 (d, J = 7.6 Hz, 2H, ArH), 7.03 (t, J = 7 Hz, 1H, ArH), 7.28–7.35 (m, 2H, ArH). Anal. Calcd for C$_9$H$_9$NO (147.18): C, 73.45; H, 6.16; N, 9.52. Found: C, 73.00; H, 5.92; N, 9.57.

3.3. Product analysis

Both kinetic (Section 3.4 below) and reaction product analyses were conducted using a Chemical Data System (CDS) custom-made pyrolyzer comprising an insulated aluminium alloy block fitted with a platinum resistance thermocouple connected to a Comark microprocessor thermometer for reactor temperature read-out. The temperature of the reactor is controlled by means of a Eurotherm 093 precision temperature regulator.

Each of the substrates (0.2 g) was introduced in the reaction tube, which is cooled in liquid nitrogen, sealed under vacuum and placed in the pyrolyzer for 900 s at a temperature comparable with that used to achieve complete pyrolysis in the kinetic studies. The contents of the tube were then analysed by NMR and LC/MS, and quantitative estimates were obtained by HPLC. A sample of known mass was subjected to complete pyrolysis. The pyrolysate was dissolved in a known volume of solvent and then injected in the HPLC chromatograph. The percentage yield of each product was estimated by comparing the area under the peak of the product with that of an authentic sample of known concentration. The spectral data of the pyrolysates were compared with reference spectra.

3.4. Kinetic runs and data analysis

A stock solution (7 mL) was prepared by dissolving 6–10 mg of the substrate in acetonitrile as solvent to give a concentration of 1000–2000 ppm. An internal standard was then added, the amount of which was adjusted to give the desired peak area ratio of substrate to standard (2.5:1). The solvent and the internal standard are selected because both are stable under the conditions of pyrolysis, and because they do not react with either substrate or product. The internal standard used in this study is chlorobenzene, 1,3-dichlorobenzene or 1,2,4-trichlorobenzene. Each solution was filtered to ensure that a homogeneous solution is obtained. The weight ratio of the substrate with respect to the internal standard was calculated from the ratio of the substrate peak area to the peak area of the internal standard. The kinetic rate was obtained by tracing the rate of disappearance of the substrate with respect to the internal

standard as follows: An aliquot part (0.2 mL) of each solution containing the substrate and the internal standard is pipetted into the reaction tube, which is then placed in the pyrolyzer for 6 min under non-thermal conditions. A sample is then analyzed using a Waters HPLC probe (pump model 515, UV detector model 2487), or a Metrohm HPLC (pump model 7091C, and SPD 10 AV Shimadzo UV detector) and UV detector at wavelength of 256 nm, and the standardization value (A_0) was then calculated. Several HPLC measurements were obtained with an accuracy of $\geq 2\%$. HPLC columns used for the analysis were Supelco (25 cm length, 4.6 mm ID) ABZ^+, LC-8 and LC-18. The temperature of the pyrolysis (aluminium) block is then raised and held for ca. 900 s to allow approximately 10% pyrolysis to take place at this temperature. This procedure is repeated after each 10–15 °C rise in the temperature of the pyrolyzer until $\geq 90\%$ pyrolysis takes place. The relative ratios of the integration values of the sample and the internal standard (A) at the pyrolysis temperature are then calculated. A minimum of three kinetic runs were carried out at each reaction temperature, following every 10–15 °C rise in the temperature of the pyrolyzer, in order to ensure reproducible values of (A). Treatment of the kinetic data has been detailed elsewhere.[1,15–16]

Acknowledgements

References and notes

1. Al-Awadi, N.; Kaul, K.; El-Dusouqui, O. M. E. *J. Phys. Org. Chem.* **2000**, *13*, 499–504.
2. Al-Awadi, S. A.; Abdallah, M. R.; Hasan, M. A.; Al-Awadi, N. A. *Tetrahedron* **2004**, *60*, 3045–3049.
3. Al-Juwaiser, I. A.; Al-Awadi, N. A.; El-Dusouqui, O. M. E. *Can. J. Chem.* **2002**, *80*, 499–503.
4. Rotinov, A.; Chuchani, G.; Machado, R. A.; Rivas, C.; Quijano, J.; Yepes, M. S.; Restrepo, I. *Int. J. Chem. Kinet.* **1992**, *24*, 909–915.
5. Natrio, R.; Quijano, J.; Quijano, J. C.; Gutierrez, L. P.; Suarez, W. A.; Chamorro, E. *J. Phys. Chem. A* **2002**, *106*, 4377–4383.
6. *Titan, Tutorial and User's Guide*; Wavefunction, Inc., 18401 Von Karman Avenue: U.S.A., 1999.
7. Scott, A.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502–16513.
8. Lai, S. M. F.; Orchison, J. J. A.; Whiting, D. A. *Tetrahedron* **1989**, *45*, 5895–5906.
9. Ahn, Y.; Cohen, T. *J. Org. Chem.* **1994**, *59*, 3142–3150.
10. Powell, S. G. *J. Am. Chem. Soc.* **1923**, *45*, 2708–2711.
11. Rehberg, C. E.; Dixon, M. B. *J. Am. Chem. Soc.* **1950**, *72*, 2205–2206.
12. Davis, F. A.; Friedman, A. J.; Nadir, U. K. *J. Am. Chem. Soc.* **1978**, *100*, 2844–2852.
13. Hurd, C. D.; Gershbein, L. *J. Am. Chem. Soc.* **1947**, *69*, 2328–2335.
14. Bachmann, G. B.; Levine, H. A. *J. Am. Chem. Soc.* **1948**, *70*, 599–601.
15. Al-Awadi, N. A.; Elnagdi, M. H.; Kaul, K.; Ilingovan, S.; El-Dusouqui, O. M. E. *J. Phys. Org. Chem.* **1999**, *12*, 654–656.
16. Al-Awadi, N. A.; El-Dusouqui, O. M. E.; Kaul, K.; Dib, H. H. *Int. J. Chem. Kinet.* **2000**, *32*, 403–407.