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Kinetics and mechanisms of the gas-phase elimination of arylethyl *N,N*-dimethylcarbamates and ω-phenylalkyl *N,N*-dimethylcarbamates

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ABSTRACT: The gas-phase elimination kinetics of several arylethyl *N,N*-dimethylcarbamates and ω-phenylalkyl *N,N*-dimethylcarbamates were determined in the temperature range 299.6–399.9 °C and pressure range 18–95 Torr. The reactions in a static system, seasoned with allyl bromide, and in the presence of a free radical suppressor are homogeneous and unimolecular and follow a first-order rate law. The rate coefficients are given by the Arrhenius equations: for 4-phenethyl *N,N*-dimethylcarbamate, $\log[k_1\ (s^{-1})] = (11.32 \pm 0.22) - (166.9 \pm 2.5)$ kJ mol^{-1} $(2.303RT)^{-1}$; for methylphenethyl *N,N*-dimethylcarbamate, $\log[k_1\ (s^{-1})] = (12.07 \pm 0.36) - (178.6 \pm 4.3)$ kJ mol^{-1} $(2.303RT)^{-1}$; for 4-methoxyphenethyl *N,N*-dimethylcarbamate, $\log[k_1\ (s^{-1})] = (11.03 \pm 0.60) - (167.3 \pm 7.1)$ kJ mol^{-1} $(2.303RT)^{-1}$; for 4-nitrophenethyl *N,N*-dimethylcarbamate, $\log[k_1\ (s^{-1})] = (11.31 \pm 0.54) - (163.7 \pm 6.1)$ kJ mol^{-1} $(2.303RT)^{-1}$; for 3-(4-methoxyphenyl)propyl *N,N*-dimethylcarbamate, $\log[k_1\ (s^{-1})] = (13.52 \pm 0.54) - (208.4 \pm 6.8)$ kJ mol^{-1} $(2.303\ RT)^{-1}$; for 4-phenyl-1-butyl *N,N*-dimethylcarbamate, $\log[k_1\ (s^{-1})] = (12.00 \pm 0.34) - (185.2 \pm 4.2)$ kJ mol^{-1} $(2.303\ RT)^{-1}$; and for 5-phenyl-1-pentyl *N,N*-dimethyl carbamate, $\log[k_1\ (s^{-1})] = (11.79 \pm 0.31) - (182.2 \pm 3.9)$ kJ mol^{-1} $(2.303RT)^{-1}$. The results imply the absence of anchimeric assistance of the phenyl group, while the acidity of the benzylic β-hydrogen appears to be responsible for a small but significant rate augmentation in these eliminations. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: arylethyl *N,N*-dimethylcarbamates; ω-phenylalkyl *N,N*-dimethylcarbamates; gas-phase elimination; kinetics; mechanism

INTRODUCTION

The use of several structure–reactivity relationships for the gas-phase elimination kinetics of a considerable number of 2-substituted-ethyl *N,N*-dimethylcarbamates[1] gave meaningless results, except for Taft original σ^* values. Three good slopes were originated at σ^* $(CH_3) = 0.00$. Mechanisms were suggested on the basis of this relationship. However, the point positions of phenyl (C_6H_5) and isopropenyl [$CH_2{=}C(CH_3)$] as substituents Z in $(CH_3)_2NCOOCH_2CH_2Z$ were found to fall far above the three slopes of the lines. These substituents were believed to enhance the rate of elimination due to neighboring group participation or to the acidity of the benzylic and allylic C_β—H bond.

In association with the above considerations, and previous work on the gas-phase pyrolytic elimination of 2-phenethyl chloride,[2] the presence of the methoxy (OCH_3) group at the 4-position of pheneylethyl chloride suggested the participation of the aromatic nuclei by a significant increase in the rate of HCl elimination. In addition to this work, the phenyl susbtituent was also found to assist anchimerically the gas-phase elimination of ω-phenylalkyl methanesulfonates.[3] The C_6H_5 substituent at the 2- and 4-positions with respect to the C—O bond of the methanesulfonate confirmed participation in the rate of pyrolysis. Moreover, the five-membered structure which is favorable for anchimeric assistance yielded to some extent a cyclic product, tetralin. Neighboring phenyl group participation at the 3-position was found to be absent.

Because of the dichotomy as to whether the anchimeric assistance of the phenyl substituent or the acidity of the benzylic C_β—H bond enhanced the rate of elimination of 2-substituted-ethyl *N,N*-dimethylcarbamates, the present work was aimed at examining the gas-phase pyrolysis kinetics of several arylethyl *N,N*-dimethylcarbamates and ω-phenylalkyl *N,N*-dimethylcarbamates, and it was possible to reveal which of these two factors affects the rate of elimination of these carbamates.

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Table 1. Stoichiometry of the reactions

Substrate	Temperature (°C)	Parameter	Value				
4-Methylphenethyl *N,N*-dimethylcarbamate	339.6	Time (min)	5	10	20	31	
		Reaction (%) (pressure)	20.0	37.1	58.9	73.6	
		Olefin (%) (GLC)	18.5	35.8	59.2	73.3	
4-Methoxyphenethyl *N,N*-dimethylcarbamate	349.9	Time (min)	6	8	10	15	20
		Reaction (%) (pressure)	29.4	37.7	42.7	58.8	62.8
		Olefin (%) (GLC)	28.2	36.8	43.0	56.5	62.4
4-Nitrophenethyl *N,N*-dimethylcarbamate[a]	—	—	—	—	—	—	—
3-(4-Methoxyphenyl)propyl *N,N*-dimethylcarbamate	379.6	Time (min)	5	6	7	8	
		Reaction (%) (pressure)	17.4	22.2	25.0	30.8	
		Olefin (%) (GLC)	16.9	22.5	25.7	31.9	
4-Phenyl-1-butyl *N,N*-dimethylcarbamate	369.6	Time (min)	4	6	8	10	15
		Reaction (%) (pressure)	22.7	31.6	39.6	46.4	59.0
		Olefin (%) (GLC)	21.8	31.6	38.3	46.0	58.5
5-Phenyl-1-pentyl *N,N*-dimethylcarbamate	379.1	Time (min)	4	5	6	8	10
		Reaction (%) (pressure)	28.9	33.9	39.2	44.6	53.9
		Olefin (%) (GLC)	29.0	33.5	40.0	44.2	54.1

[a] The stoichiometry was difficult to determine because the olefin product could not be obtained quantitatively.

RESULTS AND DISCUSSION

The unimolecular elimination of 2-substituted-ethyl *N,N*-dimethylcarbamates in the gas phase is described by the reaction

$$(CH_3)_2NCOOCH_2CH_2Z \rightarrow (CH_3)_2NCOOH + CH_2{=}CHZ \quad (1)$$
$$\downarrow$$
$$(CH_3)_2NH + CO_2$$

where Z = 4-$CH_3C_6H_4$, 4- $CH_3OC_6H_4$, 4- $NO_2C_6H_4$, 4- $CH_3OC_6H_4CH_2$, 4- $C_6H_5CH_2CH_2$ or 4- $C_6H_5CH_2$-CH_2CH_2. The stoichiometry of reaction (1) implies for a long reaction time $P_f/P_0 = 3$, where P_f and P_0 are the final and initial pressure, respectively. The average P_f/P_0 values at four temperatures and ten half-lives were 2.8 for 4-methylphenethyl *N,N*-dimethylcarbamate, 2.9 for 4-methoxyphenethyl *N,N*-dimethylcarbamate, 3.0 for 4-nitrophenethyl *N,N*-dimethylcarbamate, 2.1 for 3-(4-methoxyphenyl)propyl *N,N*-dimethylcarbamate, 3.0 for 4-phenyl-1-butyl *N,N*-dimethylcarbamate and 2.9 for 5-phenyl-1-pentyl *N,N*-dimethylcarbamate. The departure from $P_f/P_0 < 3$ for 3-(4-methoxyphenyl)propyl *N,N*-dimethylcarbamate may be due to some significant condensation or polymerization of the corresponding product 3-(4-methoxyphenyl)-1-propene. An authentic sample of this unsaturated product, when introduced into the reaction vessel, gave rise to a decrease in pressure to yield an unidentified solid. The stoichiometry of reaction (1), up to 30–74% reaction, was checked by comparing the extent of decomposition of the substrates from pressure measurements with that obtained from quantitative gas—liquid chromatographic (GLC) analyses of the corresponding olefin formation (Table 1).

The elimination reaction (1) was found to be homogeneous, since no significant variations in rates were obtained when using packed and unpacked seasoned vessels with allyl bromide with a surface-to-volume ratio of 6.0 relative to that of the normal vessel. (Table 2). However, the packed and unpacked clean Pyrex vessels showed a marked effect on 4-nitrophenethyl *N,N*-dimethylcarbamate and 5-phenyl-1-pentyl *N,N*-dimethylcarbamate.

The effect of addition of different proportions of the free radical inhibitor cyclohexene or toluene is described in Table 3. Nevertheless, the pyrolyses of these carbamates were carried out in the presence of at least twice the amount of the inhibitor in order to avoid any possible free radical chain reactions. No induction period was observed. The rate coefficients were reproducible with a relative standard deviation not greater than 5% at a given temperature.

The first-order rate coefficients of the carbamates calculated from $k_1 = (2.303/t)\log[2P_0/(3P_0 - P_t)]$ were found to be independent of the initial pressure (Table 4). A plot of $\log(3P_0 - P_t)$ vs time gave a good straight line up to 30–70% decomposition. The temperature dependence of the rate coefficient and the corresponding Arrhenius equations are given in Table 5 (95% confidence coefficient from least-squares procedure).

According to the data in Table 6, if neighboring group participation is the paramount factor affecting the rate of elimination of these phenethyl *N,N*-dimethylcarbamates, the 4-CH_3 and 4-OCH_3 substituents in the benzene ring should have given a significant augmentation in rates compared with 4-H and 4-NO_2 groups. On the other hand, the relative rates depicted in Scheme 1 suggest that the assistance of the benzylic β-hydrogen may be responsible for a small but significant rate increase in the rate of elimination.

A further approach to elucidating whether neighboring

Table 2. Homogeneity of the reactions

Compound	*S/V* (cm^{-1})[a]	10^4 k_1 (s^{-1})[b]	10^4 k_1 (s^{-1})[c]
4-Methylphenethyl *N,N*-dimethylcarbamate at 339.6 °C	1	7.29	7.30
	6	7.18	7.07
4-Methoxyphenethyl *N,N*-dimethylcarbamate at 349.9 °C	1	9.01	9.55
	6	9.20	9.50
4-Nitrophenethyl *N,N*-dimethylcarbamate at 330.2 °C	1	12.1[d]	13.0
	6	12.5[d]	13.6
3-(4-Methoxyphenyl)propyl *N,N*-dimethylcarbamate at 379.6 °C	1	7.96	7.21
	6	8.16	7.31
4-Phenyl-1-butyl *N,N*-dimethylcarbamate at 369.6 °C	1	9.40	9.55
	6	9.22	9.39
5-Phenyl-1-pentyl *N,N*-dimethylcarbamate at 379.1 °C	1	13.2	15.5
	6	10.7	15.8

[a] S = Surface area; V = volume.
[b] Clean Pyrex vessel.
[c] Vessel seasoned with allyl bromide.
[d] k Value up to 20% decomposition.

group participation may influence the rate of elimination is to examine the effect of the C_6H_5 ring along the carbon chain of ω-phenylalkyl *N,N*-dimethylcarbamates. The comparative rates in Scheme 2 suggest the absence of anchimeric assistance of the C_6H_5 group at the 2-position for a three-membered structure and at the 4- and 5-positions for more favorable five- and six-membered structures. This argument is derived from the lack of rate increase and possible formation of ring-closed products. The experimental findings imply that the acidity of the benzylic C_β—H bond assists the elimination process, while the rate decreased on interposition of a CH_2 group with respect to the *N,N*-dimethylcarbamate.

Table 3. Effect of the free radical inhibitor on rates[a]

Substrate	Temperature (°C)	P_s (Torr)[b]	P_i (Torr)[b]	P_i/P_s	10^4 k_1 (s^{-1})
4-Methylphenethyl *N,N*-dimethylcarbamate	349.7	77.5	—	—	11.6
		65	52	0.8	11.7
		51	83.5	1.6	11.6
		75.5	187.5	2.5	11.8
		37	136	3.7	11.7
4-Methoxyphenethyl *N,N*-dimethylcarbamate	349.9	31	—	—	9.42
		50.4	73.5	1.5	9.54
		68	108	1.6	9.35
		40	129	3.2	9.03
4-Nitrophenethyl *N,N*-dimethylcarbamate	330.2	41	—	—	13.0
		84	90.5	1.1	13.2
		27.5	40	1.5	13.1
		18	51.5	2.9	13.2
		24.5	107.5	4.4	13.0
		32	163.5	5.1	13.2
3-(4-Methoxyphenyl)propyl *N,N*-dimethylcarbamate	399.2	54.5	—	—	22.1
		51	45.5	0.9	22.2
		64	86.5	1.4	22.0
		43	146.5	3.4	21.9
		32	168	5.3	22.4
4-Phenyl-1-butyl *N,N*-dimethylcarbamate	369.6	54	—	—	9.61
		62.5	47	0.8	9.63
		64.5	97	1.5	9.39
		51	173	3.4	9.83
5-Phenyl-1-pentyl *N,N*-dimethylcarbamate	379.1	32	—	—	27.7
		63	54	0.9	15.1
		52	74	1.4	15.6
		53.5	134.5	2.5	15.5
		37	125.5	3.4	15.7

[a] Temperature <360 °C with cyclohexene inhibitor, >360 °C, with toluene inhibitor.
P_s, Pressure of the substrate; P_i, pressure of the inhibitor.

Table 4. Invariability of the rate coefficients from initial pressure

Substrate	Temperature (°C)	Parameter	Value				
4-Methylphenethyl *N,N*-dimethylcarbamate	359.1	P_0 (Torr)	27	45	79	95	
		$10^4 k_1$ (s^{-1})	19.8	20.2	20.0	20.2	
4-Methoxyphenethyl *N,N*-dimethylcarbamate	349.9	P_0 (Torr)	21.4	31.4	40	50.4	
		$10^4 k_1$ (s^{-1})	9.35	9.42	9.03	9.54	
4-Nitrophenethyl *N,N*-dimethylcarbamate	330.2	P_0 (Torr)	18	24.5	32	41	84
		$10^4 k_1$ (s^{-1})	13.2	13.0	13.2	13.1	13.2
3-(4-Methoxyphenyl)propyl *N,N*-dimethylcarbamate	390.6	P_0 (Torr)	40.5	51	63	82.5	
		$10^4 k_1$ (s^{-1})	12.7	12.8	12.9	12.9	
4-Phenyl-1-butyl *N,N*-dimethylcarbamate	369.6	P_0 (Torr)	48	51	64	79.5	
		$10^4 k_1$ (s^{-1})	9.49	9.83	9.39	9.50	
5-Phenyl-1-pentyl *N,N*-dimethylcarbamate	379.1	P_0 (Torr)	30	48	52	63	
		$10^4 k_1$ (s^{-1})	15.5	15.3	15.6	15.3	

EXPERIMENTAL

General procedure. The arylethanol or the ω-phenylalkanol (0.15 mol) was added to *N,N*-dimethylcarbamyl chloride (0.15 mol) in 50 ml of carbon tetrachloride and the reaction mixture was heated until no more HCl gas was evolved.

2-Phenethyl N,N-dimethylcarbamate. This compound was prepared as reported previously.[1]

4-Methylphenethyl N,N-dimethylcarbamate. This substrate was distilled several times to 99.5% purity as determined by GLC (DB-5MS capillary column, 30 m × 0.250 mm i.d., 0.25 μm). B.p. 124 °C at 2 Torr (1 Torr = 133.3 Pa), yield 61%. ^{1}H NMR, δ 2.3 (s, 3H, CH_3), 2.8 (m, 8H, $2CH_3$, —CH_2O—), 4.2 (t, 2H, CH_2), 7.1 (m, 4H, C_6H_5). MS, *m/z* 207 (M^+), 119 $[CH_3C_6H_4CH_2CH_2]^+$.

4-Methoxyphenethyl N,N-dimethylcarbamate. Several distillations of this carbamate gave a purity of 99.6% as determined by GLC (FFAP–Chromosorb W AW, 80–100 mesh). B.p. 160 °C at 2 Torr, yield 70%. ^{1}H NMR, δ 2.9 (m, 8H, $2CH_3$, —CH_2O—), 4.2 (t, 2H, CH_2), 6.8–7.1 (m, 4H, C_6H_4), 7.8 (s, 3H,CH_3O). MS, *m/z* 237 (M^+), 133 $[CH_3OC_6H_4CH_2CH_2]^+$ 121 $[CH_3OC_6H_4CH_2]^+$.

4-Nitrophenethyl N,N-dimethylcarbamate. This solid compound was recrystallized several times with water to 99.0% purity. M.p. 81 °C, yield 66%. ^{1}H NMR, δ 2.8–2.9 (s, 3H, $3CH_3$), 3.1 (t, 2H, —CH_2O—), 4.3 (t, 2H, CH_2) 7.4–8.2 (m, 4H, C_6H_4). MS, *m/z* 236 (M^+), 150 $[NO_2C_6H_4CH_2CH_2]^+$, 120 $[NO_2C_6H_4]^+$, 88 $[(CH_3)_2NCOO]^+$, 72 $[(CH_3)_2NCO]^+$, 46 $[NO_2]^+$, 44 (CO_2).

3-(4-Methoxyphenyl)-propyl N,N-dimethylcarbamate. This starting material was prepared by the above-mentioned method. B.p. 165 °C at 1 Torr, yield 65%. After several distillations the purity was 99.4% as determined by GLC (DB-5MS capillary column, 30 m × 0.250 mm i.d., 0.25 μm). ^{1}H NMR, δ 1.8–1.9 (q, 2H, C—CH_2—C), 2.6–2.8 (m, 2H, CH_2—C), 2.8–2.9 [s, 6H, $(CH_3)_2$N], 3.7 (s, 3H, OCH_3), 3.8–4.1(t, 2H, —CH_2O—), 6.8–7.1 (m, 4H, C_6H_4). MS, *m/z* 237 (M^+), 147 $[CH_3OC_6H_4CH_2CH_2CH_2]^+$, 133 $[CH_3OC_6H_4CH_2CH_2]^+$, 119 $[CH_3OC_6H_4CH_2]^+$, 72 $[(CH_3)_2NCO]^+$, 44 (CO_2).

4-Phenylbutyl N,N-dimethylcarbamate. The above method was used for the preparation of this substrate. B.p. 150 °C at 22 Torr, yield 67%. Several distillations gave a 98.9% purity by GLC (DB-5MS capillary column, 30 m × 0.250 mm i.d., 0.25 μm). ^{1}H NMR, δ 1.7 (m, 4H, CH_2CH_2), 2.6 (t, 2H, CH_2Ph), 2.9 [s, 6H, $(CH_3)_2$N], 4.1 (t, 2H, OCH_2), 7.2–7.3 (m, 5H, C_6H_5). MS, *m/z* 221 (M^+), 133 $[C_6H_5CH_2CH_2CH_2CH_2]^+$, 119 $[C_6H_5CH_2CH_2CH_2]^+$, 105 $[C_6H_5CH_2CH_2]^+$, 91 $[C_6H_5CH_2]^+$, 72 $[(CH_3)_2NCO]^+$, 44 (CO_2).

5-Phenylpentyl N,N-dimethylcarbamate. This compound was prepared by the above procedure. B.p. 158 °C at 2 Torr, yield 80.0%. Several distillations gave a 99.0% purity by GLC (DB-5MS capillary column, 30 m × 0.250 mm i.d., 0.25 μm). ^{1}H NMR, δ 1.4 (m, 2H, C—CH_2—C), 1.7 (m, 4H, CH_2—C—CH_2), 2.6 (t, 2H, CH_2Ph), 2.9 [s, 6H, $(CH_3)_2$N], 4.0 (t, 2H, OCH_2), 7.1–7.3 (m, 5H, C_6H_5). MS, *m/z* 235 (M^+), 147 $[C_6H_5CH_2CH_2CH_2CH_2CH_2]^+$, 133 $[C_6H_5CH_2CH_2CH_2CH_2]^+$, 119 $[C_6H_5CH_2CH_2CH_2]^+$, 105 $[C_6H_5CH_2CH_2]^+$, 91 $[C_6H_5CH_2]^+$, 72 $[(CH_3)_2NCO]^+$, 44 (CO_2).

Quantitative chromatographic analyses of the unsaturated olefinic products were performed by GLC with a DB-5MS capillary column, 30 m × 0.250 mm i.d., 0.25 μm film thickness. However, 4-Methoxystyrene was analyzed by GLC with an FFAP–Chromosorb W AW, 80–100 mesh column. The solid product 4-nitrostyrene was difficult to analyze quantitatively using different types of GLC columns. The identifications of substrates and products were performed by GLC–MS

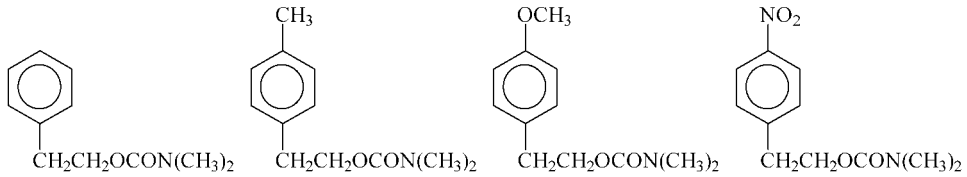
Table 5. Variation of rate coefficients with temperature

Substrate	Parameter	Value						
Phenethyl *N,N*-dimethylcarbamate	Temperature (°C)	318.5	328.8	338.6	343.2	349.2	354.2	
	$10^4 k_1$ (s^{-1})	3.86	6.84	11.3	15.5	20.3	26.5	
	Rate equation	$\text{Log}[k_1\ (s^{-1})] = (11.32 \pm 0.22) - (166.9 \pm 2.5)$ kJ mol^{-1} $(2.303\ RT)^{-1}$, $r = 0.9995$						
4-Methylphenethyl *N,N*-dimethylcarbamate	Temperature (°C)	319.6	330.6	339.6	349.7	359.1	370.3	378.8
	$10^4 k_1$ (s^{-1})	2.13	3.97	7.29	11.7	20.1	36.6	57.8
	Rate equation	$\text{Log}[k_1\ (s^{-1})] = (12.07 \pm 0.36) - (178.6 \pm 4.3)$ kJ mol^{-1} $(2.303\ RT)^{-1}$, $r = 0.9997$						
4-Methoxyphenethyl *N,N*-dimethylcarbamate	Temperature (°C)	319.3	330.5	339.6	349.9	359.6	370.0	
	$10^4 k_1$ (s^{-1})	1.94	3.28	5.95	9.55	13.4	27.5	
	Rate equation	$\text{Log}[k_1\ (s^{-1})] = (11.03 \pm 0.60) - (167.3 \pm 7.1)$ kJ mol^{-1} $(2.303\ RT)^{-1}$, $r = 0.9991$						
4-Nitrophenethyl *N,N*-dimethylcarbamate	Temperature (°C)	299.6	309.4	320.0	330.2	337.6	347.8	
	$10^4 k_1$ (s^{-1})	2.35	4.37	8.18	13.0	19.9	35.5	
	Rate equation	$\text{Log}[k_1\ (s^{-1})] = (11.31 \pm 0.54) - (163.7 \pm 6.1)$ kJ mol^{-1} $(2.303\ RT)^{-1}$, $r = 0.9993$						
3-(4-Methoxyphenyl)propyl *N,N*-dimethylcarbamate	Temperature (°C)	359.1	370.9	379.6	390.6	399.3		
	$10^4 k_1$ (s^{-1})	2.02	4.20	7.21	12.8	22.1		
	Rate equation	$\text{Log}[k_1\ (s^{-1})] = (13.52 \pm 0.54) - (208.4 \pm 6.8)$ kJ mol^{-1} $(2.303\ RT)^{-1}$, $r = 0.9997$						
4-Phenyl-1-butyl *N,N*-dimethylcarbamate	Temperature (°C)	349.7	359.3	370.8	380.8	390.3	399.1	
	$10^4 k_1$ (s^{-1})	2.84	5.18	9.28	15.7	25.5	40.7	
	Rate equation	$\text{Log}[k_1\ (s^{-1})] = (12.00 \pm 0.34) - (185.2 \pm 4.2)$ kJ mol^{-1} $(2.303\ RT)^{-1}$, $r = 0.9997$						
5-Phenyl-1-pentyl *N,N*-dimethylcarbamate	Temperature (°C)	359.5	371.5	379.1	389.8	399.9		
	$10^4 k_1$ (s^{-1})	5.57	10.5	15.5	27.6	43.9		
	Rate equation	$\text{Log}[k_1\ (s^{-1})] = (11.79 \pm 0.31) - (182.2 \pm 3.9)$ kJ mol^{-1} $(2.303\ RT)^{-1}$, $r = 0.9999$						

Table 6. Kinetic and thermodynamic parameters for pyrolysis of $ZCH_2CH_2OCON(CH_3)_2$ at 360 °C

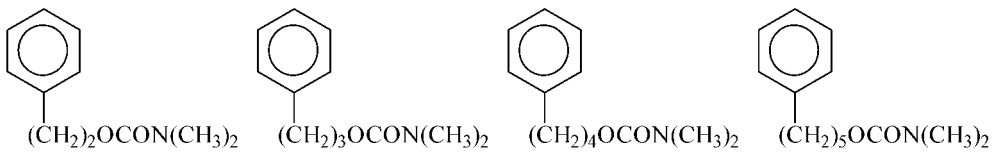
Z	$k_1\times10^{-4}$ (s^{-1})	E_a (kJ mol^{-1})	Log A (s^{-1})	$\Delta S^{\neq}$ (J $mol^{-1}K^{-1}$)	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
C_6H_5	35.3	166.9 ± 2.5	11.32 ± 0.22	−42.74	161.6	188.7
$C_6H_5CH_2$[a]	5.72	181.2 ± 3.2	11.71 ± 0.26	−35.27	175.9	198.2
4-$CH_3OC_6H_4CH_2$	2.10	208.4 ± 6.8	13.52 ± 0.54	−0.62	203.1	203.5
$C_6H_5CH_2CH_2$	5.22	185.2 ± 4.2	12.00 ± 0.34	−29.72	179.9	198.7
$C_6H_5CH_2CH_2CH_2$	5.69	182.2 ± 3.9	11.79 ± 0.31	−33.73	176.9	198.3
4-$CH_3C_6H_4$	21.5	178.6 ± 4.3	12.07 ± 0.36	−28.38	173.3	191.3
4-$CH_3OC_6H_4$	16.8	167.3 ± 7.1	11.03 ± 0.60	−48.28	162.0	192.6
4-$NO_2C_6H_4$	63.4	163.7 ± 6.1	11.31 ± 0.54	−42.92	158.4	185.6

[a] From Ref. 1.



Rel. rate at 360°C: 1.0 | 0.6 | 0.5 | 1.8

Scheme 1



Rel. rate at 360°C: 1.0 | 0.16 | 0.15 | 0.16

Scheme 2

(Saturn 2000, Varian) with a DB-5MS capillary column, 30 m × 0.250 mm i.d., 0.25 μm film thickness.

Kinetics. The pyrolyses kinetics were studied in a static system as described[4,5] with some modifications and additions of modern electronic and electrical devices. The reaction vessel was seasoned with allyl bromide, and the experiments were performed in the presence of at least twice the amount of the free radical inhibitor cyclohexene or toluene. The rate coefficients were determined manometrically or by quantitative chromatographic analyses of the olefinic products. The temperature was controlled by a resistance thermometer controller, Shinko DIC-PS 25RT, and an Omega Solid State SSR240AC45, maintained within ±0.2 °C and measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was found along the reaction vessel. The substrates 4-methoxyphenethyl *N,N*-dimethylcarbamate dissolved in dioxane, 4-nitrophenethyl *N,N*-dimethylcarbamate dissolved in chlorobenzene and the other carbamates in pure liquid form were injected with a syringe through a silicone rubber septum directly into the reaction vessel.

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