# Steric Factors in the Gas Phase Elimination Kinetics of Ethyl N-Benzyl-N-Cyclopropylcarbamate and Ethyl Diphenylcarbamate

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ABSTRACT: The elimination kinetics of ethyl N-benzyl-N-cyclopropylcarbamate and ethyl diphenylcarbamate were investigated over the temperature range of 349.9–440.0°C and the pressure range of 31–106 Torr. These reactions have been found to be homogeneous, unimolecular, and obey a first-order rate law. The products are ethylene, carbon monoxide, and the corresponding secondary amine. The rate coefficient is expressed by the following Arrhenius equations:

For ethyl N-benzyl-N-cyclopropylcarbamate

 $\log k_1(s^{-1}) = (12.94 \pm 0.09) - (198.5 \pm 0.9) \text{ kJ mol}^{-1}(2.303 \text{RT})^{-1}$ 

For ethyl diphenylcarbamate

 $\log k_1(s^{-1}) = (12.91 \pm 0.18) - (208.2 \pm 2.4) \text{ kJ mol}^{-1}(2.303 \text{ RT})^{-1}$ 

The presence of phenyl and bulky groups at the nitrogen atom of the ethylcarbamate showed a decrease in the rate of elimination. Steric factor may be operating during the process of decomposition of these substrates. These reactions appear to undergo a semipolar six-membered cyclic transition type of mechanism. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 34: 67–71, 2002

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#### INTRODUCTION

The first pyrolysis of a carbamate in the gas phase, the ethyl ester of N-methyl-N-phenylcarbamate, showed to give N-methylaniline, ethylene, and CO<sub>2</sub> gas [1].

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Substrate	Temperature (°C)	$P_{\rm o}$ (Torr)	$P_{\rm f}$ (Torr)	$P_{\rm f}/P_{\rm o}$	Average
Ethyl N-benzyl-	382.2	78	231	2.96	2.98
<i>N</i> -cyclopropylcarbamate	391.2	35	106	3.03	
	400.7	66	195	2.95	
	412.0	76	225	2.96	
Ethyl diphenylcarbamate	400.0	51	151	2.87	2.78
	410.1	50	140	2.81	
	420.7	59	158	2.69	
	430.6	37	101	2.73	

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

Additional works on the thermal decomposition of alkyl esters of dimethylcarbamates suggested the mechanism of a six-membered cyclic transition state [reaction (1)], which is similar to the designated transition state for the gas phase pyrolyses of acetates, carbonates, and xanthates [2–6].



A later work on the gas phase pyrolysis of *tert*-butyl arylcarbamates [7] revealed enhancement in rates with electron-withdrawing substituents at the aromatic nuclei, whereas electron-releasing substituents decreased the *k*-values.

Table II Homogeneity of the Reaction

Compound	S/V (cm <sup>-1</sup> )	$\frac{k_1}{(10^{-4}\mathrm{s}^{-1})^a}$	$(10^{-4}  \mathrm{s}^{-1})^b$
Ethyl <i>N</i> -benzyl- <i>N</i> - cyclopropylcarbamate at 369 8°C	1 6	7.61 8.89	7.54 8.42
Ethyl diphenylcarbamate at 400.0°C	1 6	5.75 8.34	5.82 8.72

<sup>a</sup>Clean Pyrex vessel.

<sup>b</sup>Vessel seasoned with allyl bromide.

A recent investigation showed that branching of alkyl groups at the 2-position of ethyl N,N- diethylcarbamates increased the rate of elimination in the order *tert*-butyl > isopropyl > ethyl [8]. Moreover, the presence of different substituents other than carbon at the acid side of the ethyl ester gave a good Taft-Topsom method of correlation [8]. According to this relationship, the field (inductive effect) of the substituent has the greatest influence on rate increase, while the polarizability (steric) and resonance effects assist very little to the elimination process.

With this background, some additional information on carbamates pyrolyses may be of interest, such as how the presence of bulky or crowded groups attached to the nitrogen atom may affect the rate of elimination. Consequently, the present work aimed at examining the pyrolysis kinetics of ethyl *N*-benzyl-*N*-cyclopropylcarbamate and ethyl *N*, *N*-diphenylcarbamate in the gas phase.

## **EXPERIMENTAL**

Ethyl *N*-benzyl-*N*-cyclopropylcarbamate (98%) and ethyl N,N-diphenylcarbamate (99%) were acquired



**Figure 1** Plot of  $\log [(3P_0 - P_t)/2P_0]$  vs. time for the pyrolysis kinetics of ethyl *N*-benzyl-*N*-cyclopropylcarbamate at 392.2°C.

$P_{\rm o}$ (Torr)	$P_{\rm i}$ (Torr)	$P_{\rm i}/P_{\rm o}$	$k_1 \ (10^{-4} \ \mathrm{s}^{-1})$		
40	-	-	13.54		
51	57.5	1.1	13.81		
50	77	1.5	13.29		
66	245	3.7	13.57		
59	_	_	9.76		
106.5	82	0.8	9.55		
78	126	1.6	9.89		
41	91	2.2	9.36		
	P <sub>o</sub> (Torr) 40 51 50 66 59 106.5 78 41	$\begin{array}{c c} \hline P_{\rm o} \ ({\rm Torr}) & P_{\rm i} \ ({\rm Torr}) \\ \hline 40 & - \\ 51 & 57.5 \\ 50 & 77 \\ 66 & 245 \\ 59 & - \\ 106.5 & 82 \\ 78 & 126 \\ 41 & 91 \\ \end{array}$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$		

 Table III
 Effect of the Inhibitor Toluene on Rates

 $P_0$  = pressure of the substrate;  $P_i$  = pressure of toluene inhibitor.

**Table IV**Variation of Rate Coefficients with InitialPressure

Substrate	$P_{\rm o}$ (Torr)	$k_1 (10^{-4} \text{ s}^{-1})$
Ethyl N-benzyl-	31	13.48
<i>N</i> -cyclopropylcarbamate	40	13.31
at 380.4°C	60	13.37
	78	13.17
	98	13.10
Ethyl diphenylcarbamate	35	9.70
at 410.0°C	42	9.35
	51	9.09
	68	9.89
	106	9.55

 Table V
 Variation of Rate Coefficient with Temperature

Substrate	Temperature (°C)	$k_1 \ (10^{-4} \ \mathrm{s}^{-1})$
Ethyl N-benzyl-	349.5	1.90
N-cyclopropylcarbamate <sup><math>a</math></sup>	360.4	3.80
	372.2	7.54
	382.2	13.30
	391.2	21.60
	400.7	35.70
	412.0	63.20
Ethyl diphenylcarbamate <sup>b</sup>	380.8	1.94
	390.5	3.40
	400.8	5.66
	410.1	9.69
	420.7	14.40
	430.6	29.27
	440.6	46.42

<sup>*a*</sup>Rate equation: log  $k_1$  (s<sup>-1</sup>) = (12.94 ± 0.09) – (198.5 ± 0.9) kJ mol<sup>-1</sup> (2.303*RT*)<sup>-1</sup>; r = 0.99997.

<sup>b</sup>Rate equation: log  $k_1$  (s<sup>-1</sup>) = (12.91 ± 0.18) – (208.2 ± 2.4) kJ mol<sup>-1</sup> (2.303*RT*)<sup>-1</sup>; r = 0.99967.



**Figure 2** Plot of  $\log [(3P_0 - P_t)/2P_0]$  vs. time for the pyrolysis kinetics of ethyl *N*,*N*-diphenylcarbamate at 410.2°C.

from Aldrich. The quantitative analyses of the substrates were determined by GLC (Pennwalt 223/KOH, 80–100 mesh). The product ethylene was analyzed in a column of Porapak Q (80–100 mesh). The verification of the substrates and identification of the products were carried out by GLC/MS (Saturn 2000, Varian). Capillary column DB-5MS, 30 mm  $\times$  0.250 mm., i.d. 0.25  $\mu$ m.

The pyrolysis experiments were carried out in a static reaction system as described before [9,10] with some additions and modifications of modern electronic and electric devices. The reaction vessel was seasoned with the product of decomposition of allyl bromide. The rate coefficients were determined by measurements of pressure increase. The temperature was controlled by a SHINKO DIC-PS 25TR resistance thermometer controller maintained within  $\pm 0.2^{\circ}C$ and measured with a calibrated platinum/platinum-13% rhodium thermocouple. No temperature gradient was found along the reaction vessel. The substrates ethyl N-benzyl-N-cyclopropylcarbamate and ethyl N-N-diphenylcarbamate were dissolved in dimethylformamide, and injected directly into the reaction vessel through a silicone-rubber septum.

	<i>k</i> 1		E		$\Delta S^{\neq}$	$\Delta H^{\neq}$	$\Delta G^{\neq}$	
Z	$(10^{-4} \mathrm{s}^{-1})$	Rel. rate	(kJ/mol)	$\log A \ (\mathrm{s}^{-1})$	(J/mol K)	(kJ/mol)	(kJ/mol)	Ref.
(CH <sub>3</sub> ) <sub>2</sub> N	18.20	1.0	$185.5\pm5.3$	$12.10\pm0.22$	-6.74	180.1	184.5	14
CH <sub>3</sub> PhN	17.75	0.98	$189.9\pm4.5$	$12.44\pm0.19$	-5.18	184.5	187.9	1
PhCH <sub>2</sub> (C <sub>3</sub> H <sub>5</sub> )N	11.52	0.63	$198.5\pm0.9$	$12.94\pm0.09$	-2.89	193.1	195.0	а
Ph <sub>2</sub> N	1.80	0.10	$208.2\pm2.4$	$12.91\pm0.18$	-3.03	202.8	204.8	а

Table VI Comparative Rates and Kinetic Parameters for the Pyrolysis of ZCOOCH<sub>2</sub>CH<sub>3</sub> at 380.0°C

<sup>a</sup>This work.

### **RESULTS AND DISCUSSION**

The products formation of these carbamates are described in reaction (2)



Ph<sub>2</sub>NCOOCH<sub>2</sub>CH<sub>3</sub>

$$\longrightarrow \left[ \begin{array}{c} Ph_2NCOOH \\ \downarrow \end{array} \right] + CH_2 = CH_2$$

$$ph_2NH + CO_2$$

The stoichiometry based on reaction (2) required that, for long reaction time  $P_f/P_o = 3.0$ , where  $P_f$ and  $P_o$  are the final and initial pressure, respectively. The average experimental  $P_f/P_o$  values at four different temperatures and 10 half-lives were 2.98 for ethyl *N*-benzyl-*N*-cyclopropylcarbamate and 2.78 for ethyl *N*,*N*-diphenylcarbamate (Table I). The small departure in ethyl diphenylcarbamate was due to a small polymerization of the product diphenylamine.

The homogeneity of these reactions was examined by carrying out several runs in a vessel with a surfaceto-volume ratio of 6.0 relative to that of the normal vessel, taken as 1.0 (Table II). The clean and seasoned Pyrex vessel had no effect on rate. However, the packed clean and packed seasoned Pyrex vessel resulted in a significant heterogeneous effect in the rate coefficients. The pyrolysis of these carbamate substrates were not affected by the presence of different proportions of a free radical inhibitor such as toluene (Table III). No induction period was obtained. The *k*-values are reproducible with a relative standard deviation not greater than 5% at a given temperature.

The first-order rates of the carbamates, calculated from  $k_1 = (2.303/t) \log [2P_0/(3P_0 - P_t)]$ , were found to be invariable of the initial pressure. A plot of  $\log (3P_0 - P_t)$  vs time t gave a good straight line up to 60–70% decomposition (Table IV, Figs. 1 and 2). The temperature dependence of the rate coefficients and the corresponding Arrhenius equations are given in Table V (90% confidence coefficient from the leastsquares method).

The influence of the phenyl group at the N atom of the ethyl carbamates shown in Table VI suggests that steric factors may be affecting the rate of elimination. The replacement of a methyl group in the  $(CH_3)_2N$  by a phenyl group results in a small decrease in k-value due to steric factor. This consideration appears to be evident when the remaining CH<sub>3</sub> at N atom of the carbamate is replaced by an additional phenyl group i.e. diphenyl carbamate (Table VI). Augmentation in bulkiness of  $CH_3PhN$  by  $PhCH_2(C_3H_5)N$  also gives rise to a small but significant decrease in rate, which may also be due to steric factor. The effect of the substituent PhNH as Z in ZCOOCH<sub>2</sub>CH<sub>3</sub>, i.e. PhNHCOOCH<sub>2</sub>CH<sub>3</sub>, was not included in Table VI, because this compound was reported to give poor kinetic reproducibility [11]. It was believed that some parallel reaction should take place; the formation of isocyanate and alcohol has been reported [1,12-14], when the alkyl side of the phenylcarbamate is primary or secondary.

With regard to the results of the present work, the mechanisms for reactions described in reaction (2) may be explained in terms of a semipolar six-membered cyclic transition state as pictured in reaction (1).

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