# The Gas-Phase Elimination Kinetics of Ethyl 2-Furoate and Ethyl 2-Thiophenecarboxylate

LILIANY ESPITIA,[1] RUBY MENESES,[1] ROSA M. DOMINGUEZ,[2] MARIA TOSTA,[2]
ARMANDO HERIZE,[2] JESUS LEZAMA,[2] JENNIFER LAFONT,[1] GABRIEL CHUCHANI[2]

[1] *Departamento de Química, Universidad de Cordoba, Montería, Colombia*
[2] *Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 21827, Caracas 1020-A, Venezuela*

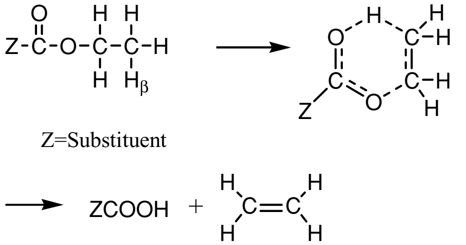
*Received 25 July 2007; revised 11 January 2008, 22 February 2008, 16 June 2008, 25 August 2008; accepted 26 August 2008*

*DOI 10.1002/kin.20382*

ABSTRACT: The gas-phase elimination kinetics of ethyl 2-furoate and 2-ethyl 2-thiophenecarboxylate was carried out in a static reaction system over the temperature range of 623.15–683.15 K (350–410°C) and pressure range of 30–113 Torr. The reactions proved to be homogeneous, unimolecular, and obey a first-order rate law. The rate coefficients are expressed by the following Arrhenius equations: ethyl 2-furoate, $\log k_1$ ($s^{-1}$) = (11.51 ± 0.17)–(185.6 ± 2.2) kJ $mol^{-1}$ (2.303 RT)$^{-1}$; ethyl 2-thiophenecarboxylate, $\log k_1$ ($s^{-1}$) = (11.59 ± 0.19)–(183.8 ± 2.4) kJ $mol^{-1}$ (2.303 RT)$^{-1}$. The elimination products are ethylene and the corresponding heteroaromatic 2-carboxylic acid. However, as the reaction temperature increases, the intermediate heteroaromatic carboxylic acid products slowly decarboxylate to give the corresponding heteroaromatic furan and thiophene, respectively. The mechanisms of these reactions are suggested and described. © 2008 Wiley Periodicals, Inc. Int J Chem Kinet 41: 145–152, 2009

## INTRODUCTION

The gas-phase pyrolysis and elimination of esters of carboxylic acids have extensively been investigated. The commonly accepted mechanism consists of a concerted six-membered cyclic transition state producing the corresponding olefin and carboxylic acid [1,2], as described in reaction (1). The presence of a $C_\beta$–H bond at the alkyl side of the ester is required for molecular elimination.



(1)

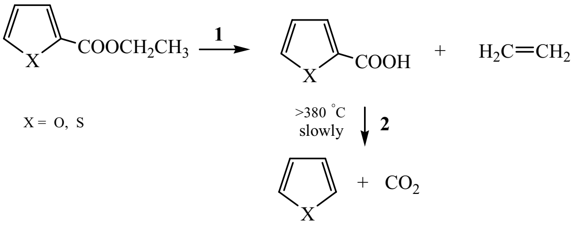
Earlier work [3] from our laboratory explored a structure reactivity correlation of ethyl esters with a carbon atom attached at the acid side of ethyl $\alpha$-substituted carboxylic acids ($ZCOOCH_2CH_3$, Z = substituent) [3]. The correlation of $\log k_z/k_0$ of $ZCOOCH_2CH_3$ (where $k_z$ is the rate coefficient of

---

*Correspondence to:* Gabriel Chuchani; e-mail: chuchani@ivic.ve.

the substrate with substituent Z and $k_0$ is the rate of the substrate of reference with substituent $Z = CH_3$) versus Taft original $\sigma^*$ (polar substituent constant) values yielded a slope of $\rho^*$ (reaction constant) $= 0.315$; $r$ (correlation coefficient) $= 0.976$, at 673.15 K (400°C) [4]. This study supported the general concept that electron-withdrawing groups at the acyl or acid side of the ester enhance the elimination rate, while electron-releasing groups tend to decrease it. The Taft–Topsom method [5] of $\log k/k_H = \sigma_\alpha \rho_\alpha + \sigma_F \rho_F + \sigma_R \rho_R$ takes into consideration the steric ($\sigma_\alpha$), electronic ($\sigma_F$), and resonance ($\sigma_R$) contributions in the quantitative study of structural and substituent effects on chemical reactivity. Using this treatment, a correlation of $\log k/k_0 = (2.09 \pm 0.11)\sigma_F$ at 673.15 K (400°C), $r = 0.979$, $SD = 0.078$, was obtained. The polarizability effect ($\sigma_\alpha$) and the resonance interactions ($\sigma_R$) were found to be minimal and may be neglected, while the field inductive effect ($\sigma_F$) appears to be the important factor influencing the elimination rates of these esters.

Although the elimination kinetics of a large number of $ZCOOCH_2CH_3$ species have been examined [3], the effect of a heteroaromatic substituent at the acid side of the ethyl ester, such as 2-furyl and 2-thienyl groups, has not been studied. Therefore, the present work aimed at examining the extent to which these heteroaromatic groups may affect the elimination kinetics of ethyl 2-furoate and ethyl 2-thiophenecarboxylate [reaction (2), step 1]. An additional question is whether the initial carboxylic acid intermediate will decarboxylate under the conditions of the reaction, due to assistance of the nucleophilicity or basicity of the heteroatom at C-2 for the abstraction of the H of the COOH group. Decarboxylation could also be promoted by double bond character or resonance interaction with the heteroaromatic nuclei [reaction (2), step 2].



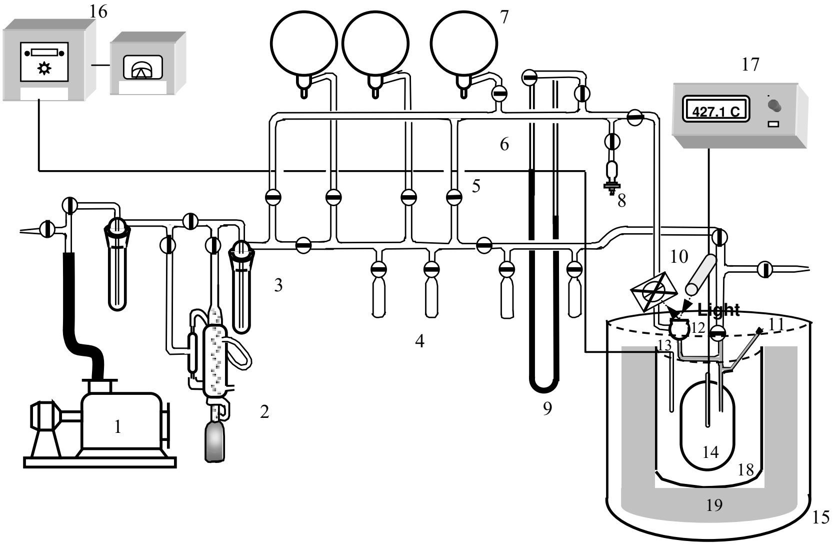
(2)

## EXPERIMENTAL

The substrates ethyl 2-furoate (Aldrich) and ethyl 2-thiophenecarboxylate (Aldrich) of 99.0% purity (GC-MS: Saturn 2000 Varian, with a DB-5MS capillary column 30 m × 0.53 mm. i.d., 0.53 µm film thickness) were used. The quantitative chromatographic analysis of ethylene product was determined by using a Gas Chromatograph Varian 3600× with a capillary column GS-Q 30 mm × 0.53 mm. The thermal conductivity detector was used to identify $CO_2$ gas. Identification of the products 2-furoic acid and 2-thiophene carboxylic acid were made by comparison with authentic samples (Aldrich) and by GC-MS analysis (Saturn 2000, Varian with a DB-5MS capillary column 30 m × 0.25 mm. i.d., 0.25 µm). In some experiments propene was used as an inhibitor to suppress free radical reactions. The reaction vessel was seasoned by the products of decomposition of allyl bromide to prevent surface effects on the decomposition of the substrate.

### Kinetics

The kinetic experiments were carried out in a static reaction system as reported before [6–8] and depicted in Fig. 1. The reaction vessel (14) of approximately 250 mL is enclosed in a thermostatic furnace (15), which is a cylindrical aluminum block 20.5 cm in diameter and 36 cm high with a central circular well 10 cm in diameter. A Nichrome heating coil of resistance 90 ohms was wound on it after insulation with asbestos (19). This furnace (15) is united to a glass diaphragm (12) and to a mercury manometer (9). The substrate for analysis is injected to the reaction vessel (14) with a syringe Perfektum of 1.0 mL through a capillary silicone rubber septum (11). The increase of pressure in the system due to the thermal decomposition of the substrate causes a small deformation of the glass diaphragm (12), which is then compensated with the introduction of air by using a valve (8). The diaphragm (12) lighted by a lamp (10) produces an indicating line that moves from the reference point when pressure increases. The variation of pressure increase seen in the mercury manometer (9) with time is measured with a chronometer. The initial pressure of the reaction at time zero is estimated by extrapolation in a graphic of pressure versus time. The temperature was maintained within ±273.35 K (0.2°C) through control with a Shinko DIC-PS 23TR resistance thermometer (16). The temperatures were determined by using a calibrated iron–constantan thermocouple (13) and measured in a Digital Multimeter Omega 3465B (17). The vacuum of this static system is accomplished by a rotatory vacuum pump (1) Hitachi LTD 3VP-C2 and can reach approximately $5.0 \times 10^{-4}$ Torr. The vacuum may be improved when using the Mercury diffusion pump (2) Edwards EMG 150 W. The pyrolysis products were trapped in the reactant storage reservoir (4). The amount of substrate used for each reaction was ~0.05–0.1 mL.



1. Vacuum pump
2. Mercury diffusion pump
3. Liquid nitrogen trap
4. Reactant storage reservoir
5. Bridge valve
6. Vacuum valve
7. Glass flask
8. Compensator valve
9. Manometer
10. Lamp
11. Capillary septum
12. Diaphragm
13. Thermocouple
14. Reaction vessel
15. Thermostatic furnace
16. Temperature control
17. Digital multimeter
18. Aluminum block
19. Asbestos logging

**Figure 1** Static reaction system.

## RESULTS AND DISCUSSION

The theoretical stoichiometry of reaction (2), in a static system, with vessels seasoned with allyl bromide, requires for step 1 a theoretical stoichiometry $P_f/P_0 = 2.0$ where $P_f$ and $P_0$ are the final and initial pressure, respectively. However, the theoretical stoichiometry of steps 1 and 2 demands $P_f/P_0 = 3.0$. The average experimental $P_f/P_0$ for step 1 up to 653.15 K (380°C) and at 10 half-lives for ethyl furoate and ethyl 2-thiophenecarboxylate is approximately 2.0. Yet, as the temperature increases above 653.15 K (380°C), the experimental $P_f/P_0$ approaches 3.0 (Table I). The increase in $P_f/P_0$ at higher temperatures is presumably due to further decomposition of the carboxylic acid product into the corresponding heteroaromatic compound and $CO_2$ gas, step 2. The verification of the stoichiometry of reaction (2), up to 60% decomposition of the substrate into 2-furoic acid and ethylene, was made by comparing the pressure measurements with the quantitative GLC analysis of ethylene formation (Table II).

The homogeneity of these reactions was examined in a vessel with a surface-to-volume ratio 6.0 times greater than the standard reactor (Table III). The reaction rates in packed and unpacked clean Pyrex vessels were significantly different. However, when the packed and unpacked vessels were seasoned with allyl bromide, no marked effect on the rate coefficients of these esters was observed. The effect of different

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

| Temperature (K) | $P_0$ (Torr) | $P_f$ (Torr) | $P_f/P_0$ |
|---|---|---|---|
| | Ethyl furoate | | |
| 643 | 102 | 231 | 2.3 |
| 653 | 66 | 152 | 2.3 |
| 663 | 123 | 312 | 2.5 |
| 673 | 117 | 318 | 2.7 |
| 683 | 109 | 306 | 2.8 |
| | Ethyl 2-thiophene carboxylate | | |
| 623 | 46 | 76 | 1.7 |
| 633.4 | 76 | 151 | 2.0 |
| 643.9 | 53 | 111 | 2.1 |
| 653.4 | 69 | 152 | 2.2 |
| 663.5 | 46 | 134 | 2.9 |
| 673.4 | 61 | 184 | 3.0 |

**Table II** Stoichiometry of the Reaction

| Substrate | Temperature (K) | Parameter | Value | | | | |
|---|---|---|---|---|---|---|---|
| Ethyl 2-furoate | 653 | Time (min) | 8 | 13 | 24 | 33 | |
| | | Reaction (%) (pressure) | 20.8 | 27.4 | 51.6 | 65.0 | |
| | | Ethylene (%) (GLC) | 21.2 | 27.2 | 50.3 | 65.7 | |
| Ethyl 2-thiophene carboxylate | 643 | Time (min) | 8 | 12 | 16 | 20 | 38 |
| | | Reaction (%) (pressure) | 17.6 | 25.3 | 31.0 | 40.0 | 60.4 |
| | | Ethylene (%) (GLC) | 18.9 | 25.0 | 32.3 | 43.0 | 60.0 |

proportions of propylene inhibitor had no effect on the rates (Table IV). No induction period was observed, suggesting the absence of significant free radical processes. Rates were reproducible with a relative standard deviation of not greater that 5% at a given temperature.

**Table III** Homogeneity of the Elimination Reactions

| Substrate | $S/V$ (cm$^{-1}$)[a] | $10^4k_1$ (s$^{-1}$)[b] | $10^4k_1$ (s$^{-1}$)[c] |
|---|---|---|---|
| Ethyl 2-furoate | 1 | 10.29 | 7.86 |
| at 663 K | 6 | 10.35 | 7.72 |
| Ethyl 2-thiophene | 1 | 9.23 | 4.33 |
| carboxylate | 6 | 9.38 | 4.10 |
| at 643 K | | | |

[a] $S$ = surface area, $V$ = volume.

[b] Clean vessel.

[c] Vessel seasoned with allyl bromide.

**Table IV** Effect of Free Radical Inhibitor Propylene on Rates

| Substrate | Temperature (K) | $P_s$ (Torr) | $P_i$ (Torr) | $P_i/P_s$ | $10^4$ $k_1$ (s$^{-1}$) |
|---|---|---|---|---|---|
| Ethyl 2-furoate | 653 | 75 | – | – | 4.41 |
| | | 113 | 57 | 0.5 | 4.31 |
| | | 95 | 141 | 1.5 | 4.41 |
| | | 77 | 169 | 2.3 | 4.42 |
| | | 66 | 187 | 2.8 | 4.50 |
| Ethyl 2-thiophene carboxylate | 643 | 30.5 | – | – | 4.47 |
| | | 56.5 | 40 | 0.7 | 4.36 |
| | | 59.5 | 60 | 1.0 | 4.38 |
| | | 72.0 | 95 | 1.3 | 4.26 |
| | | 83.0 | 184 | 2.2 | 4.25 |

$P_s$ = pressure substrate. $P_i$ = pressure inhibitor.

To obtain rate coefficients for step 1 of reaction (2), by GC analyses of ethylene, the expression of $k_1 = -(2.303/t)$ log $[(P_0 - P_{\text{ethylene}})/P_0)]$ was used and showed no significant variation with change of initial pressure (Table V). The plots log $(P_0 - P_{\text{ethylene}})/P_0$ against time $t$ are linear up to 60%–65% reaction (Figs. 2 and 3), implying a first-order rate reactions. The temperature dependence of the rate coefficients and the corresponding Arrhenius equation shown in Table VI (Figs. 4 and 5), where 90% confidence limits from a linear least-squares procedure are given.

The kinetic and thermodynamic parameters of the decomposition of furoic acid to produce furan, step 2, have recently been reported [9]. The working temperature between 688–728 K (415–455°C) and pressure range 20–50 Torr led to the following Arrhenius expression: log $k_1$ (s$^{-1}$) = (11.59 ± 0.19)–(183.8 ± 2.4) kJ mol$^{-1}$(2.303 $RT$)$^{-1}$. In the case of ethyl 2-thiophenecarboxylate, the elimination of the product 2-thiophene carboxylic acid slowly decarboxylate above 653 to give thiophene and $CO_2$ gas (step 2). To obtain the kinetic and thermodynamic parameters of step 2 from 2-thiophene carboxylic acid decomposition, several attempts to pyrolyze an authentic sample of this acid (Aldrich, 99% purity) by pressure increase and by GC analyses of the product thiophene were unreliable and irreproducible.

The kinetic and thermodynamic parameters of the 2-carboethoxy heteroaromatic substrates of step 1 are shown in Table VII. The observed log of $A$ values of 11.51 and 11.59 are reasonable for six-membered cyclic transition states [reaction (3)].

**Table V** Invariability of the Rate Coefficients with Initial Pressure

| Substrate | Temp. (K) | Parameter | Value | | | | |
|---|---|---|---|---|---|---|---|
| Ethyl 2-furoate | 653 | $P_0$ (Torr) | 66 | 75 | 77 | 95 | 113 |
| | | $10^4$ $k_1$ (s$^{-1}$)[a] | 4.41 | 4.50 | 4.42 | 4.41 | 4.31 |
| Ethyl 2-thiophene carboxylate | 643 | $P_0$ (Torr) | 30.5 | 56.5 | 59.5 | 72 | 83 |
| | | $10^4$ $k_1$ (s$^{-1}$)[a] | 4.47 | 4.36 | 4.38 | 4.26 | 4.25 |

[a] $k$-values from GLC analysis of ethylene.

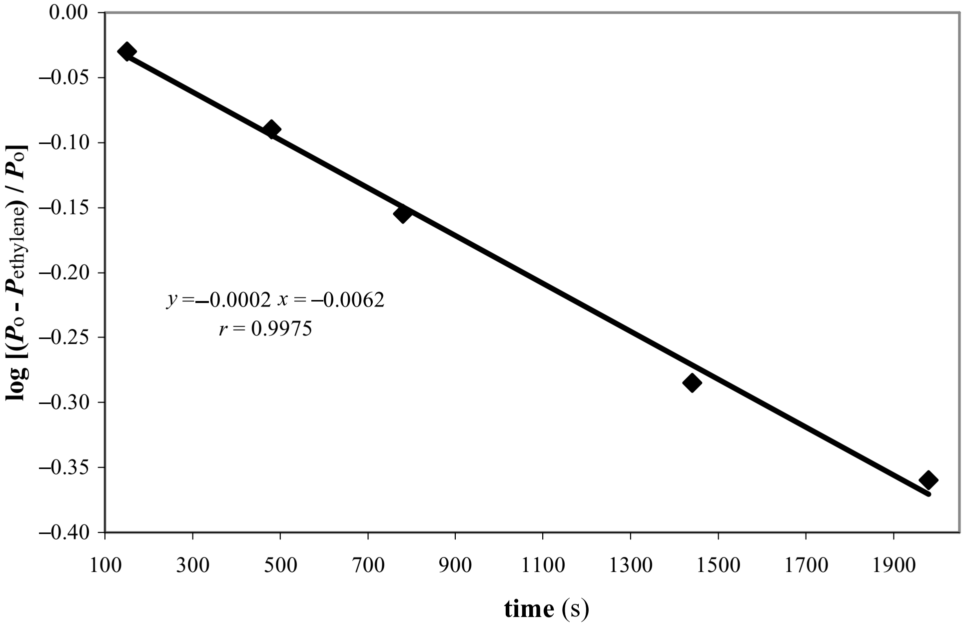


**Figure 2** Plot of log $[(P_0{-}P_{\mathrm{ethylene}})/P_0]$ against time $t$ of the gas-phase elimination of ethyl 2-furoate at 653 K.

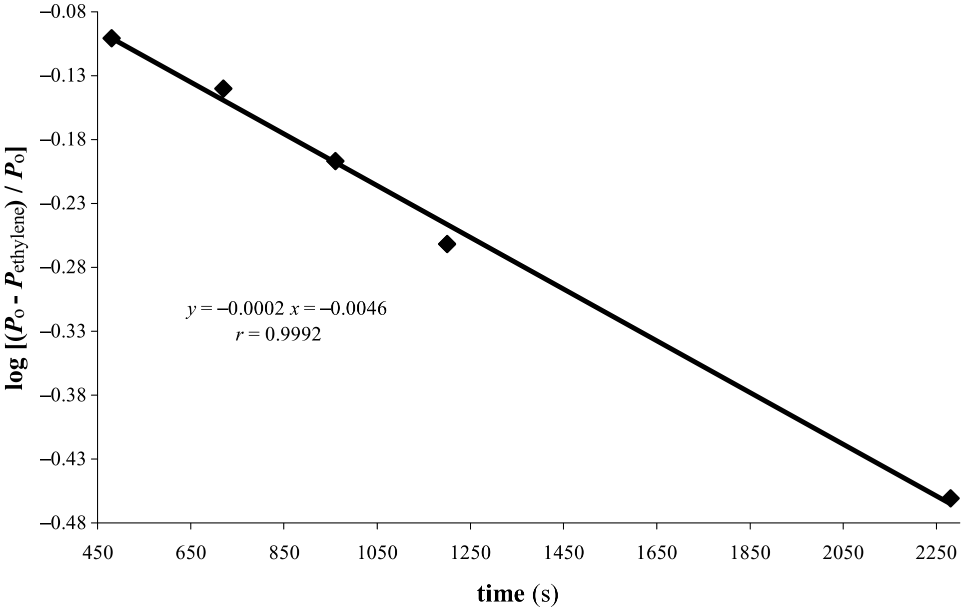


**Figure 3** Plot of log $[(P_0{-}P_{\mathrm{ethylene}})/P_0]$ against time $t$ of the gas-phase elimination of ethyl 2-thiophene carboxylate at 643 K.

**Table VI** The Variation of the Rate Coefficients with Temperatures

| Substrate | Parameter | Value | | | | | |
|---|---|---|---|---|---|---|---|
| Ethyl 2-furoate | Temp. (K) | 633 | 643 | 653 | 663 | 673 | 683 |
| | $10^4\ k_1$ (s$^{-1}$)$^a$ | 1.58 | 2.67 | 4.46 | 7.86 | 12.40 | 20.74 |
| | Rate equation log $k_1$ (s$^{-1}$) = (11.51 ± 0.17)–(185.6 ± 2.2) kJ mol$^{-1}$ (2.303 $RT$)$^{-1}$ | | | | | | |
| Ethyl 2-thiophene carboxylate | Temp. (°C) | 623 | 633.6 | 643.3 | 653.5 | 663.4 | 673.9 |
| | $10^4\ k_1$ (s$^{-1}$)$^a$ | 1.53 | 2.63 | 4.47 | 7.49 | 12.69 | 22.20 |
| | Rate equation log $k_1$ (s$^{-1}$) = (11.59 ± 0.19)–(183.8 ± 2.4) kJ mol$^{-1}$ (2.303 $RT$)$^{-1}$ | | | | | | |

[a] $k$ values from GLC analysis of ethylene.

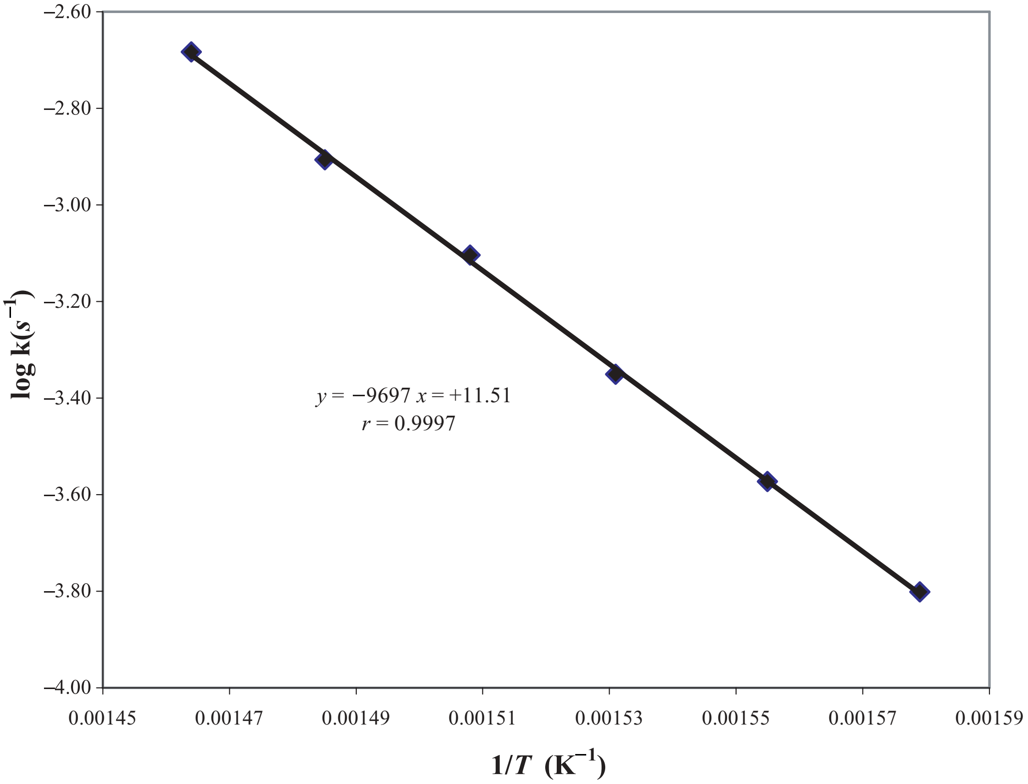


**Figure 4** Arrhenius plot of gas-phase elimination of ethyl 2-furoate.

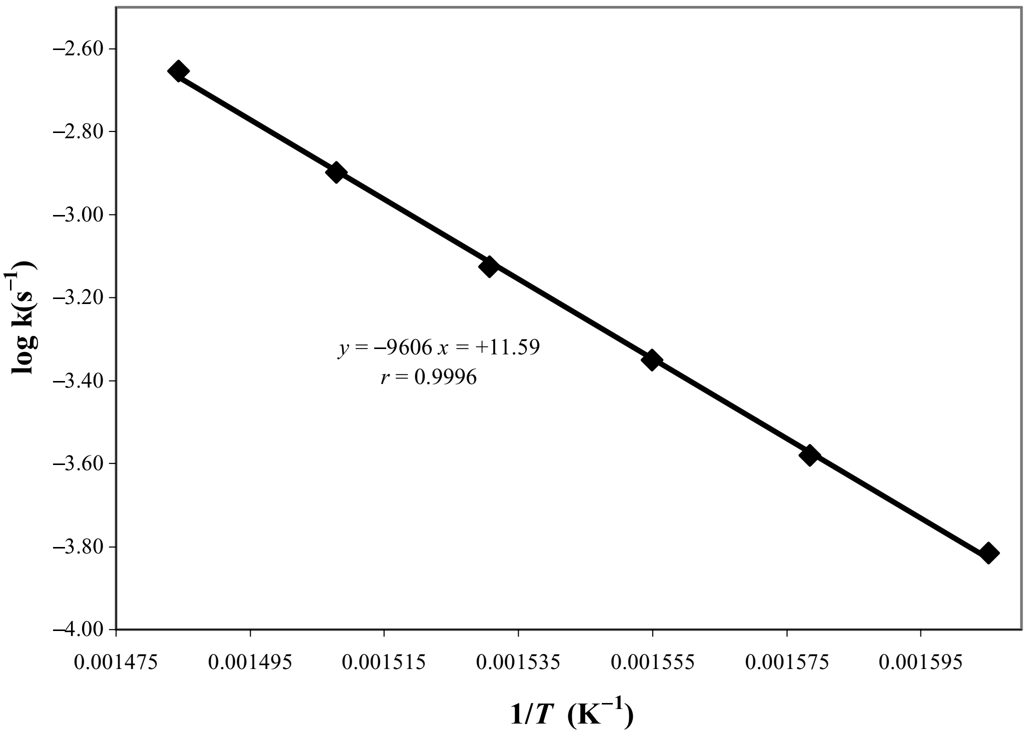
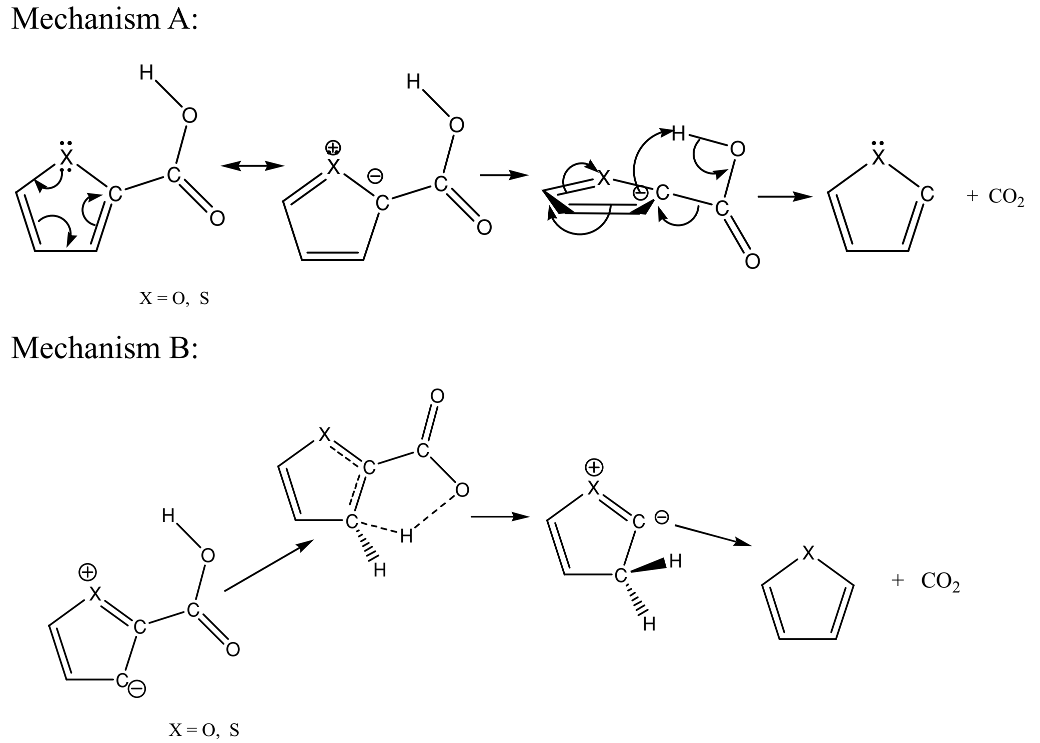


**Figure 5** Arrhenius plot of gas-phase elimination of ethyl 2-thiophene carboxylate.

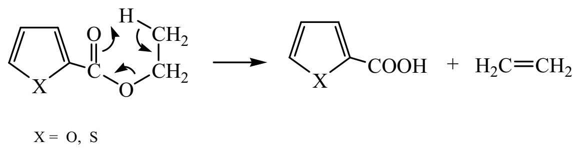
**Table VII** Kinetic and Thermodynamic Parameters at 653 K

| Substrate | $k_1 \times 10^4$ ($s^{-1}$) | $E_a$ (kJ/mol) | log $A$ ($s^{-1}$) | $\Delta S^{\ddagger}$ (J/mol K) | $\Delta H^{\ddagger}$ (kJ/mol) | $\Delta G^{\ddagger}$ (kJ/mol) |
|---|---|---|---|---|---|---|
| Ethyl 2-furoate | 4.57 | 185.6 ± 2.2 | 11.51 ± 0.17 | −39.5 | 180.2 | 205.9 |
| Ethyl 2-thiophenecarboxylate | 7.76 | 183.8 ± 2.4 | 11.59 ± 0.19 | −37.7 | 178.5 | 202.7 |


Mechanism A:

Mechanism B:

**Figure 6** The mechanism of 2-furoic acid decomposition according to kinetic and thermodynamic parameters, together with the theoretical study at the B3LYP/6–31++G**computational level.



X = O, S

(3)

The negative entropy of activation $\Delta S^{\neq}$of these reactions suggests the transition state to be more ordered with respect to the reactant with lost of degree of freedom on rotation and some approximation to planarity. The mechanism for the elimination of step 2 may be explained as recently reported, where the experimental and theoretical studies at the B3LYP/6–31++G** computational level [9] appears to be in better accord to mechanism A (Fig. 6). Attempts to carry out the gas-phase elimination kinetics of 2-thiophene carboxylic acid, X = S, in seasoned reaction vessel and in the presence of a free radical inhibitor, gave unreliable experimental data. This fact appears to suggest a complex reaction of both free radical and molecular mechanisms.

## CONCLUSION

The homogeneous, unimolecular gas-phase elimination of ethyl 2-furoate and ethyl 2-thiophenecarboxylate was found to proceed through a six-membered cyclic transition state type of mechanism to give the corresponding heteroaromatic 2-carboxylic acid and ethylene. Ethyl 2-furoate and ethyl 2-thiophenecarboxylate react 1.3 and 2.3 times faster at 653 K in comparison to the reference compound ethyl acetate [3]. These results confirm the general concept that electron-withdrawing substituents such as furan and thiophene enhance the elimination rate in the gas-phase pyrolysis of ethyl esters of the type $ZCOOCH_2CH_3$

Decarboxylation of the heteroaromatic acid intermediate 2-furoic acid is rather slow at 673 K. The mechanism is thought to be due to resonance of furan as reported [9] (Mechanism A). This mechanism differs from the gas-phase pyrolysis of picolinic acid, another type of heteroaromatic 2-carboxylic acid. Picolinic acid is 2500 times faster in $CO_2$ decomposition than that of ethyl picolinate pyrolysis at 633 K [10]. This significant decarboxylation was explained by the nucleophilic assistance of the nitrogen atom. In the case of 2-thiophene carboxylic acid, the mechanism of $CO_2$ elimination above 663 K may be explained similarly as to that of 2-furoic acid (Mechanism A).

## BIBLIOGRAPHY

1. Taylor, R. In The Chemistry of Functional Group. Supplementary Volume B, Acid Derivatives. Patai, S. (Ed.); Wiley: London, 1979; Ch. 15, pp. 859–914.
2. Holbrook, K. A. In The Chemistry of Acid Derivatives.Volume 2. Vapor and Gas Phase Reaction of Carboxylic Acids and Their Derivatives. Patai, S. (Ed.); Wiley: London, 1992; Ch. 12, pp. 703–746.
3. Chuchani, G.; Mishima, M.; Notario, Aboud, J. L. M. Structural Effects on Gas-Phase Reactivities. Volume 2. Advances in Quantitative Structure-Property Relationships. Charton, M.; Charton, B. I. (Eds.); Jai Press: Stamford, CT, 1999; pp. 35–126.
4. Hansch, C.; Leo, A. J. Substituent Constants for Correlation Analysis in Chemistry and Biology; Wiley: New York, 1979.
5. Hansch, C.; Leo, A.; Taft, R. Chem Rev 1991, 91, 165–195.
6. Maccoll, A. J. Chem Soc 1955, 965–973.
7. Swinbourne, E. S. Aust J Chem 1958, 11, 314–330.
8. Dominguez, R. M.; Herize, A.; Rotinov, A.; Alvarez-Aular, A.; Visbal, G.; Chuchani, G. J. Phys Org Chem 2004, 17, 399–408.
9. Ramirez, B.C.; Dominguez, R.M.; Herize, A.; Tosta, M.; Cordova, T.; Chuchani, G. Int J Chem Kinetic 2007, 39, 298–306.
10. Lafont, J.; Ensuncho, A.; Dominguez, R. M.; Rotinov, A.; Herize, A.; Quijano, J.; Chuchani, G J Phys Org Chem 2003, 16, 84–88.