# Homogeneous, Unimolecular Gas-Phase Elimination Kinetics of Ethyl Esters of Glyoxylic, 2-Oxo-Propanoic, and 3-Methyl-2-Oxo-Butanoic Acids

ANDREINA REYES, ROSA M. DOMINGUEZ, MARIA TOSTA, ARMANDO HERIZE, GABRIEL CHUCHANI

Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela

Received 28 July 2006; revised 9 October 2006, 30 November 2006; accepted 13 December 2006

DOI 10.1002/kin.20240 Published online in Wiley InterScience (www.interscience.wiley.com).

> ABSTRACT: The rates of elimination of several ethyl esters of 2-oxo-carboxylic acid were determined in a seasoned static reaction vessel over the temperature range 350–430°C and pressure range 33–240 Torr. The reactions, in the presence of a free-radical inhibitor, are homogeneous, unimolecular, and follow a first-order rate law. The overall and partial rate coefficients are expressed by the Arrhenius equation.

Ethyl glyoxalate

 $\log k_{1(\text{CO}_2)} (\text{s}^{-1}) = (13.43 \pm 0.25) - (213.1 \pm 3.3) \text{ kJ mol}^{-1} (2.303 \text{ } RT)^{-1}, r = 0.9996$  $\log k_{2(\text{CO})} (\text{s}^{-1}) = (14.06 \pm 0.54) - (232.9 \pm 7.0) \text{ kJ mol}^{-1} (2.303 \text{ } RT)^{-1}, r = 0.9986$  $\log k_{t(\text{overall})} (\text{s}^{-1}) = (13.72 \pm 0.25) - (216.1 \pm 3.3) \text{ kJ mol}^{-1} (2.303 \text{ } RT)^{-1}, r = 0.9997$ Ethyl 2-oxo-propionate $\log k_1 (\text{s}^{-1}) = (13.03 \pm 0.15) - (205.1 \pm 2.0) \text{ kJ mol}^{-1} (2.303 \text{ } RT)^{-1}, r = 0.9998$ 

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





Ethyl 3-methyl-2-oxo-butyrate

 $\log k_1 (s^{-1}) = (12.58 \pm 0.31) - (198.4 \pm 4.1) \text{ kJ mol}^{-1} (2.303 \text{ } RT)^{-1}, r = 0.9994$ 

The mechanisms of these elimination reactions are described in terms of concerted cyclic transition state structures. © 2007 Wiley Periodicals, Inc. Int J Chem Kinet 39: 268–275, 2007

#### INTRODUCTION

The homogeneous unimolecular gas phase elimination of ester of carboxylic acids is known to proceed through a six-membered cyclic transition state type of mechanism to give the corresponding carboxylic acid and the olefin, respectively (reaction (1)) [1,2]. The presence of a  $C_{\beta}$ —H bond at the alkyl side of the ester is necessary for molecular elimination.



Among the organic esters that contribute to the mechanistic consideration described in reaction (1) are those found from the gas-phase elimination of a considerable number of ethyl esters with alkyls attached to the acid side of  $\alpha$ -substituted carboxylic acid [3]. A correlation of these esters log  $k/k_0$  versus Taft original  $\sigma^*$  values yielded  $\rho^* = 0.315$  (r = 0.976, at 400°C) [4]. This result implied the general argument that electron-withdrawing groups at the acyl or acid side of the ester enhance the elimination rate, whereas

electron-releasing groups decrease it. Moreover, using the Taft–Topsom treatment [4], a resonance interaction and polarizability effects were found to be minimal and therefore neglected. However, the field inductive effect  $\sigma_{\rm F}$  appears to be the main factor affecting the elimination rates of this ester: log  $k/k_0 = (2.09 \pm 0.11)\sigma_{\rm F}$  at  $400^{\circ}$ C, r = 0.979, SD = 0.078.

The reported kinetic parameters and the comparative rates of different substituents other than carbon at the acid side of organic ethyl esters [5] give a similar mechanism as described in reaction (1). These organic esters showed a good Taft–Topsom correlation as depicted in Fig. 1.

The negative value of  $\rho_{\alpha} = -0.68$  suggests a modest participation of the steric effect. The greatest absolute value of  $\rho_{F^-} = +2.57$  of the field or electronic effect seems to have the most important influence on the elimination process. The value of  $\rho_R^- = -1.18$  is believed to confirm the interaction of the substituent Z with an incipient negative reaction center and implies a favorable effect for the abstraction of the  $\beta$ -hydrogen of the ethyl ester by the oxygen carbonyl in the transition state.

Substrates with the interposition of a polar group such as the carbonyl between the substituents shown



Figure 1 Taft–Topsom correlation for the pyrolysis of ZCOOCH<sub>2</sub>CH<sub>3</sub> log  $k/k_0 = -(0.68 \pm 0.12)\sigma_{\alpha} + (2.57 \pm 0.12)\sigma_{F} - (1.18 \pm 0.27)\sigma_{R}^{-}(r = 0.984, \text{ sd} = 0.119 \text{ at } 400^{\circ}\text{C}).$ 

Method	E <sub>a</sub> (kJ/mol)	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J/mol K)	$\Delta G^{\ddagger}$ (kJ/mol)	$\frac{\log A}{(s^{-1})}$	$10^4 k_1 \ (s^{-1})$
PM3	174.6	169.8	-16.7	179.4	12.64	5.29
MP2/6-3G*	173.2	168.5	-14.0	176.5	12.78	9.81
Experimental	174.3	169.5	-14.9	178.1	12.73	6.94

 Table I
 Comparative Theoretical and Experimental Activation Parameters at 300°C

in Fig. 1 and the acid side of ethyl ester, that is ethyl ester of 2-oxo-carboxylic acids, are interesting to examine for their elimination kinetics in the gas phase.

Several works related to 2-oxo substrates are found in the papers of Clark [6–8] on the kinetics of decarboxylation of oxalic and oxamic acids in several solvents (reaction (2)).

$$\begin{array}{c} O & O \\ \parallel & \parallel \\ H_2N-C-C-OH & \xrightarrow{Solvent} & O \\ 127-160^{\circ}C & H-C-NH_2 + CO_2 \end{array}$$
Solvent: Aniline  
*o*-Toluidine  
*O*uinoline  
*O*uinoline  
*O*uinoline  
*D*imethylsulfonate  
Triethylphosphate
$$\begin{array}{c} O \\ H-C-NH_2 + CO_2 \end{array}$$
(2)

Later, Lapidus et al. [9] determined the kinetics and stoichiometry of oxalic acid decomposition in the gas phase and the mechanism was described as in reaction (3).

$$HO - C - C - OH \xrightarrow{127 - 157^{\circ}C} H - C - OH + CO_{2}$$

$$HO - C - C - OH \xrightarrow{127 - 157^{\circ}C} H - C - OH + CO_{2}$$

$$HO - C - C - C = O$$

$$HO - C - C - C = O$$

$$HO - C - C - OH + CO_{2}$$

$$HO - C - C - OH + CO_{2}$$

$$HO - C - C - OH + CO_{2}$$

$$HO - C - C - OH + CO_{2}$$

$$HO - C - C - OH + CO_{2}$$

$$HO - C - OH + CO_{2}$$

Taylor carried out the thermal decomposition of pyruvic and benzoylformic acids [10,11]. The mechanism of these reactions was thought to proceed through a four-membered cyclic transition state to give carbon dioxide and the corresponding aldehyde (reaction (4)).

$$\begin{array}{ccc} \text{RCOCOOH} & \longrightarrow & \begin{bmatrix} O & O \\ R & -C & --C \\ & & & | \\ R & --Me, & -C_6H_5 \end{bmatrix} & & \text{RCOH} + CO_2 \\ & & & | \\ H & --O \end{bmatrix}$$

$$(4)$$

A joint theoretical and experimental study on the homogeneous, unimolecular gas-phase elimination kinetics of methyl oxalyl chloride was reported [12]. The reaction was found to proceed in a concerted semipolar mechanism as described in reaction (5). The semiempirical PM3 and MP2/6-31G\* calculations have been found to be in good agreement with experiments (Table I).

Recently, a few ethyl esters of 2-oxo-carboxylic acids with a nitrogen atom attached to the acid side, that is, ethyl oxamate, ethyl N,N-dimethyloxamate, and ethyl oxanilinate [13], were reported.



According to the elimination products of ethyl oxamate (reaction (6)) and ethyl oxanilinate (reaction (7)), decarbonylation was thought to be the first step of decomposition and the corresponding ethyl ester intermediate underwent subsequent parallel elimination (reactions (6) and (7)). The ethyl N,N-dimethyloxamate pyrolysis gives different elimination pathways (reaction (8)). This result was surprising, since decarbonylation was expected to be the first step of the reaction. This fact suggested the need for further work with regard to the influence of the (CH<sub>3</sub>)<sub>2</sub>N group on the ethyl ester of 2-oxo-carboxylic acid in order to explain such difference in the mechanism.

International Journal of Chemical Kinetics DOI 10.1002/kin

With the background described above, the substituents given in Fig. 1 are to be examined in the present work, that is, H, CH<sub>3</sub>, and (CH<sub>3</sub>)<sub>2</sub>CH groups.

#### EXPERIMENTAL

Ethyl glyoxalate in 50% toluene solution (Fluka, St. Louis, MO, USA), ethyl 2-oxo-propanoate (98% purity, Aldrich, St. Louis, MO, USA), and ethyl 3methyl-2-oxo-butyrate (97% purity, Aldrich, St. Louis, MO, USA) were employed. The identification and purity of these substrates were verified by GC–MS: Saturn 2000, Varian, with a DB-5MS capillary column  $30 \text{ m} \times 0.25 \text{ mm. i.d.}, 0.25 \text{-}\mu\text{m}$  film thickness. The products ethyl formate, formic acid, ethylene, acetaldehyde, isobutyraldehyde, ethylene, and carbon dioxide were identified in a GC-MS (Saturn 2000, Varian) with a DB-5MS capillary column 30 m  $\times$  0.25 mm. i.d., 0.25-µm film thickness. The quantitative analysis of the product ethylene (Matheson) and CO<sub>2</sub> was carried out by using a gas chromatograph Varian 3600X with a thermal conductivity detector (capillary column: GS-Q, 30 m long and 0.53 i.d., helium gas carrier).

#### Kinetics

The kinetic experiments were performed in a static reaction system as reported in [14–16]. The rate coefficients were calculated from the pressure increase manometrically, or by the quantitative chromatographic analyses of ethyl formate, ethylene, and  $CO_2$  products. The temperature was controlled by a Shinko DC-PS resistance thermometer controller maintained at  $\pm 0.2^{\circ}$ C and measured with a calibrated iron constantan 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  $\sim 0.05-0.2$  mL.

## **RESULTS AND DISCUSSION**

## **Ethyl Glyoxalate**

The stoichiometry based on reaction (9) cannot be determined from the pressure ratio of  $P_{\rm f}/P_0$ , where  $P_{\rm f}$  is the final and  $P_0$  is the initial pressure, respectively. The average experimental  $P_{\rm f}/P_0$  at 4 different temperatures and 10 half-lives was 2.7. However, an estimation of stoichiometry (9), up to 70% decomposition, was possible from quantitative formation of CO and CO<sub>2</sub> gases (Table II). Consequently, total ethylene formation (reaction (9)) is needed in order to estimate CO and CO<sub>2</sub> gases. The quantitative amount of  $CO_2$  gas, i.e.,  $k_1$ , is equivalent to the pressure of ethylene formation from ethyl glyoxylate decomposition, i.e.,  $P_{\text{total ethylene}} = P_{\text{ethylene from ethyl formate}} +$  $P_{\text{total CO}_2}$ . In order to estimate CO gas, we have  $P_{\text{total ethyl formate}} = P_{\text{CO}} = (P_{\text{total ethylene}} - P_{\text{CO}_2})/1 - e^{-k_3 t}$ where  $k_3$  is the rate coefficient of ethyl formate pyrolysis as reported in the literature [17]. In this manner, the  $k_2$  value of decarbonylation was obtained from the decomposition of ethyl glyoxylate. The rate coefficient of ethyl formate pyrolysis,  $k_3 = 1.64 \times 10^{-4}$ at 390°C, is not negligible. Therefore, the formation of ethyl formate or CO gas from ethyl glyoxylate must be calculated as explained above. The total rate coefficient for the decomposition of ethyl glyoxylate was calculated from the sum  $k_1 + k_2$ . The elimination products within the range of rate determination were ethyl formate, formic acid, formaldehyde, ethylene, CO, and  $CO_2$ .

 Table II
 Stoichiometry of the Reaction

Temperature (°C) Substrate Parameters Values Ethyl glyoxalate 390.0 Time (min) 5 15 20 30 45 CO<sub>2</sub>(%) (GC) 11.9 34.7 43.6 54.0 72.2 CO formation (%)<sup>a</sup> 1.3 5.5 6.7 8.7 11.9 Total (%) (GC) 13.2 40.2 50.3 62.7 84.1 398.0 Ethyl 2-oxo-propionate Time (min) 3 5 7 10 13 Reaction (%) (pressure) 20.0 30.0 40.0 50.0 60.8 Ethylene (%) (GLC) 22.6 28.3 41.5 51.2 59.6 399.5 Ethyl 3-methyl-2-oxo-butyrate Time (min) 2 3 5 7 10 Reaction (%) (pressure) 16.6 23.6 34.2 44.9 60.6 Ethylene (%) (GLC) 17.3 23.5 36.7 43.8 54.6

<sup>*a*</sup> CO formation was estimated from  $P_{\rm CO} = (P_{\rm total \ ethylene} - P_{\rm CO_2})/1 - e^{-k_3 t}$ .

Parameter	$S/V = 1 \text{ cm}^{-1a}$	$S/V = 6.2 \text{ cm}^{-1a}$
$10^4 k_1 \text{ CO}_2 (\text{s}^{-1})$	7.41	7.92
$10^4 k_2 \text{ CO} (\text{s}^{-1})$	0.90	1.12
$10^4 k_1 (s^{-1})$	21.72	21.93
$10^4 k_1  (\mathrm{s}^{-1})$	14.87	14.95
	Parameter $10^4k_1 \operatorname{CO}_2(\mathrm{s}^{-1})$ $10^4k_2 \operatorname{CO}(\mathrm{s}^{-1})$ $10^4k_1(\mathrm{s}^{-1})$ $10^4k_1(\mathrm{s}^{-1})$	Parameter $S/V = 1 \text{ cm}^{-1a}$ $10^4k_1 \text{ CO}_2 (\text{s}^{-1})$ 7.41 $10^4k_2 \text{ CO} (\text{s}^{-1})$ 0.90 $10^4k_1 (\text{s}^{-1})$ 21.72 $10^4k_1 (\text{s}^{-1})$ 14.87

Table III Homogeneity of the Elimination Reaction

S is the Surface area; V is the volume.

<sup>a</sup> Vessel seasoned with the products decomposition of allyl bromide.



The effect of the surface on the rate of elimination was carried out in a vessel with a surface to volume ratio of 6.2 relative to that of the normal vessel, which is equal to 1.0 (Table III). Packed and unpacked clean Pyrex vessel had a marked heterogeneous effect, and unreliable and irreproducible k values were obtained. However, packed and unpacked Pyrex vessel seasoned with allyl bromide showed no effect on the reaction rates. The pyrolysis experiments of this substrate were performed in the presence of an equal amount of the free-radical suppressor toluene in order to prevent any possible free-radical reaction. The effect of different proportions of toluene on the elimination reaction is shown in Table IV. No induction period was observed. The rate coefficients were reproducible with a relative standard deviation of less than  $\pm 5\%$  at a given temperature.

The rate coefficient of this elimination reaction was found to be invariable to initial pressures (Table V), and the first-order rate for decarboxylation was calculated from  $k_1 = -(2.303/t) \log[(P_0 - P_{CO_2})/P_0]$  and for decarbonylation [17] from  $k_2 = -(2.303/t) \log[(P_0 - P_{CO})/P_0]$ , where  $P_{CO} = (P_{\text{total ethylene}} - P_{CO_2})/[1 - e^{-k_{3t}}]$  and  $k_3 = 2.52 \times 10^9 e^{-40.010 \text{ cal/}RT}$ . The variation in the rate coefficients with temperature and the corresponding Arrhenius equation are given in Table VI (90% confidence coefficient from the least-squares procedure).

# Ethyl 2-Oxo-Propionate and Ethyl 3-Methyl-2-Oxo-Butyrate

Theoretical stoichiometry (10) for the gas-phase elimination of the above-mentioned compounds requires  $P_f/P_0 = 3.0$ . The average experimental  $P_f/P_0$  value at 4 different temperatures and 10 half-lives for both substrates was 2.9. Confirmation of the stoichiometry of reaction (10), up to 60% decomposition, was

**Table IV** Effect of the Free-Radical Chain Inhibitor Toluene on Rates

Substrate	Temperature (°C)	$P_{\rm s}{}^a$ (Torr)	$P_i^{b}$ (Torr)	$P_{\rm i}/P_{\rm s}$	$10^4 k_1 (s^{-1})$	$10^4 k_2 (s^{-1})$
Ethyl glyoxalate	389.7	43	С	с	$4.22^{d}$	$0.42^{e}$
		49.5	28	0.6	$4.77^{d}$	0.63 <sup>e</sup>
		50	84	1.7	$4.74^{d}$	$0.58^{e}$
		52	118	2.3	$4.74^{d}$	$0.57^{e}$
Ethyl 2-oxo-propionate	398.6	79.5	_	-	13.60	
		80.5	142	1.7	12.99	
		76.5	170	2.2	12.66	
		59	179.5	3.0	12.47	
Ethyl 3-methyl-2-oxo-butyrate	399.4	63	-	-	15.56	
		59	71	1.2	14.95	
		56	131	2.3	14.86	
		50	149	3.0	14.97	

<sup>*a*</sup>  $P_s$  is the pressure of the substrate.

<sup>*b*</sup>  $P_i$  is the pressure of the free-radical inhibitor.

<sup>c</sup> Substrate dissolved in 50% toluene.

 $e_{k_2}$  value of CO formation.

<sup>&</sup>lt;sup>*d*</sup>  $k_1$  value of CO<sub>2</sub> formation.

Substrate	Temperature (°C)	Parameters			Values		
Ethyl glyoxalate	410.5	$P_0$ (Torr)	32.5	44	51	68	78.5
		$10^4 k_{1(CO_2)} (s^{-1})$	14.40	14.08	14.47	14.32	14.14
		$10^4 k_{2(CO)} (s^{-1})$	1.76	1.86	1.78	1.68	1.88
Ethyl 2-oxo-propionate	410.8	$P_0$ (Torr)	29	55.5	71	105	
		$10^4 k_1 (s^{-1})$	21.98	21.87	21.56	21.58	
Ethyl 3-methyl-2-oxo-butyrate	409.3	$P_0$ (Torr)	46.5	59	78	98.5	
		$10^4 k_1 (s^{-1})$	26.04	26.15	25.12	24.87	

 Table V
 Invariability of the Rate Coefficients from Initial Pressure

Table VI	Variation of	of the Rate	Coefficients	with Temp	erature

Ethyl glyoxalate	Temperature (°C)	389.9	399.4	410.3	419.5	430.3		
	$10^4 k_{1(CO_2)} (s^{-1})$	4.56	7.41	14.38	23.30	41.09		
	$10^4 k_{2(CO)} (s^{-1})$	0.52	0.90	1.84	3.39	5.55		
Rate equation log $k_{1(CO_2)}$ (s <sup>-1</sup> )	$=(13.43\pm0.25)-(1000)$	$213.1 \pm 100$	3.3) kJ n	$nol^{-1}$ (2)	.303 RT)	$^{-1}, r = 0.9$	9996	
Rate equation log $k_{2(CO)}$ (s <sup>-1</sup> ) =	$=(14.06\pm0.54)-(2$	$32.9 \pm 7$	'.0) kJ m	$ol^{-1}$ (2.3	$303 RT)^{-1}$	$^{-1}, r = 0.9$	986	
Rate equation log $k_{t(\text{overall})}$ (s <sup>-1</sup>	$) = (13.72 \pm 0.25) - $	(216.1 ±	± 3.3) kJ	$mol^{-1}$ (	2.303 RI	$(T)^{-1}, r = 0$	).9997	
Ethyl 2-oxo-propionate	Temperature (°C)	369.1	378.6	389.6	398.4	410.0 4	18.9	429.6
	$10^4 k_1 (s^{-1})$	2.31	3.88	7.23	12.71	21.78 3	5.88	62.42
Rate equation $\log k_1 (s^{-1}) = (11)$	$3.03 \pm 0.15) - (205.13)$	$1 \pm 2.0)$	kJ mol <sup>−1</sup>	(2.303	$RT)^{-1}, r$	= 0.9998		
Ethyl 3-methyl-2-oxo-butyrate	Temperature (°C)	380.2	389.7	399.6	409.4	420.0		
	$10^4 k_1 (s^{-1})$	5.38	8.48	14.95	25.62	42.38		
Rate equation $\log k_1$ (s <sup>-1</sup> ) = (1)	$2.58 \pm 0.31) - (198.4)$	$4 \pm 4.1)$	kJ mol <sup>-1</sup>	(2.303	$RT)^{-1}, r$	= 0.9994		

possible when comparing between pressure measurements and the quantitative analyses of ethylene gas (Table II).

$$\begin{array}{c} O & O \\ \parallel & \parallel \\ R - C - C - C - OCH_2CH_3 \end{array} \xrightarrow{1} \left[ \begin{array}{c} O & O \\ \parallel & \parallel \\ R - C - C - OH \end{array} \right] + H_2C = CH_2$$

$$\begin{array}{c} R = CH_3, (CH_3)_2CH \\ \downarrow \\ R - CHO + CO_2 \end{array}$$

$$(10)$$

The homogeneity of these reactions (10) was examined in a vessel with a surface to volume ratio of 6.2 relative to that of the normal vessel, which is equal to 1.0 (Table III). The packed and unpacked clean Pyrex vessel had a marked heterogeneous effect, and unreliable k values were obtained. Yet, the packed and unpacked Pyrex vessel seasoned with allyl bromide gave no difference in rates. The effect of adding different proportions of the inhibitor toluene is shown in Table IV. According to this result, the elimination experiments were carried out in the presence of twice the amount of toluene with respect to these 2-oxo-esters in order to prevent any possible radical chain reactions. No induction period was observed, and the rates were reproducible with a relative standard deviation not greater than  $\pm 5\%$  at a given temperature.

The first-order rate coefficient of these substrates calculated from  $k_1 = -(2.303/t) \log 2P_0/(3P_0 - P_t)$  was independent of the initial pressure of the substrate (Table V). A plot of log  $(3P_0 - P_t)$  versus time (*t*) gave a good straight line for up to 60% of the reaction. The temperature dependence of the rate coefficients and the corresponding Arrhenius equation are given in Table VI (90% confidence coefficient from the least-squares procedure).

The comparative kinetic and thermodynamic parameters at  $400^{\circ}$ C are shown in Table VII.

Table VII Comparative Kinetic and Thermodynamic Parameters at 400°C

Z	$k_1 \times 10^4  (\mathrm{s}^{-1})$	$E_{\rm a}~({\rm kJ/mol})$	$\log A (s^{-1})$	$\Delta S^{\neq}$ (J/mol K)	$\Delta H^{\neq}$ (kJ/mol)	$\Delta G^{\neq}$ (kJ/mol)
Ethyl glyoxalate	8.91 <sup>a</sup>	$216.1 \pm 3.3$	$13.72\pm0.25$	2.7	210.5	208.7
	$7.77^{b}$	$213.1\pm3.3$	$13.43\pm0.25$	-2.9	207.8	209.7
	$0.96^{c}$	$232.9\pm7.0$	$14.06\pm0.54$	9.2	233.1	226.9
Ethyl 2-oxo-propionate	12.92	$205.1\pm2.0$	$13.03\pm0.15$	-10.6	199.5	206.6
Ethyl 3-methyl-2-oxo-butyrate	15.18	$198.4\pm4.1$	$12.58\pm0.31$	-19.2	192.8	205.7

<sup>*a*</sup> Overall rate.

<sup>*b*</sup> Rate of decarboxylation.

<sup>c</sup> Rate of decarbonylation.

# CONCLUSION

Electron-withdrawing substituents, such as chlorine in methyl oxalyl chloride and amino in ethyl oxamate and ethyl oxanilinate, proceed to a decarbonylation [12,13] process (Step 1, reactions (5)-(7)). An exception is ethyl N,N-dimethyl oxamate (reaction (8)). However, by changing the electronic transmission of the substituent to electron-releasing groups such as methyl (ethyl 2-oxo-propionate) and isopropyl (3-methyl-2oxo-butyrate), the elimination process proceeds as organic esters to give the corresponding carboxylic acid and ethylene. Step 1,  $C_{\alpha}^{\delta+} \cdots O^{\delta-}$ , is a rate-determining step and through a six-membered cyclic transition state yields the corresponding 2-oxo-acids (reaction (11)). These acids, under the reaction conditions, rapidly decarboxylate, as suggested before [10,11], to give the corresponding aldehyde. The product of ethyl 2-oxopropionate (Step 1, reaction (11)), the intermediate 2oxo-propionic acid or pyruvic acid, was reported to decompose in the gas phase [18] into acetaldehyde and  $CO_2$  in the temperature range 284–334°C with an Arrhenius expression log  $k_1$  (s<sup>-1</sup>) = 13.53 - 172.4 kJ mol<sup>-1</sup>  $(2.303 RT)^{-1}$ . These data suggest that the pyruvic acid intermediate, under the condition of the present work, changes to decarboxylate rapidly. The effect of the increase in rate on the electron release of the alkyl groups CH<sub>3</sub> and (CH<sub>3</sub>)<sub>2</sub>CH of the oxyesters may be due to the nucleophilic assistance of the oxygen of the carbonyl to the incipient positive  $C_{\gamma}$ in the transition state (reaction (11)). Consequently, the greater the electron release of the alkyl group R, the greater the nucleophilicity of oxygen carbonyl, the more the stabilization of the positive  $C_{\gamma}$ . Therefore, an augmentation on the rate of elimination is obtained.

The presence of H as a substituent in ethyl glyoxalate gives a parallel reaction (12). Step 1 of the predominant pathway A is the rate-determining step, which proceeds through a six-membered cyclic transition state to produce ethylene and glyoxylic acid.



International Journal of Chemical Kinetics DOI 10.1002/kin

(12)

Under the reaction conditions, the acid decomposes through a four-membered cyclic transition state to give formaldehyde and CO<sub>2</sub>. Since the H substituent has been defined in the Taft original  $\sigma^*$  with a positive value of +0.49 [19], this means that some electronwithdrawing property, and therefore a small amount of decarbonylation process (pathway B), is obtained. The rate-determining Step 2 in the same pathway occurs in a similar way as in methyl oxalyl chloride (reaction (5)), which is through a three-membered cyclic transition state to give ethyl formate and CO gas. Ethyl formate slowly decomposes to produce formic acid and ethylene.

#### BIBLIOGRAPHY

- Taylor, R. The Chemistry of Functional Group, Supplementary Volume B: Acid Derivatives; Patai, S. (Ed.); Wiley: London, 1979; Ch. 15, pp. 859–914.
- Holbrook, K. A. 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.
- Chuchani, G.; Mishima, M.; Notario, R.; Aboud, J. L. Structural Effects on Gas-Phase Reactivities, Volume
   Advances in Quantitative Structure-Property Relationships; Charton, M.; Charton, B. I. (Eds.); Jai Press: Stamford, CT; 1999, pp. 35–126.

- (a) Hansch, C.; Leo, A. J. Substituent Constants for Correlation Analysis in Chemistry and Biology; Wiley: New York, 1979; (b) Hansch, C.; Leo, A.; Taft, R. Chem Rev 1991, 91, 165–195.
- Herize, A.; Domínguez, R. M.; Rotinov, A.; Nuñez, O.; Chuchani, G. J Phys Org Chem 1999, 12, 201–206.
- 6. Clark, L. J Phys Chem 1961, 65, 659-661.
- 7. Clark, L. J Phys Chem 1961, 65, 180–182.
- 8. Clark, L. J Phys Chem 1961, 65, 1651–1652.
- 9. Lapidus, G.; Barton, D.; Yankwich, P. J Phys Chem 1964, 68, 1863.
- 10. Taylor, R. Int J Chem Kinet 1987, 19, 709-713.
- 11. Taylor, R. Int J Chem Kinet 1991, 23, 247-250.
- 12. Cordova, T.; Rotinov, A.; Chuchani, G. J Phys Org Chem 2004, 17, 148–151.
- Chacin, E. V.; Tosta, M.; Herize, A.; Dominguez, R. M.; Alvarado, Y.; Chuchani, G. J Phys Org Chem 2005, 18, 539–545.
- 14. Maccoll, A. J Chem Soc 1955, 965-973.
- 15. Swinbourne, E. S. Aust J Chem 1958, 11, 314–330.
- Dominguez, R. M.; Herize, A.; Rotinov, A.; Alvarez-Aular, A.; Visbal, G.; Chuchani, G. J Phys Org Chem 2004, 17, 399–408.
- 17. Makens, R. F.; Eversole, W. G. J Am Chem Soc 1939, 61, 3203–3206.
- 18. Taylor, R. Int J Chem Kinet 1987, 19, 709–713.
- (a) Hansch, C.; Leo, A. J. Substituent Constants for Correlation Analysis in Chemistry and Biology; Wiley: New York, 1979; (b) Hansch, C.; Leo, A.; Taft, R. Chem Rev 1991, 91, 165–195.