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Kinetics of the homogeneous, unimolecular elimination reactions of ethyl oxamate, ethyl *N*,*N*-dimethyloxamate and ethyl oxanilate in the gas phase

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ABSTRACT: The gas-phase elimination kinetics of the title compounds were determined over the temperature range 350–430 °C and pressure range 35–240 Torr (1 Torr = 133.3 Pa). The reactions, which were carried out in a static reactor system, seasoned with allyl bromide and in the presence of a free radical inhibitor, are homogeneous, unimolecular and obey a first-order rate law. The temperature dependences of the overall rate coefficients are given by the following Arrhenius equations: for ethyl oxamate, $\log [k_1\ (\mathrm{s}^{-1})] = (13.28 \pm 0.20) - (203.7 \pm 2.5)\ \mathrm{kJ\ mol}^{-1} (2.303RT)^{-1}$, for ethyl *N*,*N*-dimethyloxamate, $\log [k_1\,(\mathrm{s}^{-1})] = (13.06 \pm 0.34) - (206.8 \pm 4.4)\ \mathrm{kJ\ mol}^{-1}(2.303RT)^{-1}$, and for ethyl oxanilate, $\log [k_1\,(\mathrm{s}^{-1})] = (13.86 \pm 0.12)–(207.4 \pm 1.5)\ \mathrm{kJ\ mol}^{-1}(2.303RT)^{-1}$. The overall rates, the partial rates and the kinetic and thermodynamic parameters of these eliminations are presented and discussed. These reactions appear to proceed through moderately polar cyclic transition states. Copyright © 2004 John Wiley & Sons, Ltd.

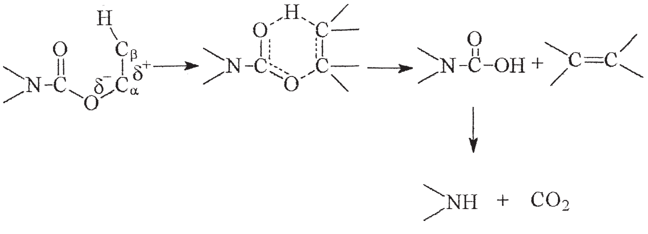
KEYWORDS: pyrolysis; elimination; kinetics; ethyl oxamate; ethyl *N*,*N*-dimethyloxamate; ethyl oxanilate

INTRODUCTION

Ethyl *N*-methyl-*N*-phenylcarbamate was the first carbamate substrate to be pyrolyzed in the gas phase.[1] This compound was found to produce *N*-methylaniline, ethylene and carbon dioxide [reaction (1)].

$$\mathrm{Ph(CH_3)NCOOCH_2CH_3 \rightarrow PhNHCH_3 + H_2C = CH_2 + CO_2} \tag{1}$$

Additional work on the elimination kinetics of *N*,*N*-dimethylcarbamates led researchers to consider a generally accepted mechanism of a six-membered cyclic transition state similar to those described for acetates, carbonates and xanthates[1–6] [reaction (2)].

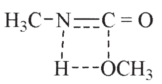


(2)

A carbamate with a hydrogen atom at the nitrogen and without a C_β—H bond at the alkyl side of the ester, such as methyl *N*-methylcarbamate,[7] yielded elimination products which differ from those of ethyl *N*-methyl-*N*-phenylcarbamate[1] [reaction (3)].

$$\mathrm{CH_3NHCOOCH_3 \rightarrow CH_3NCO + CH_3OH} \tag{3}$$

Apparently, the H atom attached to nitrogen was considered to be responsible for a different mechanistic pathway, and the decomposition process was rationalized in terms of a four-membered cyclic transition state, shown in Scheme 1.[7]



Scheme 1

Kwart and Slutsky suggested from ethyl *N*,*N*-dimethylcarbamate pyrolyses[6,8] that carbamate decomposition proceeds through an intermediate whose structure lies between a semi-concerted six-membered cyclic transition state and an intimate ion-pair type of mechanism. Further work on the elimination kinetics of 2-alkyl-2-substituted ethyl *N*,*N*-diethylcarbamates[9] revealed a rate enhancement of ethylene elimination in the order *tert*-butyl > isopropyl > ethyl, which is consistent with the sequence

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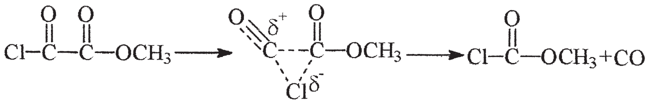
of the comparative rates for the corresponding 2-alkyl-2-substituted-ethyl *N*,*N*-dimethylcarbamates.[10] The results of these eliminations suggested that C_α—O bond polarization, in the direction $C_\alpha^{\delta+}$—$O^{\delta-}$, is important and that the mechanism proceeds according to reaction (2).

The presence of phenyl and bulky groups at the N atom of ethyl carbamates was found to decrease the rate of elimination due to steric factors.[11] The application of various correlations methods[12,13] such as the steric parameters Hancock's E_s^c, Taft's E_s, Charton's ν, the inductive σ_I values and the Taft–Topsom equation for a considerable number of 2-substituted-ethyl *N*,*N*-dimethylcarbamates,[12] $(CH_3)_2NCOOCH_2CH_2Z$, gave random points with no meaning for mechanistic interpretation. However, the plotting of log (k_Z/k_{CH_3}) against the original Taft σ^* values[13] gave rise at the origin $[\sigma^*(CH_3) = 0.00]$ to three good straight lines. This result implied that small alterations in the polarity of the transition state may be due to changes in electronic transmission at the reaction center. This means that a simultaneous effect may be operating during the process of elimination. The mechanisms were described according to each slope of the straight lines. Moreover, the point positions of Z = phenyl (C_6H_5) and isopropenyl $[CH_2{=}C(CH_3)]$ substituents were found to fall far above the three lines. These substituents were demonstrated to enhance the rate of elimination due to the acidity of the benzylic and allylic C_β—H bond.[14]

With this background and with the literature described below, it was of interest to investigate a related type of carbamate molecule, such as one with the interposition of a carbonyl group (C=O) between the N atom and the acid side of the carbonyl ester, that is, $R_2NCOCOOCH_2CH_3$. Therefore, the substrates to be examined were ethyl oxamate $(H_2NCOCOOCH_2CH_3)$, ethyl *N*,*N*-dimethyloxamate $[(CH_3)_2NCOCOOCH_2CH_3]$ and ethyl oxanilate $(PhNHCOCOOCH_2CH_3)$. The substrates containing at least an H atom attached to N may proceed in one step via a five-membered cyclic transition state to yield CO gas, ethanol and the corresponding isocyanate. However, as organic esters, they are expected to produce ethylene gas and the corresponding 2-oxo acid intermediates. These acid intermediates decarboxylate in a similar to that observed for pyruvic and benzoyl formic acids [reaction (4)].[15,16] Another possible path of elimination can be related to a recent publication on the pyrolysis kinetics of methyl oxalyl chloride[17] [reaction (5)], i.e. decarbonylation is the first step of oxamate elimination, after which the resulting carbamate decomposes to isocyanate and ethanol and/or ethylene gas and the unstable carbamic acid.

$$RCOCOOH \rightarrow RCHO + CO_2 \qquad (4)$$

$$R = Me, C_6H_5$$



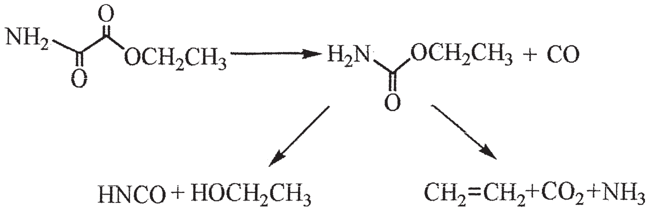
(5)

Two additional literature references have been found useful in the conception of the present research work. These are the study of the kinetics of CO_2 elimination from oxamic acid in several solvents[18–20] and the kinetics and stoichiometry of oxalic acid decomposition in the gas phase.[21]

RESULTS AND DISCUSSION

Ethyl oxamate

The products of decomposition of ethyl oxamate in a vessel seasoned with allyl bromide are ethanol and isocyanic acid and, in slightly less amounts, ethylene, CO_2 and ammonia, by reaction (6).



(6)

The theoretical stoichiometry in reaction (6) for the molecular elimination of this substrate where pathways A and B occur equally requires that the final pressure, P_f, be 3.5 times the initial pressure, P_0. The average experimental value of P_f/P_0 at four different temperatures and 10 half-lives is 3.3 (Table 1). The fact that $P_f/P_0 < 3.5$ can be attributed to the fact that the ethyl carbamate intermediate of reaction (6) does not decompose equivalently to five products (see Table 6). However, it was possible to corroborate the stoichiometry of reaction (6), up to 76% decomposition, by comparing the percentage decomposition of the substrate from pressure measurements with those obtained from the sum of the gas chromatographic (GC) analyses of the products ethanol and ethylene (Table 2). The reaction appears to be homogeneous since no significant effects on rates were obtained on using both clean and seasoned Pyrex vessels with a surface-to-volume ratio of 6.0 relative to normal, which is equal to 1.0 (Table 3). The addition of different proportions of propene, an effective free radical inhibitor, had no effect on the rates and no induction period was obtained (Table 4). The rates are reproducible with a standard deviation of <5% at a given temperature.

In view of the stoichiometry of reaction (6), where P_f/P_0 is nearly 3, the rate coefficients for elimination, calculated from $k_1 = (2.303/t)\log[2P_0/(3P_0 - P_t)]$, are

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

Compound	Temperature (°C)	P_0 (Torr)[a]	P_f (Torr)[a]	P_f/P_0	Average
Ethyl oxamate	370.3	44.8	141.8	3.2	3.3
	380.9	40.5	134.5	3.3	
	390.4	29.0	95.0	3.3	
	400.1	27.6	93.6	3.4	
Ethyl *N*,*N*-dimethyloxamate	400.2	108	302	2.8	2.8
	408.0	104	288	2.8	
	418.7	88	238	2.7	
	429.7	88	246	2.8	
Ethyl oxanilate	359.2	30.0	91.0	3.0	2.9
	370.9	76.0	225	3.1	
	378.9	54.0	147.5	2.7	
	391.7	76.0	205.0	2.7	

[a] 1 Torr = 133.3 Pa.

Table 2. Stoichiometry of pyrolysis reactions

Compound	Temperature (°C)	Parameter	Value			
Ethyl oxamate	380.9	Time (min)	5	10	15	20
		Reaction (%) (pressure)	25.5	43.5	55.0	76.2
		Ethylene (%) (GC)	9.3	15.1	20.1	26.1
		Ethanol (%) (GC)	17.8	26.3	34.0	49.4
		Sum (%) (GC)	27.1	41.4	54.1	75.5
Ethyl *N*,*N*-dimethyloxamate	408.0	Time (min)	4.5	7	8.5	20
		Reaction (%) (pressure)	38.7	51.2	63.6	81.6
		Ethylene (%) (GC)	34.0	53.1	64.1	82.3
Ethyl oxanilate	378.9	Time (min)	3	5	10	15
		Reaction (%) (pressure)	27.3	42.9	64.3	72.4
		Ethylene (%) (GC)	4.9	13.1	18.2	19.0
		Ethanol (%) (GC)	19.5	32.9	44.1	54.3
		Sum (%) (GC)	24.4	46.0	62.3	73.3

found to be invariant to the initial pressures (Table 5), and agree with the sum of the k values from the ethanol and ethylene analyses (Table 2).

The above-mentioned equation is the expression for the formation of three products, and the rate coefficients were calculated as follows:

$$\begin{array}{cccc} \mathrm{A} \rightarrow & \mathrm{B} + & \mathrm{C} + & \mathrm{D} \\ P_0 - P & P & P & P \end{array}$$

If P_0 = initial pressure, P = pressure at time t and P_T = total pressure, then

$$\begin{aligned} P_T &= P_0 - P + P + P + P = P_0 + 2P \\ P &= (P_T - P_0)/2 \end{aligned}$$

Since

$$k = -1/t \ln(C/C_0)$$

where C_0 = initial concentration and C = concentration at time t,

$$C_0 = P_0 \text{ and } C = P_0 - P = [P_0 - (P_T - P_0)/2]$$

$$C = (2P_0 - P_T + P_0)/2 = (3P_0 - P_T)/2$$

Table 3. Homogeneity of pyrolysis reactions

Compound	S/V (cm^{-1})[a]	$10^4\ k_1$ (s^{-1})[b]	$10^4\ k_1$ (s^{-1})[c]
Ethyl oxamate at 390.4 °C	1	16.9 (±0.4)	16.7 (±0.8)
	6	17.6 (±0.3)	17.5 (±0.3)
Ethyl *N*,*N*-dimethyloxamate at 400.2 °C	1	10.9 (±0.4)	10.4 (±0.3)
	6	10.6 (±0.3)	10.5 (±0.4)
Ethyl oxanilate at 370.4 °C	1	10.3 (±0.3)	10.8 (±0.4)
	6	10.0 (±0.2)	10.2 (±0.5)

[a] S = surface area; V = volume.
[b] Clean Pyrex vessel.
[c] Vessel seasoned with allyl bromide.

Table 4. Effect of free radical inhibitors on pyrolysis reactions[a]

Substrate	Temperature (°C)	P_s[b] (Torr)	P_i[c] (Torr)	P_i/P_s	$10^4 k_1$ (s^{-1})
Ethyl oxamate[d]	380.9	56	—	—	10.9 (±0.5)
		45	46	1.0	10.1 (±0.2)
		49	39	1.3	10.1 (±0.7)
		51	33	1.6	10.6 (±0.2)
Ethyl *N*,*N*-dimethyloxamate[e]	408.0	85	—	—	16.0 (±0.4)
		82	108	1.3	17.0 (±0.64)
		82	162	2.0	17.1 (±0.3)
		88	250	2.8	17.7 (±0.6)
Ethyl oxanilate[d]	370.5	76	—	—	11.3 (±0.2)
		36	27	1.3	11.2 (±0.4)
		42	28	1.6	10.3 (±0.2)
		38	85	2.2	10.3 (±0.4)

[a] Propene or toluene inhibitor.
[b] P_s, pressure of the substrate.
[c] P_i, pressure of the inhibitor.
[d] Propene inhibitor was used.
[e] Toluene inhibitor was used.

Table 5. Variation of rate coefficients with initial pressure

Compound	Temperature (°C)	Parameter	Value			
Ethyl oxamate	380.9	P_0 (Torr)	37	45	49	51
		$10^4 k_1$ (s^{-1})	10.5 (±0.5)	10.1 (±0.2)	10.1 (±0.7)	10.6 (±0.2)
Ethyl *N*,*N*-dimethyloxamate	420.2	P_0 (Torr)	71	130	169	240
		$10^4 k_1$ (s^{-1})	27.7 (±0.8)	26.6 (±0.9)	26.7(±0.8)	27.1 (±1.0)
Ethyl oxanilate	378.9	P_0 (Torr)	35	41	44	54
		$10^4 k_1$ (s^{-1})	19.1 (±0.3)	18.0 (±0.2)	18.8 (±0.3)	18.5 (±0.5)

Consequently,

$$k = (-1/t)\ln[(3P_0 - P_T)/2P_0]$$

Changing sign:

$$k = (1/t)\ln[2P_0/(3P_0 - P_T)]$$

or

$$k = (2.303/t)\ \log[2P_0/(3P_0 - P_T)]$$

The temperature dependence of the overall and partial rates of product formation [reaction (6), Table 6] gives, by the least-squares procedure and with a 90% confidence limit, the following Arrhenius equations:

$$\text{Ethyl oxamate}: \log[k(s^{-1})] = (13.28 \pm 0.20) - (203.7 \pm 2.5)\text{kJ mol}^{-1}(2.303RT)^{-1}, r = 0.9998$$

$$\text{Ethanol formation}: \log[k(s^{-1})] = (13.44 \pm 0.22) - (208.0 \pm 2.8)\text{kJ mol}^{-1}(2.303RT)^{-1}, r = 0.9997$$

$$\text{Ethylene formation}: \log[k(s^{-1})] = (12.19 \pm 0.18) - (195.9 \pm 2.3)\text{kJ mol}^{-1}(2.303RT)^{-1}, r = 0.9998$$

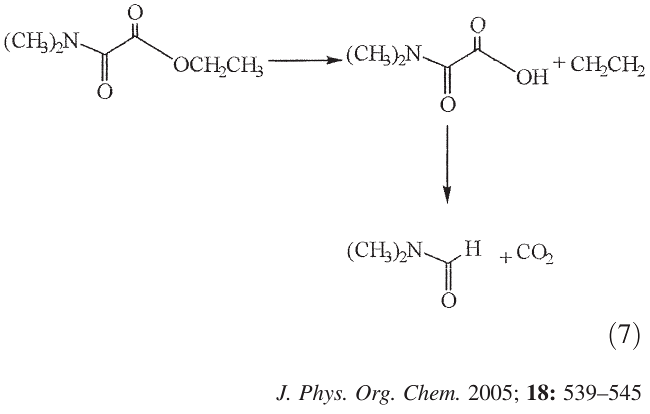
Table 6. Temperature dependence of the rate coefficients of ethyl oxamate

	$10^4 k$ (s^{-1})		
T (°C)	Chromatography[a]	Ethanol[b]	Ethylene[c]
359.5	2.91	1.86 (±0.1)	1.05 (±0.1)
370.3	5.43	3.47 (±0.1)	1.96 (±0.1)
380.9	10.1	6.60 (±0.2)	3.52 (±0.2)
390.4	17.2	11.4 (±0.3)	5.80 (±0.2)
400.1	30.6	20.4 (±0.3)	10.2 (±0.2)

[a] Sum of the rate coefficients obtained from the quantitative chromatographic analyses of ethanol and ethylene.
[b] Rate from quantitative chromatographic analysis of ethanol formation.
[c] Rate from quantitative chromatographic analysis of ethylene formation.

Ethyl *N,N*-dimethyloxamate

The elimination products of ethyl *N*,*N*-dimethyloxamate are dimethylformamide, ethylene and CO gas [reaction (7)].



(7)

The theoretical stoichiometry suggests a P_f/P_0 ratio of 3. The average experimental P_f/P_0 value at four temperatures and 10 half-lives is 2.8 (Table 1). The small departure of the stoichiometry of reaction (7) from the theoretical value may be due to some polymerization of the substrate or the products. Additional verification of the stoichiometry of reaction (7), up to 80% decomposition, was obtained by comparing the pressure measurements with the quantitative GC analysis of ethylene formation (Table 2). Elimination reaction (7) is homogeneous (Table 3), since no significant variation in the rate coefficients was obtained in these experiments when using both clean Pyrex and seasoned Pyrex vessels with a surface-to-volume ratio of 6.0 to both normal clean Pyrex and seasoned Pyrex vessels, which are equal to 1.0. The effect of the addition of different proportions of toluene inhibitor is shown in Table 4. Therefore, the elimination experiments were carried out in the presence of at least twice the amount of toluene with respect to the substrate in order to prevent any possible free radical chain reactions. The rate coefficients were reproducible with a standard deviation not greater than 5% at a given temperature.

The first-order rate coefficients of this substrate calculated from $k_1 = (2.303/t) \log 2P_0/(3P_0 - P_t)$ was independent of initial substrate pressure (Table 5). A plot of $\log(3P_0 - P_t)$ against time (t) gave a good straight line for up to 80% reaction. The variation of the rate coefficients with temperature is given in Table 7 (90% confidence limits from a least-squares procedure) with the following Arrhenius expression:

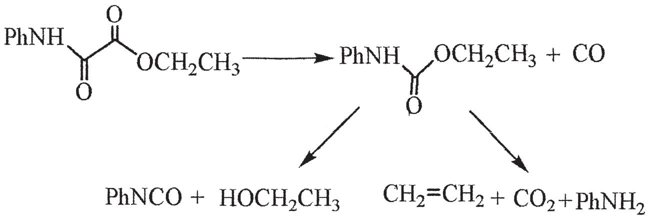
$$\text{Ethyl } N,N-\text{dimethyloxamate}: \log[k_1(\text{s}^{-1})] = (13.06 \pm 0.34) - (206.8 \pm 4.4)\,\text{kJ mol}^{-1}(2.303RT)^{-1},\quad r = 0.9991$$

Ethyl oxanilate

The products from this pyrolysis reaction are phenyl isocyanate and ethanol, and, in lesser amounts, aniline, ethylene and carbon dioxide from ethyl oxanilate [reaction (8)].

Table 7. Temperature dependence of the rate coefficients of ethyl *N*,*N*-dimethyloxamate

T (°C)	$10^4 k$ (s^{-1})
377.8	2.93 (±0.1)
389.1	5.69 (±0.2)
400.2	10.4 (±0.3)
408.0	17.4 (±0.3)
418.7	27.0 (±0.9)
429.7	49.7 (±0.9)



(8)

Apparently, the theoretical stochiometry, on the assumption of 1:1 parallel elimination, requires $P_f/P_0 = 3.5$. However, the average experimental P_f/P_0 value at four temperatures and 10 half-lives was 2.9 (Table 1). The result is evidently not a 1:1 ratio of parallel decomposition of the substrate. Therefore, the confirmation of the stoichiometry of reaction (8), up to 72% decomposition, was possible by comparing the pressure measurements with the sum of the quantitative (GC) analyses of the ethanol and ethylene formation (Table 2). The homogeneity of this reaction was examined in a vessel with a surface-to-volume ratio 6.0 times greater than normal, and determined as equal to 1.0 (Table 3). The packed and unpacked clean and seasoned Pyrex vessels showed no difference in rates. Therefore, reaction (8) may be said to be homogeneous. The effect of adding different proportions of propene inhibitor is shown in Table 4. According to this result, the pyrolysis experiments had to be carried out in the presence of at least twice the amount of propene with respect to this substrate in order to prevent any possible radical reactions. No induction period was observed and the rates were reproducible with a relative standard deviation not greater than 5% at a given temperature.

The rate coefficient of this elimination was found to be independent of initial pressures (Table 5), and the first-order rate coefficient estimated from $k_1 = (2.303/t) \log[2P_0/(3P_0 - P_t)]$ agrees with the sum of the k-values for ethylene and ethanol formation. The variation of the overall and partial rate coefficients with temperature is given in Table 8 [reaction (8)], and the corresponding Arrhenius equations are expressed as follows (90% confidence coefficient from the least-squares procedure):

Table 8. Variation of rate coefficient of ethyl oxanilate

	$10^4 k$ (s^{-1})		
T (°C)	Chromatography[a]	Ethanol[b]	Ethylene[c]
350.4	3.08	2.34 (±0.1)	0.74 (±0.0)
359.2	5.30	3.95 (±0.2)	1.35 (±0.0)
370.4	10.6	8.00 (±0.2)	2.60 (±0.1)
379.5	18.3	13.5 (±0.2)	4.80 (±0.1)
391.0	35.2	26.0 (±0.5)	9.20 (±0.3)

[a] Sum of the rate coefficients obtained from the quantitative chromatographic analyses of ethanol and ethylene.
[b] Rate from quantitative chromatographic analysis of ethanol formation.
[c] Rate from quantitative chromatographic analysis of ethylene formation.

Table 9. Kinetic and thermodynamic parameters of $ZCOCOOCH_2CH_3$ at 400 °C

Z	Reaction	$k \times 10^{-4}$ (s^{-1})	E_a ($kJ\,mol^{-1}$)	Log [A (s^{-1})]	$\Delta S^{\neq}$ ($J\,mol^{-1}\,K)^{-1}$	$\Delta H^{\neq}$ ($kJ\,mol^{-1}$)	$\Delta G^{\neq}$ ($kJ\,mol^{-1}$)
$N(CH_3)_2$	Overall rate	10.2	206.8 ± 4.4	13.06 ± 0.34	−10.0	201.2	207.9
NH_2	Overall rate	29.5	203.7 ± 2.5	13.28 ± 0.20	−5.79	198.1	202.0
	Ethanol formation	20.0	208.0 ± 2.8	13.44 ± 0.22	−2.73	202.4	204.2
	Ethylene formation	9.77	195.9 ± 2.3	12.19 ± 0.18	−26.7	190.3	208.3
PhNH	Overall rate	57.9	207.4 ± 1.5	13.86 ± 0.12	5.31	201.8	198.2
	Ethanol formation	42.0	205.2 ± 2.2	13.55 ± 0.18	−0.62	199.6	200.0
	Ethylene formation	15.6	214.1 ± 2.2	13.81 ± 0.18	4.36	208.5	205.6

$$\text{Ethyl oxanilate} : \log[k(s^{-1})] = (13.86 \pm 0.12) - (207.4 \pm 1.5)\text{kJ mol}^{-1}(2.303RT)^{-1}, r = 0.9999$$

$$\text{Ethanol formation} : \log[k(s^{-1})] = (13.55 \pm 0.18) - (205.2 \pm 2.2)\text{kJ mol}^{-1}(2.303RT)^{-1}, r = 0.9998$$

$$\text{Ethylene formation} : \log[k(s^{-1})] = (13.81 \pm 0.18) - (214.1 \pm 2.2)\text{kJ mol}^{-1}(2.303RT)^{-1}, r = 0.9999$$

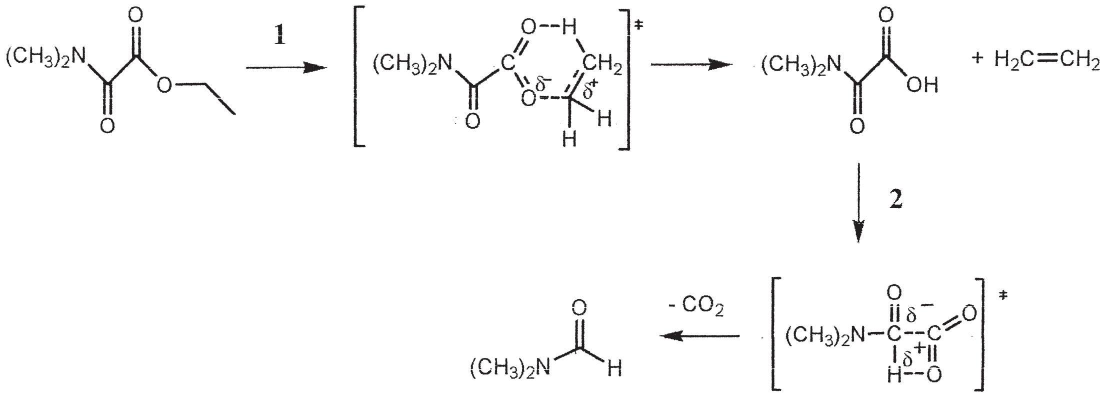
The kinetic and thermodynamic parameters for the overall and parallel eliminations of the several ethyl esters of oxamic acid derivatives are given in Table 9. According to these data and the formation of the products of ethyl *N,N*-dimethyloxamate [Table 9, reaction (9)], which has no H atom bonded to N, the elimination process of this substrate is similar to that of an alkyl ester of a carboxylic acid, which proceeds through a concerted six-membered cyclic transition state type of mechanism [step 1, reaction (9)]. The 2-oxo acid intermediate at the working temperature is unstable and decarboxylates, as in reaction (4), very rapidly, possibly through a four-membered cyclic transition state [step 2, reaction (9)] to give dimethylformamide.

The elimination products of ethyl oxamate [reaction (6)] and ethyl oxanilate [reaction (8)] and the data in Table 9 suggest decarbonylation to be the first steps of decomposition [reaction (10), step 1]. Apparently, the mechanisms may involve a semi-polar concerted three-membered cyclic transition state similar to that in reaction (5). However, the corresponding ethyl ester intermediate may undergo subsequent fragmentations. Thus, step 2 leads to the formation of an isocyanate, perhaps through a concerted four-membered cyclic transition state, while step 3 affords ethylene and the corresponding carboxylic acid. This acid intermediate could then decarboxylate by way of a concerted cyclic four-membered transition state (step 4). The fact that the partial rate coefficient for the formation of phenyl isocyanate from ethyl oxanilate is greater than that for the formation of isocyanic acid from ethyl oxamate (Table 9) may be due to the more facile abstraction of a hydrogen atom from the PhNH group than from NH_2 group (step 2).

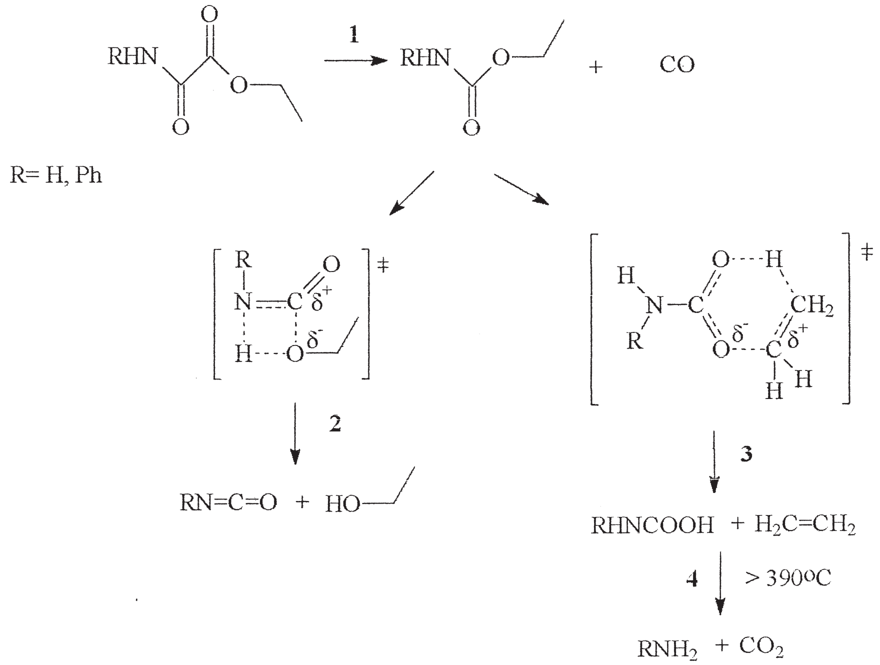
Because of the different elimination pathways in the *N,N*-dimethyloxamate pyrolysis, the overall rate coefficient of this substrate cannot be compared with the overall *k* values for ethyl oxamate and ethyl oxanilate (Table 9). This result is surprising, since decarbonylation was expected to be the first step of the reaction. Further studies relative to the influence of the $(CH_3)_2N$ group in the ethyl ester of the 2-oxocarboxylic acid may be needed in order to explain the difference in mechanism.

EXPERIMENTAL

Ethyl oxamate (Aldrich), ethyl *N,N*-dimethyloxamate (Aldrich) and ethyl oxanilate (Aldrich) of >98% purity were employed [GC–MS: Varian Saturn 2000 with a DB-5MS capillary column (30 m × 0.53 mm. i.d., 0.53 μm film thickness)]. The products of ethyl oxamate, which are hydrocyanic acid, ammonia, carbon dioxide, ethylene and ethanol, were identified as gases by GC–MS (Varian Saturn 2000) with a DB-5MS capillary column (30 m ×



(9)



(10)

0.25 mm. i.d., 0.25 μm). The quantitative analysis of the product ethylene (Matheson) was carried out by using an HP 5710A gas chromatograph with a Porapak Q (80–100 mesh) column. Ethanol (Merck) was quantitatively analyzed by using a 3 m column of Porapak S (80–100 mesh).

Phenyl isocyanate and aniline as products of ethyl oxanilate were identified as 1,3-diphenylurea and some amount of phenyl isocyanate. 1,3-Diphenylurea results from condensation of phenyl isocyanate with aniline when collected in the trap. However, ethanol and ethylene were collected as gases and quantitatively analyzed as described above. All these products were identified by GC–MS (Varian Saturn 2000) with a DB-5MS capillary column (30 m × 0.25 mm. i.d., 0.25 μm).

The pyrolysis products of ethyl *N*,*N*-dimethyloxamate were examined and identified as dimethylformamide, ethylene and CO_2 by GC–MS (Varian Saturn 2000).

Kinetics

The kinetic determinations were carried out in a static reaction system as reported previously.[22–24] At each temperature, 6–12 runs were carried out. The rate coefficients were calculated from the pressure increase measured manometrically and/or by the sum of ethylene and ethanol products. The temperature was maintained within ± 0.2 °C through control with a Shinko DIC-PS 23TR resistance thermometer and was measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was observed along the reaction vessel. The starting materials were all injected directly into the reaction vessel with a syringe through a silicone rubber septum. The amount of substrate used for each reaction was ~0.05–0.2 ml.

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