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Kinetics of the gas-phase homogeneous unimolecular elimination of selected ethyl esters of 2-oxo-carboxylic acids

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The gas-phase elimination kinetics of selected ethyl esters of 2-oxo-carboxylic acid have been studied over the temperature range of 270–415 °C and pressures of 37–114 Torr. The reactions are homogeneous, unimolecular, and follow a first-order rate law in a seasoned static reaction vessel, with an added free radical suppressor toluene. The observed overall and partial rate coefficients are expressed by the following Arrhenius equations:

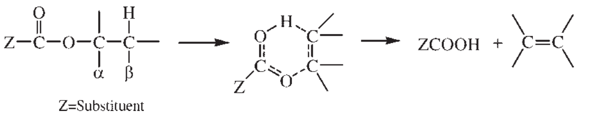
Ethyl oxalyl chloride
$\log k_{\text{overall}}\ (\text{s}^{-1}) = (13.22 \pm 0.45) - (179.4 \pm 4.9)\ \text{kJ mol}^{-1}\ (2.303\ RT)^{-1}$
Ethyl piperidineglyoxylate
$\log k_{(\text{CO2})}\ (\text{s}^{-1}) = (12.00 \pm 0.30) - (191.2 \pm 3.9)\ \text{kJ mol}^{-1}\ (2.303\ RT)^{-1}$
$\log k_{(\text{CO})}\ (\text{s}^{-1}) = (12.60 \pm 0.09) - (210.7 \pm 1.2)\ \text{kJ mol}^{-1}\ (2.303\ RT)^{-1}$
$\log k_{\text{t(overall)}}\ (\text{s}^{-1}) = (12.22 \pm 0.26) - (193.4 \pm 3.4)\ \text{kJ mol}^{-1}\ (2.303\ RT)^{-1}$
Ethyl benzoyl formate$\log k_{(\text{CO2})}\ (\text{s}^{-1}) = (12.89 \pm 0.72) - (203.8 \pm 9.0)\ \text{kJ mol}^{-1}\ (2.303\ RT)^{-1}$
$\log k_{(\text{CO})}\ (\text{s}^{-1}) = (13.39 \pm 0.31) - (213.3 \pm 3.9)\ \text{kJ mol}^{-1}\ (2.303\ RT)^{-1}$
$\log k_{\text{t(overall)}}\ (\text{s}^{-1}) = (13.24 \pm 0.60) - (205.8 \pm 7.6)\ \text{kJ mol}^{-1}\ (2.303\ RT)^{-1}$

The kinetic and thermodynamic parameters of these reactions, together with those reported in the literature, lead to consider three different mechanistic pathways of elimination. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: ethyl benzoyl formate; ethyl oxalyl chloride; ethyl piperidineglyoxylate; gas-phase elimination; kinetics; mechanism

INTRODUCTION

The unimolecular gas-phase decomposition of organic carboxylic esters has been postulated to proceed through a six-membered cyclic transition state type of mechanism to yield the corresponding carboxylic acid and the olefin, respectively [reaction (1)].[1,2] The presence of a C_β—H bond at the alcoxy side of the ester is necessary for molecular elimination.



(1)

The kinetic parameters and the comparative rates of substituents (Z) other than carbon at the acid side of the organic ethyl esters[3] indicate that the substituted compounds still react via the mechanism described in reaction (1). Substituent effects on reaction rates are often examined by the Taft–Topsom method[4] of $\log k/k_H = \sigma_\alpha\rho_\alpha + \sigma_F\rho_F + \sigma_R\rho_R$ which takes into consideration the steric (σ_α), electronic (σ_F), and resonance (σ_R) contributions in the quantitative study of structural and substituent effects on chemical reactivity. The substituent constant σ_α is defined as the polarizability or steric effect, σ_F as the field or electronic effect, while σ_R as the resonance effect.[4] The ρ value is defined as the nature of the reaction. The plot of this method between the experimental data ($\log k/k_H$) and the three substituent parameters σ_α, σ_F, and σ_R was found to be approximately linear.

$$\log k/k_H = -(0.68 \pm 0.12)\sigma_\alpha + (2.57 \pm 0.12)\sigma_F - (1.18 \pm 0.27)\sigma_{R^-}$$
$$(r = 0.984,\ \text{sd} = 0.119\ \text{at}\ 400^\circ\text{C})$$

The negative value of $\rho_\alpha = -0.68$ suggests the polarizability or steric effect has a little participation on the rate of elimination of ethene, while the positive value of $\rho_{F^-} = +2.57$ suggests that the field or electronic effect appears to have the major influence in the elimination process. Finally, $\rho_{R^-} = -1.18$ suggests an interaction of the substituent Z with an incipient negative reaction center, thus favoring the abstraction of the β-hydrogen of the ethyl ester by the oxygen carbonyl in the transition state.

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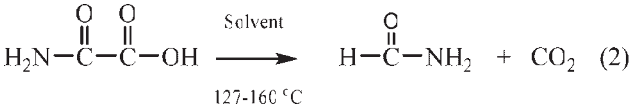
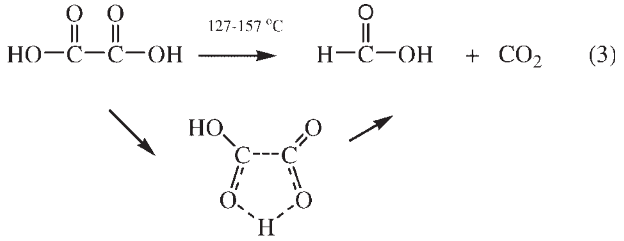
Investigation of the gas-phase elimination kinetics of some compounds having the interposition of a carbonyl between the substituents Z and the acid side of ethyl ester, that is, ethyl esters of 2-oxo-carboxylic acids, has recently been reported.[5] It seemed interesting to find if some correlation with substituent Z may be obtained. Otherwise, the migration of Z to the ethoxycarbonyl with loss of CO may occur rather than a simple formation of ethylene in the gas-phase elimination of ethyl esters.

It seemed interesting to inquire the works on the thermal decomposition of 2-oxoacids and their alkyl esters in solution and in the gas phase. Thermolyses of oxalic and oxamic acids in several solvents [reaction (2)] have been described.[6–8] The polar nature of the solvents was found to affect the rate of decomposition. The fact that oxo-acids are being referred is because they may be the intermediates of the corresponding 2-oxo-esters decomposition, and they are generally found to be unstable at the working temperatures.



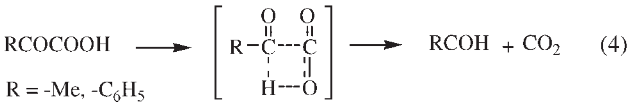
$$H_2N-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[127\text{-}160\,^{\circ}C]{\text{Solvent}} H-\overset{O}{\overset{\|}{C}}-NH_2 + CO_2 \quad (2)$$

In related works, the mechanism and kinetics of the gas-phase decomposition of oxalic acid was reported [reaction (3)][9]



$$HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{127\text{-}157\,^{\circ}C} H-\overset{O}{\overset{\|}{C}}-OH + CO_2 \quad (3)$$

The thermal decomposition of pyruvic and benzoylformic acids[10,11] was found to proceed through a concerted mechanism with semi-polar type transition states to give carbon dioxide and the corresponding aldehydes [reaction (4)]

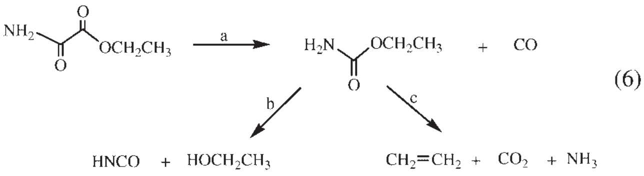


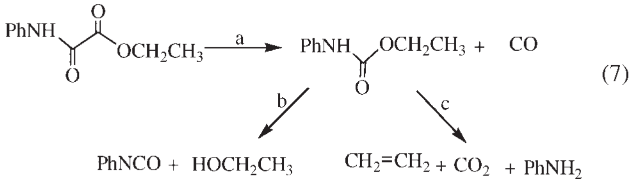
$$RCOCOOH \longrightarrow \left[R-\overset{O}{\overset{\|}{C}}---\overset{O}{\overset{\|}{C}} \;\; H---O \right] \longrightarrow RCOH + CO_2 \quad (4)$$

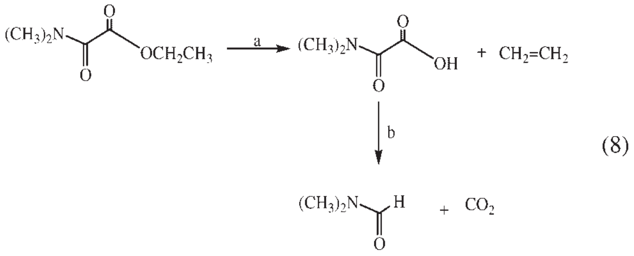
$R = \text{-Me}, \text{-}C_6H_5$

A theoretical and experimental study on the gas-phase elimination kinetics of methyl oxalyl chloride[12] suggested a concerted semi-polar type transition state [reaction (5)], in which the Cl atom migrates to the adjacent carbonyl group as CO gas is eliminated. Semi-empirical PM3 and MP2/6-31G* calculations have been found to be in good agreement with experiments.

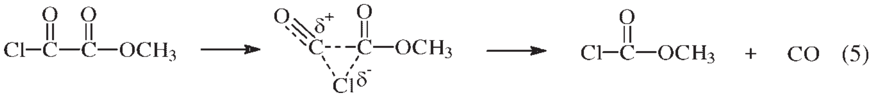
Few years ago, the decomposition of some ethyl esters of 2-oxo-carboxylic acids with a nitrogen atom attached at the acid side, that is, ethyl oxamate, ethyl *N,N*-dimethyloxamate, and ethyl oxanilinate [reactions (6–8)], was described.[5]



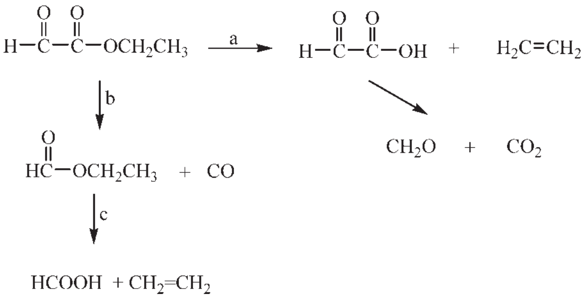




Experimental results of the decomposition products of ethyl oxamate [reaction (6a)] and ethyl oxanilinate [reaction (7a)] indicated decarbonylation as the first step of decomposition due to bond polarization of the N—C═O rate determining step, thus favoring migration of the amino group. The corresponding ethyl ester intermediate subsequently undergoes parallel eliminations [reactions (6b, c;7b, c)]. Ethyl *N,N*-dimethyloxamate decomposition proceeds via different elimination pathways [reaction (8)]. This result was surprising, since decarbonylation was expected to be the first step of the reaction. This fact may well be due to the electron release of the two methyl groups on the N atom reducing the electronegativity of this substituent when compared to a Cl atom [reaction (5)]. Several additional works showed that ethyl glyoxylate undergoes a parallel and consecutive homogeneous decomposition as depicted in reaction (9),[13] while ethyl 2-oxo-propanoate and ethyl 3-methyl-2-oxo-butyrate eliminate ethylene to give the



$$Cl-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OCH_3 \longrightarrow \left[\overset{\delta+}{O{\equiv}C}---\overset{O}{\overset{\|}{C}}-OCH_3 \;\; Cl^{\delta-} \right] \longrightarrow Cl-\overset{O}{\overset{\|}{C}}-OCH_3 + CO \quad (5)$$



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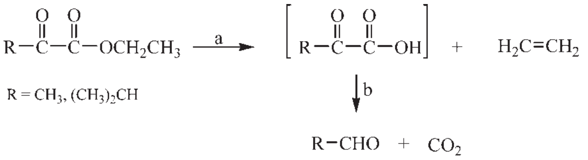


(10)

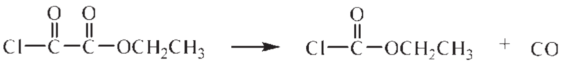
corresponding 2-oxocarboxylic acid [reaction (10)]. The oxocarboxylic acids are unstable under the conditions of the reaction and rapidly decarboxylate to produce the corresponding aldehyde.

In view of the several types of decomposition pathways found with different substituents Z in $ZCOCOOCH_2CH_3$ (Z = amino groups, hydrogen atoms, and alkyls), further research was thought of interest to examine the gas-phase decomposition of a series of 2-oxo-esters. Consequently, the present work aimed at studying the mechanisms of the gas-phase elimination kinetics and the effect of such compounds containing electron-withdrawing substituents (Z) such as chlorine Cl, piperidyl $C_5H_{10}N$, and phenyl C_6H_5, i.e., ethyl oxalyl chloride, ethyl piperidine glyoxylate, and ethyl benzoyl formate.

RESULTS AND DISCUSSION

Ethyl oxalyl chloride

The stoichiometry for the decomposition of ethyl oxalyl chloride via reaction (11) requires $P_f/P_0 = 2$, where P_f and P_0 are the initial and final pressures, respectively. The average



$$Cl-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OCH_2CH_3 \longrightarrow Cl-\overset{O}{\overset{\|}{C}}-OCH_2CH_3 + CO \qquad (11)$$

experimental P_f/P_0 at four different temperatures and ten half-lives was 1.93 (Table 1). Additional examination of the above stoichiometry of reaction (11) was made by comparing, up to 55% decomposition, the pressure measurements with the results of quantitative analyses of ethyl chloroformate (Table 2). The comparison is found in reasonable agreement.

Table 1. Ratio of final (P_f) to initial (P_0) pressure

Compound	Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	Average
Ethyl oxalyl chloride	279.9	63	115	1.83	1.93
	300.3	78	152	1.95	
	309.5	79	154	1.95	
	319.3	54	107	1.98	
Ethyl piperidine glyoxylate	365.0	42.0	120	2.86	2.96
	375.0	42.5	129.0	3.04	
	384.7	27.5	80.0	2.91	
	395.8	60.0	181.0	3.02	
Ethyl benzoyl formate	399.6	66.5	129.0	1.94	1.94
	414.0	128.5	242.5	1.90	
	426.5	88.0	175.0	1.99	

Table 2. Stoichiometry of the reaction

Substrate	Temperature (°C)	Parameters	Value				
Ethyl oxalyl chloride	390.0	Time (min)	7	10	12	15	20
		Reaction (%) (pressure)	26.9	34.6	40.4	46.8	56.4
		Ethyl chloroformate (%) (GC)	26.2	33.5	41.0	46.8	54.8
Ethyl piperidine glyoxylate	395.9	Time (min)	5	10	15	20	
		Substrate reaction (%) (GC)	34.2	57.1	71.7	87.0	
		Piperidine formate (%) (GC)	31.0	51.4	64.2	77.5	
		Piperidine (%) (GC)	3.2	5.7	7.5	9.5	
Ethyl benzoyl formate	379.6	Time (min)	6	12	20	25	
		Substrate reaction (%) (GC)	27.1	41.5	56.3	72.9	
		Benzaldehyde (%) (GC)	16.0	29.4	36.9	45.7	
		Ethyl benzoate (%)[a]	11.1	12.1	19.4	27.2	

[a] Ethyl benzoate was estimated by using the equation $\%P_{\text{ethyl benzoate}} = [P_0 - P_{\text{substrate}} - P_{\text{benzaldehyde}}/P_0] \times 100 = \%P_{CO}$

The effect of the surface on the rate of elimination was tested by carrying out several runs 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 3). No effect on the reaction rates was observed in packed and unpacked Pyrex vessels seasoned with allyl bromide. However, with clean Pyrex vessels the results with packed and unpacked reactors indicated a dramatic heterogeneous effect and unreliable and irreproducible *k*-values were obtained. The effect of the free radical inhibitor toluene is shown in Table 4. The kinetic determinations had to be carried out with at least two-fold excess of toluene in order to prevent any possible free radical processes of the substrate and/or products. No induction period was observed. The rate coefficients were reproducible with a relative standard deviation of ±5% at any given temperature.

The first-order rate coefficient of this substrate from $k_1 = -(2.303/t)\log[(2P_0 - P_t)/P_0]$ was independent of the initial pressure (Table 5). A plot of $\log(2P_0 - P_t)$ against time *t* gave a good straight line up to 55% reaction at all working temperatures. The variation of the rate coefficients with temperature and the corresponding Arrhenius equation are given in Table 6 (Fig. 1; 90% confidence coefficient from least-squares procedure).

Ethyl piperidine glyoxylate

The experimental stoichiometry for the gas elimination of ethyl piperidine glyoxylate in the gas phase [reaction (12)] showed $P_f/P_0 = 2.96$ (Table 1). However, since different proportions of parallel reaction products are obtained, stoichiometry reaction (12) was checked, up to 70% decomposition, by comparing the quantitative chromatographic analyses of the substrate with the quantitative chromatographic analyses

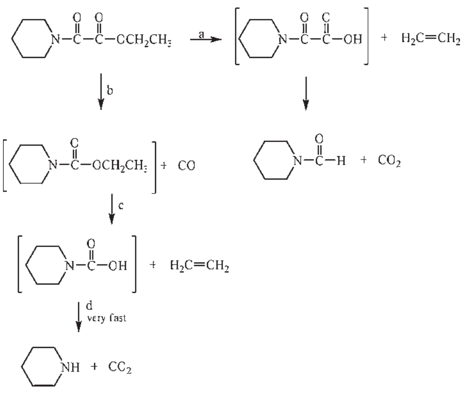


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Table 3. Homogeneity of the elimination reaction

Substrate	Parameter	$S/V = 1\ \mathrm{cm}^{-1}$[a]	$S/V = 6.2\ \mathrm{cm}^{-1}$[a]
Ethyl oxalyl chloride at 300.2 °C	$10^4\ k_T\ (s^{-1})$	7.05	7.70
Ethyl piperidine glyoxylate at 395.6 °C	$10^4\ k_T\ (s^{-1})$	13.32	13.52
Ethyl benzoyl formate at 389.8 °C	$10^4\ k_T\ (s^{-1})$	10.79	[b]

S = Surface area; *V* = Volume.

[a] In a vessel seasoned with allyl bromide.

[b] Unreliable and irreproducible.

Table 4. Effect of the free radical chain inhibitor toluene on rates

Substrate	Temperature (°C)	P_s (Torr)	P_i (Torr)	P_i/P_s	$10^4\ k_T\ (s^{-1})$
Ethyl oxalyl chloride	300.4	84	—	—	7.10
		74	90	1.2	6.97
		70	137.5	2.0	6.88
		63	194	3.1	6.99
Ethyl piperidine glyoxylate	375.5	42.0	—	—	5.23
		34.0	59.0	1.7	5.05
		42.0	92.0	2.2	4.91
		42.5	156.0	3.7	4.99
Ethyl benzoyl formate	398.8	63.0	—	—	15.97
		29.0	95.0	3.3	16.57
		26.5	91.5	3.5	16.63
		26.0	107.0	4.1	18.20
		31.5	159.0	5.1	18.65

P_s = Pressure of substrate. P_i = Pressure of free radical inhibitor. k_T = total rate coefficient

Table 5. Variation of the rate coefficients from initial pressure

Substrate	Temperature (°C)	Parameters	Value			
Ethyl oxalyl chloride	290.2	P_0 (Torr)	37	88	121	157
		$10^4\ k_T (s^{-1})$	3.80	3.71	3.94	3.86
Ethyl piperidine glyoxylate	405.6	P_0 (Torr)	44	63	73	114
		$10^4\ k_T\ (s^{-1})$	22.27	21.82	22.16	21.37
Ethyl benzoyl formate	379.6	P_0 (Torr)	19.5	25	44	47
		$10^4\ k_T\ (s^{-1})$	6.73	6.57	6.19	6.27

Table 6. Temperature dependence of the rate coefficients

Ethyl oxalyl chloride	Temperature (°C)	270.2	279.9	290.2	300.2	320.1
	$10^4\ k_1\ (s^{-1})$	1.01	1.80	3.82	7.00	29.36
Rate equation $\log k_1\ (s^{-1}) = (13.22 \pm 0.45) - (179.5 \pm 4.9)\ kJ\ mol^{-1}\ (2.303\ RT)^{-1}$, $r = 0.9990$						
Ethyl piperidine glyoxylate	Temperature (°C)	395.6	405.8	415.8		
	$10^4\ k_a\ (s^{-1})$	11.95	19.30	32.11		
	$10^4\ k_b\ (s^{-1})$	1.41	2.48	4.24		
	$10^4\ k_T\ (s^{-1})$	13.36	21.78	36.35		
Rate equation $\log k_a\ (s^{-1}) = (12.00 \pm 0.30) - (191.2 \pm 3.9)\ kJ\ mol^{-1}\ (2.303\ RT)^{-1}$, $r = 0.9998$						
Rate equation $\log k_b\ (s^{-1}) = (12.60 \pm 0.09) - (210.7 \pm 1.2)\ kJ\ mol^{-1}\ (2.303\ RT)^{-1}$, $r = 0.9999$						
Rate equation $\log k_T\ (s^{-1}) = (12.22 \pm 0.26) - (193.4 \pm 3.4)\ kJ\ mol^{-1}\ (2.303\ RT)^{-1}$, $r = 0.9999$						
Ethyl benzoyl formate	Temperature (°C)	369.6	379.6	390.7	398.8	
	$10^4\ k_a\ (s^{-1})$	2.25	3.83	6.71	11.62	
	$10^4\ k_b\ (s^{-1})$	0.91	2.12	4.08	6.31	
	$10^4\ k_T\ (s^{-1})$	3.16	5.95	10.79	17.93	
Rate equation $\log k_a\ (s^{-1}) = (12.89 \pm 0.72) - (203.8 \pm 9.0)\ kJ\ mol^{-1}\ (2.303\ RT)^{-1}$, $r = 0.9961$						
Rate equation $\log k_b\ (s^{-1}) = (13.39 \pm 0.31) - (213.3 \pm 3.9)\ kJ\ mol^{-1}\ (2.303\ RT)^{-1}$, $r = 0.9993$						
Rate equation $\log k_T\ (s^{-1}) = (13.24 \pm 0.60) - (205.8 \pm 7.6)\ kJ\ mol^{-1}\ (2.303\ RT)^{-1}$, $r = 0.9973$						

of the products piperidine formate plus piperidine (Table 2). The product piperidine results from the rapid decomposition of ethyl piperidine formate, which is unstable at the working temperature. The sum of quantitative analysis of the products piperidine and piperidine formate agrees with the quantitative amount of the substrate ethyl piperidine glyoxylate decomposition.

Table 3 indicates that reaction (12) is homogeneous in seasoned and clean packed and unpacked Pyrex vessels. The effect of the free radical suppressor is shown in Table 4. The kinetic determinations had to be carried out in the presence of toluene (the concentration of toluene is at least two times the initial pressure of this substrate) to inhibit any possible chain reactions of the substrate and/or products. No induction period was observed. The rate coefficients are reproducible with a relative standard deviation not greater than ±5% at a given temperature.

The first-order rate coefficient was found to be independent of the initial pressure (Table 5). The temperature dependence of the rate coefficients and the corresponding Arrhenius equation are given in Table 6 (Fig. 2; 90% confidence coefficient from least-squares procedure).

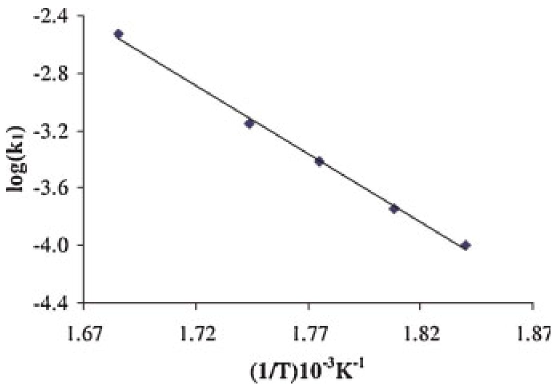
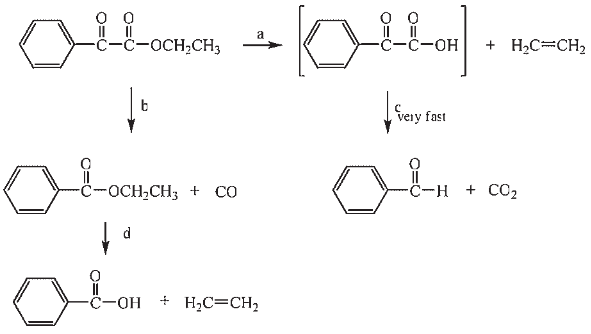


Figure 1. Arrhenius plot for the elimination kinetics of ethyl oxalyl chloride

Ethyl benzoyl formate

The gas elimination of this substrate proceeds according to reaction (13).



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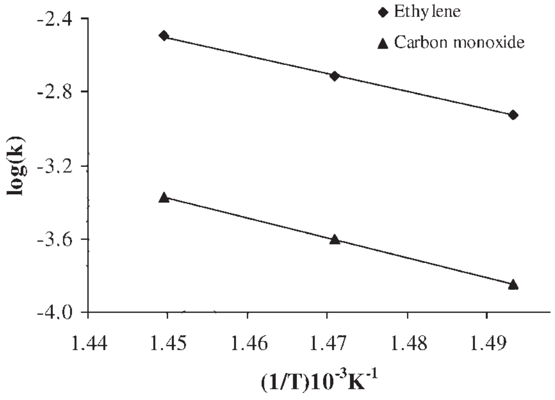


Figure 2. Arrhenius Plot for the elimination kinetics of ethyl piperidine glyoxylate

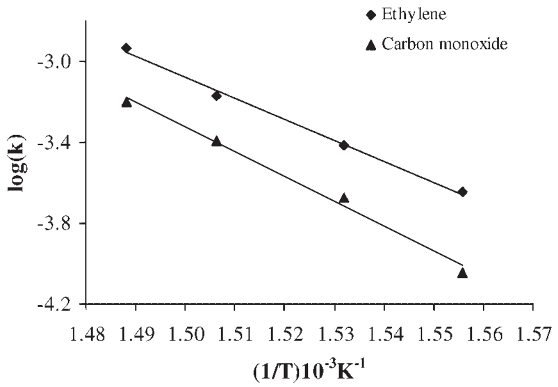


Figure 3. Arrhenius Plot for the elimination kinetics of ethyl benzoyl formate

The average experimental stoichiometry reaction (13) showed P_f/P_0 to be 1.94 (Table 1). However, to confirm stoichiometry reaction (13) was possible by comparing the quantitative chromatographic analyses of the reacted amount of substrate with the sum of products formation benzaldehyde and the CO gas ($P_{\mathrm{CO\ gas}} = P_{\mathrm{ethyl\ benzoate}} = P_0 - P_{\mathrm{substrate}} - P_{\mathrm{benzaldehyde}}$) (Table 2). The ethyl benzoate was estimated as the above equation, since it decomposes partially to ethene and benzoic acid at the working temperature. The quantitative analyses of ethene were unreliable, since CO gas impedes the condensation of the olefin. Benzoic acid was only detected. Some surface catalysis was found, even for vessels seasoned with allyl bromide. Rates were only measured in seasoned unpacked Pyrex vessels in order to obtain reproducible values (Table 3). The pyrolysis runs of the starting material were carried out with added toluene, at least five times the amount of the inhibitor in order to suppress any possible radical chain processes (Table 4). The rate coefficients are reproducible with

Table 7. Comparative kinetic and thermodynamic parameters at 400 °C

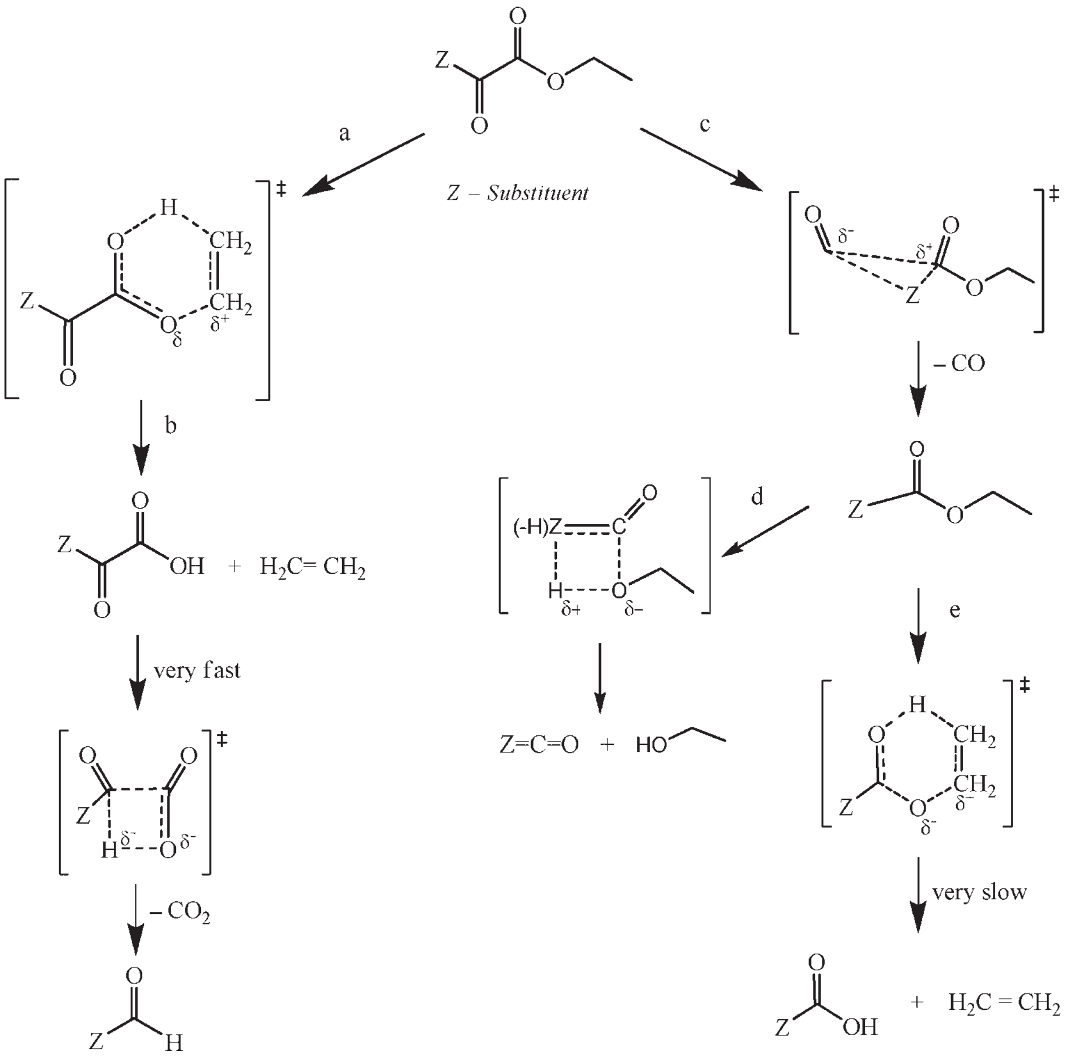
Substrate	$k_1 \times 10^4$ (s^{-1})	E_a (kJ mol^{-1})	log A (s^{-1})	ΔS$^{\neq}$ (J mol^{-1} K)	ΔH$^{\neq}$ (kJ mol^{-1})	ΔG$^{\neq}$ (kJ mol^{-1})	Ref.
Ethyl glyoxalate $HCOCOOCH_2CH_3$	8.91[a]	216.1 ± 3.3	13.72 ± 0.25	2.7	210.5	208.7	13
	7.77[b]	213.1 ± 3.3	13.43 ± 0.25	−2.9	207.8	209.7	
	0.96[c]	232.9 ± 7.0	14.06 ± 0.54	9.2	233.1	226.9	
Ethyl 2-oxo-propionate $CH_3COCOOCH_2CH_3$	12.92[a]	205.1 ± 2.0	13.03 ± 0.15	−10.6	199.5	206.6	13
Ethyl 3-methyl-2-oxo-butyrate $(CH_3)_2CHCOCOOCH_2CH_3$	15.18[a]	198.4 ± 4.1	12.58 ± 0.31	−19.2	192.8	205.7	13
Ethyl oxalyl chloride $ClCOCOOCH_2CH_3$	1968.5[a]	179.5 ± 4.9	13.22 ± 0.45	−6.9	173.8	178.5	[f]
Ethyl piperidine glyoxylate $C_5H_{10}NCOCOOCH_2CH_3$	14.67[a]	193.4 ± 3.4	12.22 ± 0.27	−26.1	187.8	205.3	[f]
	13.10[b]	191.2 ± 3.9	12.00 ± 0.30	−30.3	185.6	206.0	
	1.58[c]	210.7 ± 1.2	12.60 ± 0.09	−18.8	205.1	245.7	
Ethyl benzoyl formate $C_6H_5COCOOCH_2CH_3$	18.48[a]	205.8 ± 7.6	13.24 ± 0.60	−6.6	200.2	204.6	[f]
	11.80[b]	203.8 ± 9.0	12.89 ± 0.72	−13.2	198.2	207.1	
	6.83[e]	213.3 ± 3.9	13.39 ± 0.31	−3.7	207.7	216.9	
Ethyl oxamate $H_2NCOCOOCH_2CH_3$	29.5[a]	203.7 ± 2.5	13.28 ± 0.20	−5.79	198.1	202.0	12
	20.0[d]	208.0 ± 2.8	13.44 ± 0.22	−2.73	202.4	204.2	
	9.77[e]	195.9 ± 2.3	12.19 ± 0.18	−26.7	190.3	208.3	
Ethyl *N,N*-Dimethyl oxamate$(CH_3)_2NCOCOOCH_2CH_3$	10.2[a]	206.8 ± 4.4	13.06 ± 0.34	−10.0	201.2	207.9	12
Ethyl oxanilate $C_6H_5NHCOCOOCH_2CH_3$	57.9[a]	207.4 ± 1.5	13.86 ± 0.12	5.31	201.8	198.2	12
	42.0[d]	205.2 ± 2.2	13.55 ± 0.18	−0.62	199.6	200.0	
	15.6[e]	214.1 ± 2.2	13.81 ± 0.18	4.36	208.5	205.6	

[a] Overall rate.
[b] Rate of decarboxylation.
[c] Rate of decarbonylation.
[d] Rate of ethanol formation.
[e] Rate of ethylene formation.
[f] This work.

a relative standard deviation not greater than $\pm$5% at a given temperature.

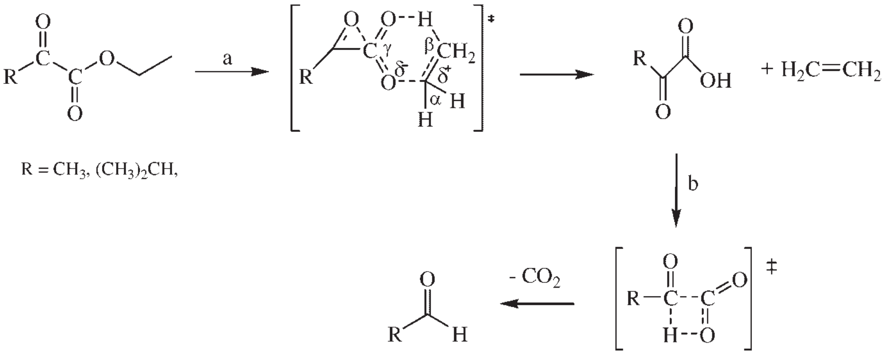
The rate coefficients were invariable to the initial pressure of the substrate chromatographic analyses (Table 5). The variation of the rate coefficients with temperature is shown in Table 6. The experimental data were fitted to the Arrhenius equation shown in Table 6 (Fig. 3), where 90% confidence limits from an unweighted least-squares procedure are given.

The kinetic and thermodynamic parameters of several ethyl esters of 2-oxo-acids reported in the literature, together with the present data, at 400 °C, are collected and shown in Table 7. The information given in Table 7 suggests, to some extent, that several types of reaction mechanisms occur in the decomposition of 2-oxo-esters. The various pathways are depicted in reaction (14). Compounds with electron-releasing groups CH_3 (ethyl 2-oxo-propionate) and $(CH_3)_2CH$ (3-methyl-2-oxo-butyrate) decompose as organic esters to produce the corresponding carboxylic acid and ethylene (14a), where the elongation and subsequent polarization of the C—O bond, in the sense $C_{\alpha}^{\delta+}....O^{\delta-}$, is the rate determining step. The corresponding 2-oxo-acids and ethylene are formed via six-membered cyclic transition state [reaction (14a)]. These oxo-acids, under the reaction conditions, are unstable and rapidly decarboxylate as reported before[10,11] to give the corresponding aldehyde. The product intermediate 2-oxo-propionic acid or pyruvic acid, from the elimination of ethyl 2-oxo-propionate [reaction (14a)], undergoes decomposition in the gas phase[14] into acetaldehyde and CO_2 in a few seconds at temperatures of 284–334 °C with an Arrhenius expression of $\log k_1(s^{-1}) = 13.53 - 172.4\,kJ\,mol^{-1}\,(2.303\,RT)^{-1}$. These data suggest the pyruvic acid intermediate, under the condition of the present work, will decarboxylate rapidly. To rationalize the rate increase caused by electron releasing alkyl groups CH_3 and $(CH_3)_2CH$ of the oxy-esters, one may invoke nucleophilic assistance of the oxygen carbonyl leading to charge stabilization of the incipient positive C_γ in the transition state [reaction (15)]. Thus, 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_γ, and the faster the rate of elimination. In contrast to the above, electron-withdrawing substituents Cl (ethyl oxalyl chloride), and NH_2 (ethyl oxamate), C_6H_5NH (ethyl oxanilinate), C_5H_5N (ethyl piperidine glyoxylate), and C_6H_5 (ethyl benzoyl formate) lead to decarbonylation[12,13] via (14c). The presence of an H attached to the nitrogen substituent may lead to subsequent elimination of ethanol (14d) or ethylene (14e). Surprisingly, the exception is $Z = (CH_3)_2N$ in ethyl *N*,*N*-dimethyl oxamate, because no migration of this substituent to the carboethoxy group takes place [reaction (14)]. Apparently, some re-examination of the elimination kinetics of these compounds may be needed to confirm the reported results.



(14)

In the case of Z = H (ethyl glyoxalate) gives a parallel decomposition (14a, 14c), where reaction (14a) is more important than reaction (14c). Because of the apparent electron-withdrawing property of H, this atom undergoes a little migration to the carboethoxy group (14c). This fact finds support from Taft original substituent effect of H,[15] $\sigma^* = +0.49$. Consequently, a small amount of decarbonylation (14c) occurs.



(15)

CONCLUSIONS

The gas-phase elimination kinetics of ethyl oxalyl chloride, ethyl piperidineglyoxilate, and ethyl benzoyl formate has been found to be homogeneous, unimolecular, and follow a first-order rate law.

Ethyl oxalyl chloride undergoes only decarboxylation process, while ethyl piperidineglyoxilate and ethyl benzoyl formate proceed to a parallel decomposition of decarboxylation and decarbonylation reactions.

The mechanisms of these decomposition reactions are described in terms of concerted discrete polar cyclic transition state structures.

EXPERIMENTAL

The substrates ethyl oxalyl chloride (98%) and ethyl piperidine glyoxalate (99%) were acquired from Acros Organics, while ethyl benzoyl formate (99%) from Aldrich. The identification and purity of these substrates were verified by GC-MS: Saturn 2000, Varian, with a DB-5MS capillary column 30 m × 0.25 mm. i.d., 0.25 μm film thickness. The products ethyl chloroformate, piperidine, piperidine formate, benzaldehyde, ethyl benzoate, ethylene, and carbon dioxide were identified in a GC-MS (Saturn 2000, Varian) with a DB-5MS capillary column 30 m × 0.25 mm. i.d., 0.25 μm. Analysis of the products ethylene (Matheson) and CO_2 was carried out by using a Gas Chromatograph Varian 3600× with a thermal conductivity detector (capillary column: GS-Q, 30 m long and 0.53 id., Helium gas carrier). Ethyl chloroformate, ethyl benzoyl formate, and benzaldehyde were quantitatively analyzed using a chromatograph Hewlett-Packard Model 5710-A with a flame ionization detector and a 2 m packed column of 10% SP-1200, 1% H_3PO_4 Chromosorb WAW 80/100 mesh. Ethyl piperidineglyoxylate, piperidine, and piperidine formate were analyzed in the same Hewlett-Packard 5710-A, but with a 1.5 m packed column of Chromosorb 103 100/120 mesh.

Kinetics

The kinetic experiments were performed in a static reaction system as previously reported.[16–18] The reactor was seasoned by the decomposition product of allyl bromide. The rate coefficients of ethyl oxalyl chloride were calculated from the pressure increased manometrically, according to following equation described below:

$$k_1 = -(2.303/t)\ \log\left[(2P_0 - P_t)/P_0\right]$$

or by the quantitative chromatographic analyses of ethyl chloroformate, thus

$$k_1 = -(2.303/t)\ \log\left[(P_0 - P_{\text{ethyl chloroformare}})/P_0\right]$$

The rate of decomposition of ethyl piperidineglyoxylate is given by Eqn (1) [reaction (12)]:

$$k_{\text{Total}} = -\frac{1}{t}\ln\left(\frac{P_{\text{Substrate}}}{P_0}\right) \tag{1}$$

For piperidine formate [reaction (12a)]

$$\frac{dP_{\text{piperidine formate}}}{dt} = k_{a(\text{piperidine formate})}\left(P_{\text{Substrate}}\right) \tag{2}$$

For piperidine [Eqn (3)]

$$\frac{dP_{\text{piperidine}}}{dt} = k_{b(\text{piperidine})}\left(P_{\text{Substrate}}\right) \tag{3}$$

Therefore, the ratio of piperidine formate/piperidine is shown in Eqn (4)

$$\frac{P_{\text{piperidine formate}}}{P_{\text{piperidine}}} = \frac{k_{a(\text{piperidine formate})}}{k_{b(\text{piperidine})}} \tag{4}$$

The values of the rate coefficients of product formation $k_{\text{a(piperidine formate)}}$ and $k_{\text{b(piperidine)}}$ were determined by Eqn (5)

$$\begin{cases} \text{k}_{\text{Total}} = \text{k}_{\text{a(piperidine formate)}} + \text{k}_{\text{b(piperidine)}} \\ \dfrac{k_{a(\text{piperidine formate})}}{k_{b(\text{piperidine})}} = \dfrac{P_{\text{piperidine formate}}}{P_{\text{piperidine}}} \end{cases} \tag{5}$$

The rate of piperidine formation is given by the following expression [Eqn (6)]:

$$k_{b(\text{piperidine})} = P_0\frac{k_{b(\text{piperidine})}}{k_{\text{Total}}}\left(1 - e^{-k_{\text{Total}}t}\right) \tag{6}$$

Substituting Eqn (6) in Eqn (5), we obtain the rate of formation of piperidine formate [Eqn (7)]

$$k_{a(\text{piperidine formate})} = \frac{P_{(\text{piperidine formate})} k_{\text{Total}}}{(1 - e^{-k_{\text{Total}} t})} \qquad (7)$$

In the case of piperidine formation, the $k_{\text{piperidine}}$ is calculated as shown in Eqn (8)

$$k_{\text{piperidine}} = k_{\text{Total}} - k_{\text{piperidine formate}} \qquad (8)$$

Because the intermediate ethyl piperidine carboxylate from (12b) decomposes rapidly above the reported pyrolysis temperatures (341–391 °C) into piperidine, ethylene, and CO_2,[19], the parallel reaction (12b) was possible to calculate according to Eqn (8).

With regard to ethyl benzoyl formate, the estimation of rate coefficients was made by using the similar equations as in ethyl piperidineglyoxylate [Eqn (1)–(8)], but substituting in the above equations the subscript piperidineformate by benzaldehyde, and piperidine by CO formation.

The temperature was controlled by a Shinko DC-PS resistance thermometer controller maintained at ±0.2 °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 ~0.05–0.2 ml.

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