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Kinetics and mechanisms of gas-phase elimination of 2,2-diethoxyethyl amine and 2,2-diethoxy-*N,N*-diethylethanamine

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The gas-phase elimination kinetics of 2,2-diethoxyethyl amine and 2,2-diethoxy-*N,N*-diethylethanamine (320–380 °C; 40–150 Torr) in a seasoned reaction vessel are homogeneous, unimolecular and obey a first-order rate law. These elimination processes involve two parallel reactions. The first gives ethanol and the corresponding 2-ethoxyethenamine. The latter compound further decomposes to ethylene, CO and the corresponding amine. The second parallel reaction produce ethane and the corresponding ethyl ester of an α -amino acid. The following Arrhenius expressions are given as:

For 2,2-diethoxyethyl amine

$$\log k_{\text{I}}(\text{EtOH}) (\text{s}^{-1}) = (13.99 \pm 0.27) - (201.1 \pm 3.2) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}, r = 0.9995$$

$$\log k_{\text{II}}(\text{EtH}) (\text{s}^{-1}) = (13.77 \pm 0.18) - (203.8 \pm 2.1) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}, r = 0.9996$$

$$\log k_{\text{III}}(\text{CH}_2=\text{CH}_2) (\text{s}^{-1}) = (11.88 \pm 0.09) - (172.2 \pm 1.0) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}, r = 0.9996$$

For 2,2-diethoxy-*N,N*-diethylethanamine

$$\log k_{\text{I}}(\text{EtOH}) (\text{s}^{-1}) = (13.94 \pm 0.20) - (202.3 \pm 2.4) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}, r = 0.9995$$

$$\log k_{\text{II}}(\text{EtH}) (\text{s}^{-1}) = (14.03 \pm 0.22) - (203.9 \pm 2.6) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}, r = 0.9996$$

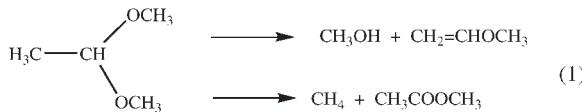
$$\log k_{\text{III}}(\text{CH}_2=\text{CH}_2) (\text{s}^{-1}) = (12.02 \pm 0.19) - (178.1 \pm 2.3) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}, r = 0.9996$$

Comparative kinetic and thermodynamic parameters of the overall, the parallel and the consecutive reactions lead to consider two types of mechanisms in terms of a concerted polar cyclic transition state structures. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: 2,2-diethoxyethyl amine; 2,2-diethoxy-*N,N*-diethylethanamine; kinetics; gas-phase elimination; mechanism

INTRODUCTION

Molera *et al.*^[1] were first to report the gas-phase thermal decomposition of ethylal, dimethyl acetal and diethyl acetal, in a static system, over the temperature range of 389–530 °C. Ethylal was believed to decompose mainly by a chain mechanism. In the case of dimethyl and diethyl acetals a rearrangement process were assumed to be important. Thus, dimethyl acetal reaction was found to follow, up to 50% decomposition, a first-order rate law to yield the products as described in the reaction (1).

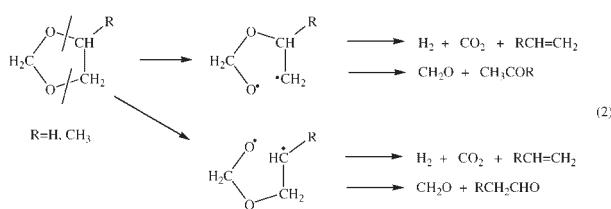


Further works on aliphatic ketals, the gas-phase pyrolysis kinetics of methylal^[2] were carried out at 472–520 °C, while that of ethylene methylal and propylene methylal^[3] were carried out at 512–572 °C. These substrates were thought to proceed through a biradical mechanism as depicted in the reaction (2).

A revisited investigation of methylal thermal decomposition under a dynamic flow system at 600–732 °C^[4,5] showed a more

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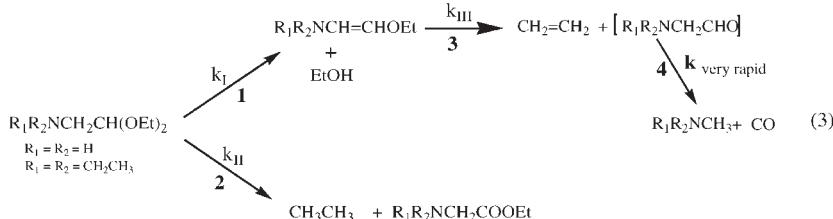


complicated process with different results due to higher working temperature than in the static system. A complex radical reaction takes place even in the presence of inhibitors.

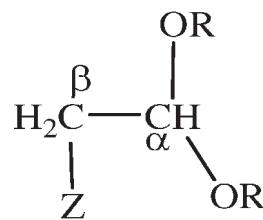
Since the gas-phase thermal decomposition of limited number of ketals have shown to proceed through radical process at very high temperatures, it seemed interesting to study these type of organic compounds under homogeneous and molecular elimination. This means, deactivation of the reaction vessel properly and to suppress any free radical reaction by using an effective inhibitor. Moreover, it was also thought to examine how important is the participation of the hydrogen atom present at the C_{α} —H bond or C_{β} —H bond in the transition state mechanism of ketals described in the Scheme 1. The intramolecular competition for the hydrogen abstraction by the leaving alkoxy nucleophile may define the lability of the C_{β} —H bond in the elimination process. To add more interest in ketals thermal decomposition reaction, the presence of an electron withdrawing substituent such as an amino group at the β -carbon (Scheme 1) may increase the acidities of C_{β} —H bond for a more facile participation. Consequently, the present work aimed at studying the elimination kinetics of some amino ketals in the gas-phase, but through a molecular process. The amino ketals to be examined are 2,2-diethoxyethyl amine and 2,2-diethoxy-*N,N*-diethylethanamine.

RESULTS AND DISCUSSION

The molecular elimination of the amino ketal substrates in the gas-phase is described according to the reaction (3).



The experimental stoichiometry of reaction (3) could not be measured from the ratio of P_f/P_o , where P_f and P_o are the final and initial pressures, respectively. This fact is due to parallel and consecutive process of elimination with both substrates. However, to verify stoichiometry (3) for 2,2-diethoxyethyl amine (Table 1, Fig. 1) and for 2,2-diethoxy-*N,N*-diethylethanamine (Table 2, Fig. 2), up to 85% reaction, was made by comparing the extent of decomposition of the substrate from quantitative chromatographic (GLC) analyses with that obtained from the sum of the quantitative gas chromatographic (GLC) analyses of ethanol and ethane formation at the six different temperatures. Tables 1 and 2 show the quantitative analyses at one of these temperatures (340 °C).



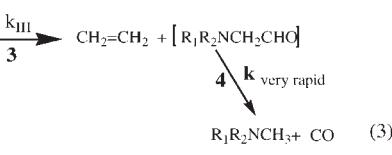
Z = Substituent
 R = Alkyl

Scheme 1. Scheme 1

The effect of the surface on the rate of elimination was examined by carrying out several runs in a vessel packed with small cylindrical glasses, with a surface-to-volume ratio of 6 relative to that of the normal unpacked vessel which is equal to 1. The rates of elimination of both substrates were unaffected in seasoned packed and unpacked vessel. However, clean packed and unpacked Pyrex vessel showed a marked heterogeneous effect on the rate coefficients (Table 3)

The effect of different proportions of the free radical inhibitor cyclohexene on the elimination reactions is given in Table 4. No induction period was observed and the rates were reproducible with a relative standard deviation not greater than 5% at a given temperature.

The total rate coefficients for the amino ketals calculated from $k_{\text{total}} = -(2.303/t) \log [P_{\text{substrate}}/P_0]$ were found to be independent of the initial pressure (Table 5). A plot of $\log (P_{\text{substrate}})$ against time gave a good straight line up to 85% decomposition. The temperature dependence of the total and partial rate coefficients are given in Table 6 (95% confidence coefficients from a least-squares method). Therefore, these reactions, carried out in seasoned vessels, are homogeneous, unimolecular, and follow a first order rate law. The rate coefficient is expressed by the following Arrhenius equations (Figs 3, 4).



For 2,2-diethoxyethyl amine

$$\log k_{1(\text{EtOH})} (\text{s}^{-1}) = (13.99 \pm 0.27) - (201.1 \pm 3.2) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}, r = 0.9995$$

$$\log k_{1(\text{EtOH})} (\text{s}^{-1}) = (13.77 \pm 0.18) - (203.8 \pm 2.1) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}, r = 0.9996$$

$$\log k_{1(\text{EtOH})} (\text{s}^{-1}) = (11.88 \pm 0.09) - (172.2 \pm 1.0) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}, r = 0.9996$$

Table 1. Stoichiometry of 2,2-diethoxyethyl amine at 340 °C

Time (s)	Substrate (chrom.) (%)	Ethanol (chrom.) (%)	Ethane (chrom.) (%)	Ethylene (chrom.) (%)	Substrate (sum EtOH + EtH) ^a (%)
60	5.8	4.1	1.5	0.2	5.6
120	10.1	8.0	3.0	0.7	11.0
180	16.1	11.9	4.4	1.6	16.3
240	20.9	15.2	5.6	2.7	20.8
300	25.1	18.5	6.8	4.0	25.3
360	29.5	21.6	8.0	5.5	29.6
420	34.0	24.5	9.0	7.1	33.5
480	37.1	27.2	10.0	8.9	37.2
900	57.6	42.6	15.7	22.4	58.3
1200	69.9	50.3	18.6	31.8	68.9
1400	75.0	54.3	20.0	37.6	74.3
1600	78.6	57.6	21.3	42.7	78.9
1800	83.1	60.4	22.3	47.2	82.7
1900	84.9	61.5	22.7	49.3	84.2
2000	85.6	62.7	23.0	51.2	85.7

^a Reaction (%) estimated from the sum of (%)ethanol and (%) ethane (GLC) analyses.

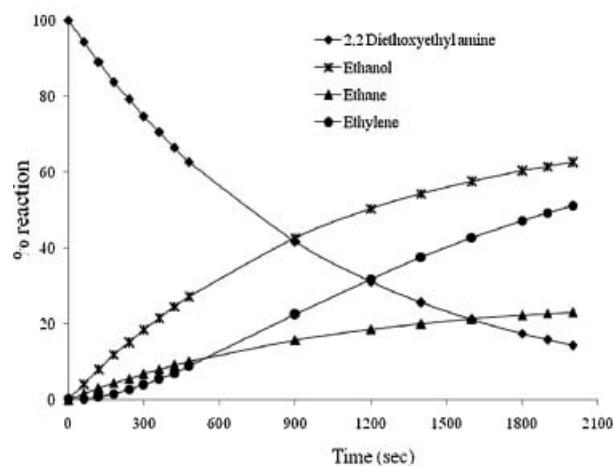


Figure 1. Kinetic profile for gas-phase elimination of 2,2-diethoxyethyl amine at 340 °C

For 2,2-diethoxy-*N,N*-diethylethanamine

$$\log k_{I(EtOH)}(s^{-1}) = (13.94 \pm 0.20) - (202.3 \pm 2.4) \text{ kJ mol}^{-1}$$

$$(2.303 RT)^{-1}, r = 0.9995$$

$$\log k_{II(EtH)}(s^{-1}) = (14.03 \pm 0.22) - (203.9 \pm 2.6) \text{ kJ mol}^{-1}$$

$$(2.303 RT)^{-1}, r = 0.9996$$

$$\log k_{III(CH_2=CH_2)}(s^{-1}) = (12.02 \pm 0.19) - (178.1 \pm 2.3) \text{ kJ mol}^{-1}$$

$$(2.303 RT)^{-1}, r = 0.9996$$

An analysis of Table 7, the results of log A values greater than 13.2 for the formation of ethanol [reaction (4), **Step 1**] and of

Table 2. Stoichiometry of 2,2-diethoxy-*N,N*-diethylethanamine at 340 °C

Time (s)	Substrate (chrom.) (%)	Ethanol (chrom.) (%)	Ethane (chrom.) (%)	Ethylene (chrom.) (%)	Substrate (sum EtOH + EtH) ^a (%)
60	6.2	3.0	2.7	—	5.7
120	10.6	5.7	5.4	0.2	11.1
180	16.2	8.3	7.6	0.5	15.9
240	21.4	10.7	9.8	0.9	20.5
300	23.6	13.1	11.7	1.4	24.8
360	28.5	15.5	13.8	1.9	29.3
420	33.8	17.4	15.8	2.5	33.2
480	37.4	19.0	17.4	3.2	36.4
900	56.2	30.3	27.8	9.0	58.1
1200	69.8	35.8	32.7	13.7	68.5
1400	74.7	38.7	35.2	16.8	73.9
1600	77.1	41.1	37.5	19.9	78.6
1800	82.2	43.1	39.4	22.9	82.5
1900	84.3	43.9	40.1	24.3	84.0
2000	84.5	44.7	40.6	25.7	85.3

^a Reaction (%) estimated from the sum of (%)ethanol and (%) ethane (GLC) analyses.

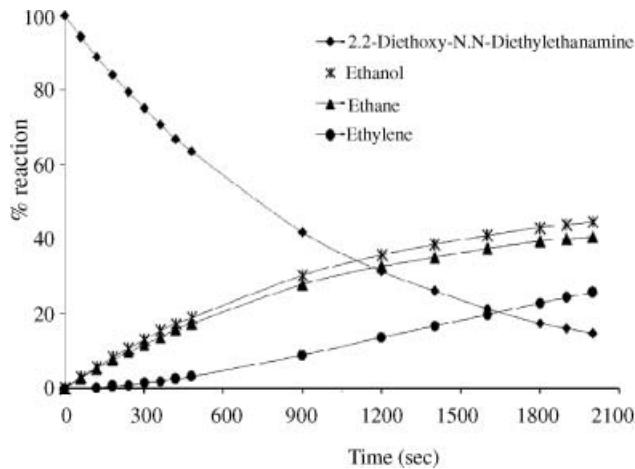


Figure 2. Kinetic profile for gas-phase elimination of 2,2-diethoxy-*N,N*-diethylethanamine at 340 °C

Table 3. Homogeneity of elimination reactions at 340 °C

S/V (cm ⁻¹) ^a	10 ⁴ k _{total} (s ⁻¹) ^b	10 ⁴ k _{total} (s ⁻¹) ^c
2,2-Diethoxyethyl amine		
1	31.4 ± 7.92	9.72 ± 0.15
6	87.5 ± 15.1	9.81 ± 0.21
2,2-Diethoxy- <i>N,N</i> -diethylethanamine		
1	33.6 ± 3.10	9.60 ± 0.08
6	96.2 ± 10.1	9.47 ± 0.11

^a S = surface area, V = volume.

^b Clean Pyrex vessel.

^c Vessel seasoned with allyl bromide.

Table 4. Effect of free radical inhibitor cyclohexene on rates at a 340 °C

P_0 (Torr)	P_i (Torr)	P_i/P_0	$10^4 k_I(s^{-1})$	$10^4 k_{II}(s^{-1})$
2,2-Diethoxyethyl amine				
55	0	0	7.12	2.62
135	71	0.5	7.09	2.61
76	74	1.0	7.16	2.64
91	144	1.6	7.07	2.60
69	163	2.4	7.09	2.61
57	178	3.1	7.11	2.62
2,2-Diethoxy- <i>N,N</i> -diethylethanamine				
62	0	0	5.07	4.61
115	63	0.5	5.00	4.55
55	49	0.9	5.06	4.59
43	74	1.7	5.04	4.58
58	145	2.5	5.08	4.62
60	175	2.9	5.02	4.56

 P_0 = Pressure of the substrate. P_i = Pressure of the inhibitor.

ethane [reaction (4), **Step 2**] in the elimination of both aminoketal substrates suggests a commonly accepted value for a four-membered cyclic transition state type of mechanism.^[6,7] This mechanistic consideration appears to be supported from the outcome of a positive entropy of activation [ΔS^\ddagger (J mol⁻¹ K⁻¹)]. Therefore **Step 1** and **Step 2** are determining factor in the elimination of ethanol and ethane, respectively [reaction (4)]. The positive entropy of activation for **Step 1** and **Step 2** of reaction (4) implies a polar cyclic transition state. In the case of the intermediate aminovinyl ethyl ether, the elimination process with a log A of approximately 12.0 [**Step 3**, reaction (4)] and a very negative entropy of activation implies a concerted six-membered cyclic transition state structure.

To rationalize the mechanism of **Step 1**, the bond polarization of C_α —bond of the ethoxy group, in the sense $C_\alpha^{\delta+} \cdots O^{\delta-}$, is the rate-determining step. Consequently, the CH_3CH_2O group as a nucleophile will abstract the hydrogen of the β -carbon to produce through a four-membered cyclic transition state the ethanol product and the corresponding aminovinyl ethyl ether. Then, the later product proceeds through a concerted six-membered cyclic transition (**Step 3**) to form ethylene and the corresponding amine. The mechanism of **Step 3** is similar to the well-known gas-phase thermal decomposition of alkyl vinyl ether.^[8-10] In the case of formation of ethane and the corresponding ethyl ester of the amino acid (**Step 2**) an alternative mechanism may be considered. In this pathway, as a competitive bond polarization of **Step 1**, the direction of $O^{\delta-} \cdots C_\gamma^{\delta+}$ of the alkoxy group is the rate determining step. The $O^{\delta-}$ may stabilize toward the C_α to form the carbonyl, while the H atom is forced to migrate to the C_γ to form the corresponding ethyl ester of the amino acid and ethane gas. Otherwise, the nucleophilicity of $O^{\delta-}$ from polarization of the $C_\gamma^{\delta+}$ may abstract the labile hydrogen atom of the β -carbon to form an enolic ester and ethane. The enolic ester will rapidly produce the corresponding ethyl ester of the amino acid. The mechanistic consideration described above may need further investigations in order to decide the most reasonable pathway of **Step 2** in the gas-phase elimination of ketals.

Table 5. Invariability of the rate coefficients with initial pressure at 340 °C^a

2,2-Diethoxyethyl amine					
P_0 (mmHg)	55	76	91	135	152
$10^4 k_{total}(s^{-1})$	9.74	9.80	9.67	9.70	9.71
2,2-Diethoxy- <i>N,N</i> -diethylethanamine					
P_0 (mmHg)	43	62	80	115	130
$10^4 k_{total}(s^{-1})$	9.62	9.80	9.70	9.61	9.60

^a Seasoned with allyl bromide.**Table 6.** Variation of the rate coefficients with temperature^a

Temp (°C)	$10^4 k_{total}(s^{-1})$	$10^4 k_I (EtOH)(s^{-1})$	$10^4 k_{II} (EtH)(s^{-1})$	$10^4 k_{III} (\text{ethylene}) (s^{-1})$
2,2-Diethoxyethyl amine				
321	2.93 ± 0.07	2.17 ± 0.08	0.76 ± 0.05	5.62 ± 0.08
331	5.23 ± 0.19	3.82 ± 0.16	1.41 ± 0.08	9.65 ± 0.09
340	9.72 ± 0.15	7.10 ± 0.08	2.62 ± 0.20	16.3 ± 0.31
349	18.5 ± 0.29	13.6 ± 0.13	4.92 ± 0.11	28.0 ± 0.15
360	34.8 ± 0.12	25.6 ± 0.30	9.24 ± 0.17	47.4 ± 0.13
370	63.6 ± 0.18	46.2 ± 0.21	17.4 ± 0.14	79.0 ± 0.16
2,2-Diethoxy- <i>N,N</i> -diethylethanamine				
321	2.76 ± 0.09	1.45 ± 0.05	1.31 ± 0.04	2.52 ± 0.01
331	5.15 ± 0.06	2.71 ± 0.01	2.44 ± 0.05	4.34 ± 0.12
340	9.60 ± 0.08	5.03 ± 0.06	4.57 ± 0.03	7.16 ± 0.10
349	17.9 ± 0.16	9.37 ± 0.07	8.51 ± 0.10	12.8 ± 0.33
360	33.4 ± 0.29	17.5 ± 0.19	15.9 ± 0.11	22.0 ± 0.30
370	62.1 ± 0.13	32.2 ± 0.06	29.9 ± 0.08	38.8 ± 0.17

^a Seasoned with allyl bromide.

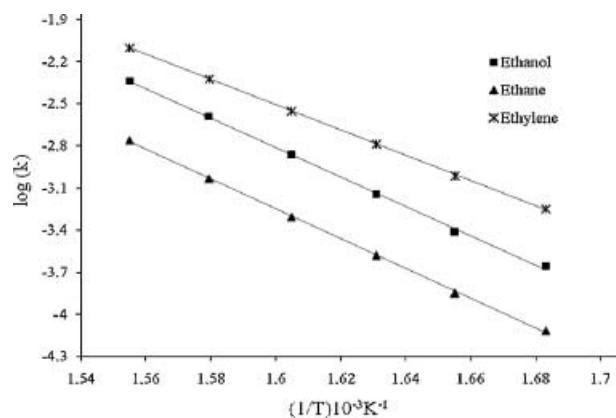


Figure 3. Graphic representation of the Arrhenius plot for the gas-phase elimination of 2,2-diethoxyethyl amine

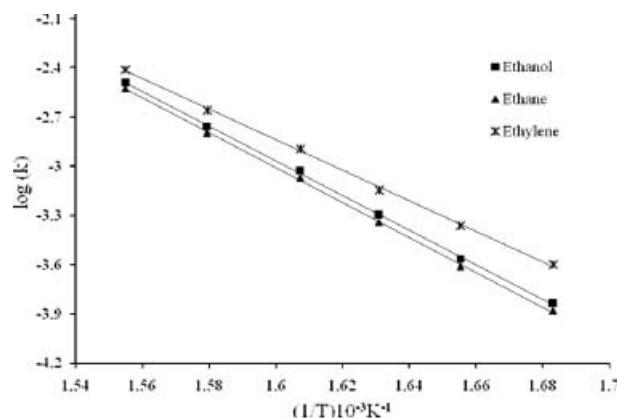


Figure 4. Graphic representation of the Arrhenius plot for the gas-phase elimination of 2,2-diethoxy-N,N-diethylethanamine

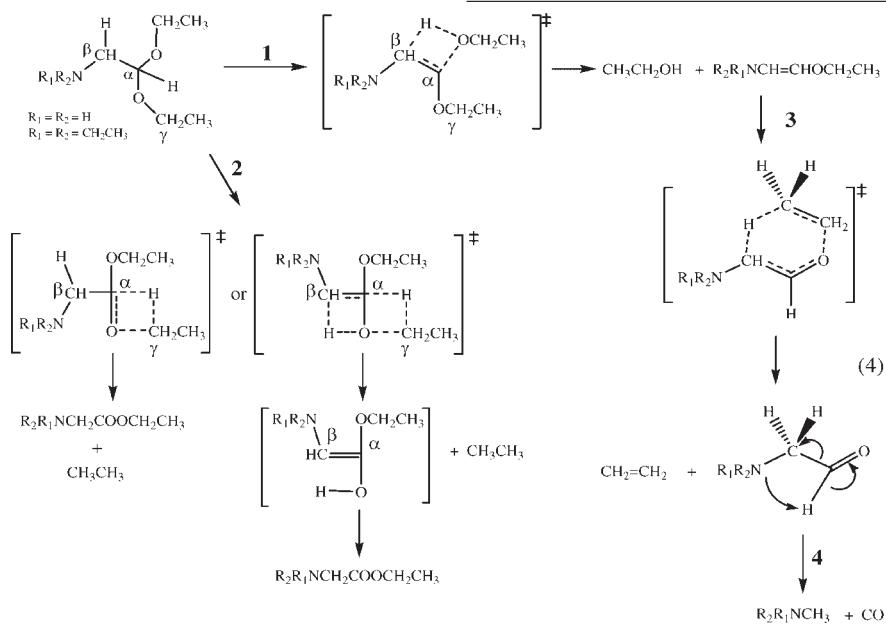
Table 7. Kinetic and thermodynamic parameters at 340 °C.

Reaction	$10^4 k(\text{s}^{-1})$	$E_a (\text{kJ mol}^{-1})$	$\log(A) (\text{s}^{-1})$	$\Delta S^\ddagger (\text{J mol}^{-1} \text{K}^{-1})$	$\Delta H^\ddagger (\text{kJ mol}^{-1})$	$\Delta G^\ddagger (\text{kJ mol}^{-1})$
2,2-Diethoxyethyl amine						
Total ^a	9.72 ± 0.15	—	—	—	—	—
Ethanol	7.10 ± 0.08	201.1 ± 3.2	13.99 ± 0.27	8.60	196.0	190.2
Ethane	2.62 ± 0.20	203.8 ± 2.1	13.77 ± 0.18	4.39	198.7	196.0
Ethylene	16.3 ± 0.31	172.2 ± 1.0	11.88 ± 0.09	-31.79	167.1	186.6
2,2-Diethoxy-N,N-diethylethanamine						
Total ^a	9.60 ± 0.08	—	—	—	—	—
Ethanol	5.03 ± 0.06	202.3 ± 2.4	13.94 ± 0.20	7.64	197.2	192.6
Ethane	4.57 ± 0.03	203.9 ± 2.6	14.03 ± 0.22	9.37	198.8	193.0
Ethylene	7.16 ± 0.10	178.1 ± 2.3	12.02 ± 0.19	-29.11	173.0	190.8

^a Total = Ethanol + Ethane.

Table 7 shows a small difference in the total rate coefficients between the two substrates. However, since the NH_2 has a greater electron-withdrawing effect than NEt_2 , then a faster

elimination of ethanol is obtained (**Step 1** reaction 4, Table 7). In other words, and as discussed in the 'Introduction', the β -hydrogen of the adjacent $\text{C}_\beta-\text{H}$ bond to the NH_2 substituent (Scheme 1) is more labile than NEt_2 group for abstraction by the



leaving ethoxy group. Therefore, $\text{NH}_2 > \text{NEt}_2$ is assisting the elimination of ethanol.

EXPERIMENTAL

2,2-Diethoxyethyl amine and 2,2-diethoxy-*N,N*-diethylethanamine were acquired from Aldrich. These substrates were better than 98.7% purity, when analyzed by GC-MS (Saturn 2000 Varian) using a DB-5MS capillary column (30 × 0.25 mm i.d., 0.25 μm film thickness). The quantitative analyses of the product ethanol, ethane, ethylene were determined by using a GC Column of Porapak S, 80–100 mesh, 3 mts. The quantitative chromatographic analysis of 2,2-diethoxyethyl amine was carried out by using a Column of Chromosorb 103, 80–100 mesh, 3 mts, while 2,2-diethoxy-*N,N*-diethylethanamine was performed in a Column 3% Versamid, 3 mts. The verification of the substrates and identification of the intermediates corresponding 2-ethoxyethenamine and products was examined with the Varian Saturn GC-MS instrument with a DB-5MS capillary column.

Kinetics

The kinetics were carried out in a static reaction system as described.^[11–13] The rate coefficients were determined by the quantitative chromatographic analyses of substrates and products. The rate of decomposition of *N,N*-substituted 2,2-diethoxyethyl amine is given by Eqn (1):

$$k_{\text{total}} = -\frac{1}{t} \ln \left(\frac{P_{\text{substrate}}}{P_0} \right) \quad (1)$$

When estimating each step of the reaction (4), Eqn (2) describes the formation of ethanol and ethane with time.

For ethanol (**Step 1**)

$$\frac{dP_{\text{EtOH}}}{dt} = k_{\text{I}(\text{EtOH})}(P_{\text{substrate}}) \quad (2)$$

For ethane (**Step 2**)

$$\frac{dP_{\text{EtH}}}{dt} = k_{\text{II}(\text{EtH})}(P_{\text{substrate}}) \quad (3)$$

Therefore, the ratio of ethanol/ethane is shown in Eqn (4)

$$\frac{P_{\text{EtOH}}}{P_{\text{EtH}}} = \frac{k_{\text{I}(\text{EtOH})}}{k_{\text{II}(\text{EtH})}} \quad (4)$$

The values of the rate coefficients of product formation, $k_{\text{I}(\text{EtOH})}$ and $k_{\text{II}(\text{CH}_2=\text{CH}_2)}$, were determined by Eqn (5)

$$\left\{ \begin{array}{l} k_{\text{total}} = k_{\text{I}(\text{EtOH})} + k_{\text{II}(\text{EtH})} \\ \frac{k_{\text{I}(\text{EtOH})}}{k_{\text{II}(\text{EtH})}} = \frac{P_{\text{EtOH}}}{P_{\text{EtH}}} \end{array} \right. \quad (5)$$

The expression which describes the ethylene formation (**Step 3**) is given by Eqn (6)

$$P_{(\text{CH}_2=\text{CH}_2)} = P_0 \left[\frac{k_{\text{I}(\text{EtOH})}}{k_{\text{total}}} (1 - e^{-k_{\text{total}}t}) - \frac{k_{\text{I}(\text{EtOH})}}{k_{\text{III}(\text{CH}_2=\text{CH}_2)} - k_{\text{total}}} (e^{-k_{\text{total}}t} - e^{-k_{\text{III}(\text{CH}_2=\text{CH}_2)}t}) \right] \quad (6)$$

In view that the value of $k_{\text{III}(\text{CH}_2=\text{CH}_2)}$ described in Eqn (6) could not be estimated directly, we have proceeded to use the Newton Method.^[14]

The temperature was controlled by a resistance thermometer controller, SHINKO DIC-PS 25RT, maintained within $\pm 0.2^\circ\text{C}$ and measured with a calibrated platinum-platinum-13% rhodium thermocouple. No temperature gradient was found along the reaction vessel. The substrates were injected (0.05–0.1 ml) directly into the reaction vessel with a syringe through a silicone rubber septum.

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