JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. **12**, 201–206 (1999)

Gas-phase elimination kinetics of ethyl, isopropyl and *tert*-butyl *N,N*-diethylcarbamates. Application of Taft–Topsom correlation for substituents other than carbon at the acid side of organic ethyl esters

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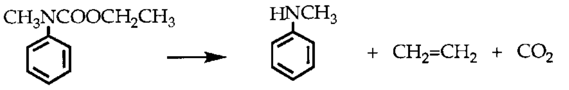
Received 20 March 1998; revised 1 June 1998; accepted 5 June 1998

ABSTRACT: The elimination kinetics of ethyl, isopropyl and *tert*-butyl *N,N*-diethylcarbamates were investigated in a static reaction vessel over the temperature range 220–400 °C and pressure range 17–160 Torr. These reactions are homogeneous, unimolecular and follow a first-order rate law. The temperature dependance of the rate coefficients is given by the following equations: for ethyl *N,N*-diethylcarbamate, $\log k_1\ (\mathrm{s}^{-1}) = (11.47 \pm 0.25) - (178.4 \pm 3.1)\ \mathrm{kJ\ mol}^{-1}\ (2.303\ RT)^{-1}$, for isopropyl *N,N*-diethylcarbamate, $\log k_1\ (\mathrm{s}^{-1}) = (12.83 \pm 0.70) - (179.8 \pm 7.9)\ \mathrm{kJ\ mol}^{-1}\ (2.303\ RT)^{-1}$; and for *tert*-butyl *N,N*-diethylcarbamate, $\log k_1\ (\mathrm{s}^{-1}) = (12.87 \pm 0.62) - (158.6 \pm 6.2)\ \mathrm{kJ\ mol}^{-1}\ (2.303\ RT)^{-1}$. The branching of the alkyl groups at the alcohol side of the ester exerts a significant effect on the rates in the order *tert*-butyl > isopropyl > ethyl. In addition, the presence of different substituents other than carbon at the acid side of organic ethyl esters gives the best correlation when using the Taft–Topsom equation: $\log k/k_\mathrm{H} = -(0.68 \pm 0.12)\sigma_\alpha + (2.57 \pm 0.12)\sigma_\mathrm{F} - (1.18 \pm 0.27)\sigma_\mathrm{R}$ ($r = 0.984 \pm 0.119$ at 400 °C). According to this relationship, the field (inductive) effect of the substituent has the greatest influence on rate enhancement, while the polarizability (steric) and resonance factors, although small in effect, favour the elimination process. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: alkyl *N,N*-diethylcarbamates; elimination kinetics; Taft–Topsom correlation

INTRODUCTION

The homogeneous, unimolecular thermal decomposition of a carbamate in the gas phase was first reported by Daly and Ziolkowski.[1] The substrate ethyl *N*-methyl-*N*-phenylcarbamate was found to produce *N*-methylaniline, ethylene and carbon dioxide [reaction 1]. The generally accepted mechanism of this elimination process consisted of a six-membered cyclic transition state (Scheme 1) similar to those described for acetates, carbonates, and xanthates.[1–4]



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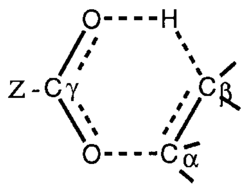

Scheme 1

Further examination of carbamate pyrolysis using methyl *N*-methylcarbamate[5] shows that its decomposition process differs from that of ethyl *N*-methyl-*N*-phenylcarbamate [reaction 2].

$$\mathrm{CH_3NHCOOCH_3 \longrightarrow CH_3NCO + CH_3OH} \qquad (2)$$

The presence of a hydrogen at the nitrogen atom was believed to be responsible for the different mechanistic pathway, and the elimination reaction was explained in terms of a four-membered cyclic transition-state mechanism (Scheme 2).

An additional study of the gas-phase pyrolysis of ethyl *N,N*-dimethylcarbamate[4,6] led to the conclusion that carbamate decomposition proceeds through an intermediate whose structure lies between a semi-concerted

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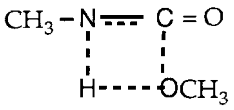
Contract/grant sponsor: Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT); *Contract/grant number:* S1-97000005.

CCC 0894–3230/99/030201–06 $17.50



Scheme 2

six-centered cyclic transition state and an intimate ion-pair type of mechanism.

The kinetics of pyrolysis of esters of carboxylic acids of the type ZCOOR, where R is an alkyl group and Z is an electron-releasing or -withdrawing aliphatic substituent, were correlated by plotting the log $k_{rel.}$ vs Taft σ^* values.[7–9] Each of these correlations gave a small positive ρ^* value. These results suggested that a negative charge has developed at the γ-carbon, where the C_α—O bond polarization, in the direction of $C_\alpha^{\delta+}\cdots O^{\delta-}$ is rate-determining step (Scheme 1).

In view of the few earlier studies on carbamate pyrolysis, the present work was aimed at examining the elimination kinetics of primary, secondary and tertiary alkyl *N,N*-diethylcarbamates and the possibility of establishing a structure–reactivity relationship of substituents Z of different ethyl esters of organic acids of the type $ZCOOCH_2CH_3$.

RESULTS AND DISCUSSION

The products of elimination of ethyl, isopropyl and *tert*-butyl esters of *N,N*-diethylcarbamic acid are the corresponding olefin, diethylamine and carbon dioxide [reaction 3].

$$(CH_3CH_2)_2NCOOCRR^1CH_3 \longrightarrow RR^1C{=}CH_2 + (CH_3CH_2)_2NH + CO_2 \qquad (3)$$

$$\text{i } R = R^1 = H$$
$$\text{ii } R = H,\ R^1 = CH_3$$
$$\text{iii } R = R^1 = CH_3$$

The stoichiometry as described in reaction 3 implies that, for long reaction times, $P_f = 3P_0$, where P_f and P_0 are final and initial pressure, respectively (Table 1). The average experimental P_f/P_0 at four different temperatures and ten half-lives were 2.85 for ethyl *N,N*-diethylcarbamate, 2.84 for isopropyl *N,N*-diethylcarbamate and 2.83 for *tert*-butyl *N,N*-diethylcarbamate.

The small departure of $P_f/P_0 < 3$ was due to the polymerization of the product diethylamine. Further examination of the stoichiometry of reaction 3, up to 40–70% reaction, was made by comparing the amount of decomposition of the substrate calculated from pressure measurements with that obtained from quantitative gas–ligun chromatographic (GLC) analyses of the unreacted carbamate (Table 2).

The decomposition reaction 3 is homogeneous, since no significant variation of the rates was observed in the experiments when using both clean Pyrex and seasoned Pyrex vessels with a surface-to-volume ratio of 6.0 relative to that of the normal vessel. The pyrolyses of these carbamate substrates were not affected by the presence of different proportions of a free radical suppressor such as cyclohexene (Table 3). 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 coefficients of the carbamates, calculated from $k_1 = (2.303/t)\log[2P_0/(3P_0\text{-}P_t)]$, were found to be independent of the initial pressure. A plot of $\log(3P_0\text{-}P_t)$ against time t gave a good straight line up to 40–70% decomposition.

The temperature dependence of the rate coefficient and the corresponding Arrhenius equations are given in Table 4 (90% confidence coefficient from the least-squares procedure).

The order of reactivity, tertiary > secondary > primary alkyl esters of *N,N*-diethylcarbamates (Table 5), is consistent with the results of the comparative rates for the corresponding *N,N*-dimethylcarbamates[10] (Table 5) and acetates.[17] This sequence is to be expected from electron

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

Compound	Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	Average
Ethyl *N,N*-diethylcarbamate	359.7	48	135	2.81	2.85
	379.9	42	122	2.90	
	389.7	50.5	144	2.85	
	399.6	66	186	2.82	
Isopropyl *N,N*-diethylcarbamate	301.6	56	160	2.86	2.84
	311.2	51.5	147	2.88	
	330.3	58	166	2.76	
	350.7	59.5	169	2.84	
tert-Butyl *N,N*-diethylcarbamate	241.7	31.5	89	2.83	2.83
	249.9	25.5	72	2.82	
	261.0	47	137	2.91	
	271.0	41.5	115	2.77	

Table 2. Stoichiometry of the reaction

Parameter	Ethyl *N*,*N*-diethylcarbamate at 380.2 °C				
Time (min)	1	3	5	8	12
Reaction (%) (pressure)	11.7	29.0	42.2	52.0	71.5
Substrate (%) (GLC)	12.2	28.4	41.5	53.5	67.0
	Isopropyl *N*,*N*-diethylcarbamate at 330.0 °C				
Time (min)	1	2	3	4	5
Reaction (%) (pressure)	8.6	19.1	26.6	34.9	39.5
Substrate (%) (GLC)	8.5	21.3	28.7	34.5	41.0
	tert-Butyl *N*,*N*-diethylcarbamate at 250.4 °C				
Time (min)	1.5	3	6	10	17
Reaction (%) (pressure)	9.6	17.8	26.5	44.8	60.2
Substrate (%) (GLC)	10.0	21.6	29.3	40.4	64.5

Table 3. Effect of the radical inhibitor cyclohexene on rate

Substrate	Temperature (°C)	P_s (Torr)[a]	P_i (Torr)[a]	P_iP_s	$10^4 k_1$ (s^{-1})
Ethyl *N*,*N*-diethylcarbamate	375.5	17	—	—	10.57
		160.5	37	0.2	10.38
		82	70	0.9	10.95
		49	94	1.9	10.91
		26	118	4.5	10.56
Isopropyl *N*,*N*—diethylcarbamate	329.9	54	—	—	17.65
		66	58	0.9	17.76
		52.5	69	1.3	17.97
		31	79	2.6	17.46
		21	133	6.3	17.04
tert-Butyl *N*,*N*-diethylcarbamate	250.0	25.5	—	—	10.43
		111	46	0.4	10.16
		59.5	65	1.1	10.90
		49	97	2.0	10.09
		17	161	9.5	10.87

[a] P_s = pressure of the substrate and P_i = pressure of the inhibitor cyclohexene.

Table 4. Variation of the rate coefficient with temperature

Parameter	Ethyl *N*, *N*-diethylcarbamate						
Temperature (°C)	340.5	349.5	359.8	369.9	380.4	389.5	399.7
$10^4 k_1$ (s^{-1})	1.71	2.99	5.06	8.52	15–34	23.14	37.89
log k_1 (s^{-1}) = 11.47 (0.25) − 178.4 (3.1) kJmol^{-1} (2.303RT)$^{-1}$; r = 0.99980							
	Isopropyl *N*,*N*-diethylcarbamate						
Temperature (°C)	291.7	301.2	310.4	320.2	330.5	340.0	350.8
$10^4 k_1$ (s^{-1})	1.48	3.22	5.51	10.30	18.14	35.57	55.37
log k_1 (s^{-1}) = 12.83 (0.70) − 179.8 (7.9) kJmol^{-1} (2.303RT)$^{-1}$; r = 0.99872							
	tert-Butyl *N*,*N*-diethylcarbamate						
Temperature (°C)	220.1	228.4	241.7	250.1	260.3	270.1	279.5
$10^4 k_1$ (s^{-1})	1.07	2.45	6.09	10.41	20.68	43.97	71.57
log k_1 (s^{-1}) = 12.87 (0.62) − 158.6 (6.2) kJmol^{-1} (2.303RT)$^{-1}$; r = 0.99900							

Table 5. Comparative rates and kinetic parameters at 320 °C

Compound	$10^4\ k_1$ (s^{-1})	E_a (kJmol)	Log A (s^{-1})	$\Delta S^{\pm}$ (J mol^{-1})	$\Delta H^{\pm}$ (kJ mol^{-1})	Reference
$(CH_3)_2NCOOCH_2CH_3$	0.58	185.5	12.10	−27.2	180.6	10
$(CH_3CH_2)_2NCOOCH_2CH_3$	0.56	178.4 ± 3.1	11.47 ± 0.25	−39.3	173.5	This work
$(CH_3)_2NCOOCH(CH_3)_2$	12.02	181.2	13.04	−9.2	176.3	10
$(CH_3CH_2)_2NCOOCH(CH_3)_2$	9.77	179.8 ± 7.9	12.83 ± 0.70	−13.3	174.9	This work
$(CH_3)_2NCOOC(CH_3)_3$	912.00	157.9	12.87	−12.3	153.0	10
$(CH_3CH_2)_2NCOOC(CH_3)_3$	794.30	158.6 ± 6.2	12.87 ± 0.62	−12.5	153.7	This work

Table 6. Kinetic parameters for the pyrolyses of $ZCOOCH_2CH_3$ at 400 °C

Z	$10^4 k_1$(s^{-1})	k/k_H	E_a (kJmol)	Log A(s^{-1})	Log k/k_H	σ^*	Reference
H	5.25	1.0	201.7	12.34	−0.280	0.49	11
CH_3	10.00	1.9	200.4	12.55	0.000	0.00	12
C_6H_5	16.60	3.2	199.5	12.70	0.220	0.60	13
$(CH_3)_2N$	50.12	9.6	185.5	12.10	0.700	0.68	14
$(CH_3CH_2)_2N$	41.69	7.9	178.4	11.47	0.620	0.62	This work
CH_3O	44.67	8.5	187.5	12.20	0.650	1.46	15
C_6H_5O	97.72	18.6	189.5	12.70	0.990	2.24	13
Cl	245.47	46.8	183.6	2.64	1.390	2.94	16

Table 7. Relatives rates and substituent parameters of $ZCOOCH_2CH_3$ at 400 °C

Z	Log k/k_H	σ_α	σ_F	σ_{R^-}
H	0.000	0.00	0.00	0.00
CH_3	0.280	−0.35	0.00	0.03
C_6H_5	0.500	−0.85	0.10	0.22
$(CH_3)_2N$	0.980	−0.44	0.10	−0.26
$(CH_3CH_2)_2N$	0.900	−0.56	0.10	−0.27
CH_3O	0.930	−0.17	0.25	−0.27
C_6H_5O	1.270	−0.38	0.38	—
Cl	1.670	−0.43	0.45	−0.12

[a] C. Hansch, A. Leo, and R. W. Taft, *Chem. Rev.* **91,** 165 (1991).

release to the reaction center, where the elongation of the C_α—O bond and polarization in the sense of $C_\alpha^{\delta+}\cdots O^{\delta-}$ is the rate-determining step of these reactions. Even though the rates for the *N*,*N*-diethylcarbamates are similar to therefor the corresponding *N*,*N*-dimethylcarbamates (Table 5), the $(CH_3CH_2)_2N$ substituent at the acid side of the ester tends to decrease the rate slightly compared with the $(CH_3)_2N$ group. This difference may be rationalized in terms of the greater electron-releasing power of the CH_3CH_2 group to the N atom than CH_3. This reduces the electron-withdrawing effect of the diethylamino group and a slight decrease in the rate of elimination results.

The observed decrease in entropy of activation from ethyl to *tert*-butyl *N*,*N*-diethylcarbamates suggests a change in the polarity of the transition state on increasing the alkyl branch of the ester. The more negative $\Delta S\ddagger$ for the ethyl ester suggests a more symmetrical arrangement and possible planarity of the transition state. This phenomenon seems to be more difficult with increasing bulkiness of the alkyl group such as isopropyl or *tert*-butyl. An alternative argument with regard to the conformation and entropy of the unactivated precursor rather than the transition state is that in the isopropyl and *tert*-butyl esters, one of the methyl groups is already in the vicinity of the carbonyl oxygen in a low-energy conformation, whereas the ethyl group will preferentially orient *anti* to the C—O bond, and thus require rotation to a less favorable orientation to achieve the cyclic transition state.

In relation to the organic esters investigated by Taylor,[13] the carbamates examined in this work confirm the proposed order of reactivity, carbonates < carbamates < benzoates < phenylacetates < acetates.

The kinetic parameters and comparative rates of different substituents other than carbon at the acid side

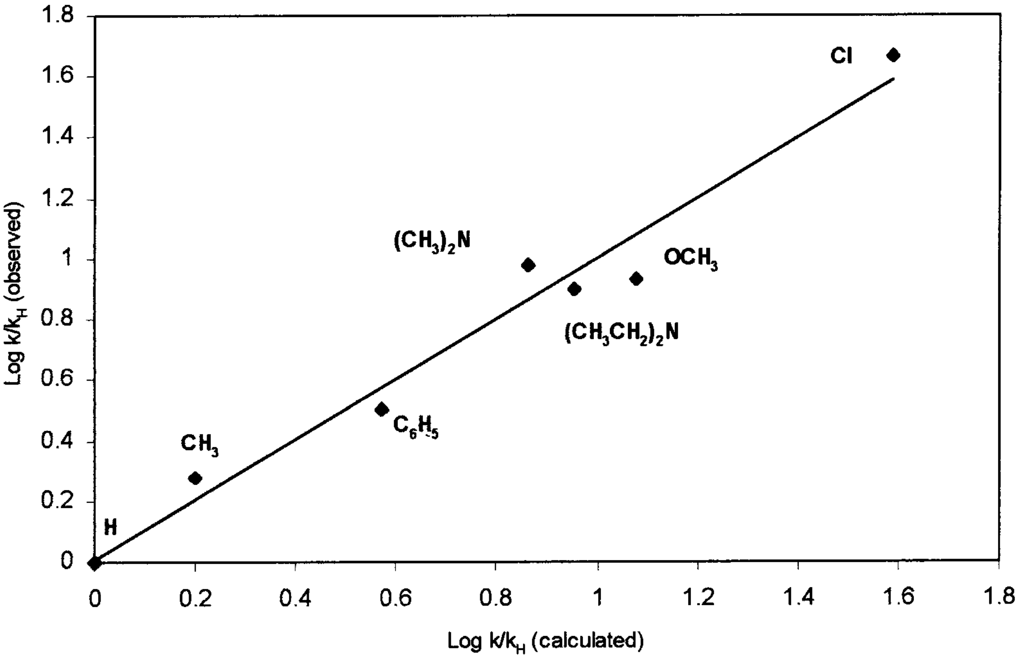


Figure 1. Taft–Topsom correlation for the pyrolysis of ZCOOCH$_2$CH$_3$ (r = 0.984 ± 0.119 at 400 °C)

of an organic ethyl ester are shown in Table 6. It is reasonable to believe that some additional effect other than just the electronic character of Z in ZCOOCH$_2$CH$_3$ may be operating in the rate of elimination of these substrates. To rationalize the above argument, on plotting log k_{rel}. against Taft σ^* values (Table 6), a poor relationship is obtained (ρ^* = 0.46 ± 0.16; r = 0.862 ± 0.295 at 400 °C). However, the Taft–Topsom treatment of log $k/k_H = \sigma_\alpha\rho_\alpha + \sigma_F\rho_F + \sigma_R\rho_R$ takes into account the steric (σ_α), electronic (σ_F) and resonance (σ_R) factors in the quantitative study of structural and substituent effects on chemical reactivity. In this respect, a good correlation is found between the experimental data and the three substituent parameters σ_α, σ_F and σ_{R^-} [Table 7; Eqn 4; Fig. 1].

$$\begin{aligned}\log k/k_H = &-(0.68 \pm 0.12)\sigma_\alpha + (2.57 \pm 0.12)\sigma_F \\ &-(1.18 \pm 0.27)\sigma_{R^-} \qquad (4) \\ &(\text{at } 400\,^\circ\text{C, r} = 0.984, \text{SD} = 0.119)\end{aligned}$$

The C$_6$H$_5$O substituent is not included in Fig. 1 because the corresponding σ_{R^-} value has not yet been defined. It is reasonable to assume that the oxygen of C$_6$H$_5$O, through delocalization to the aromatic nuclei, must exert a more powerful attraction of electrons than CH$_3$O. Consequently, the σ_{R^-} be much less negative than σ_{R^-} of CH$_3$O. If this is so, the position of the data point for the C$_6$H$_5$O group may well fall close to the line depicted in Fig. 1.

The small negative value of the coefficient ρ_α implies a modest participation of the polarizability, or steric effect, of the substituent Z on the rate of ethylene elimination. The influence of paramount importance in the process of ZCOOCH$_2$CH$_3$ decomposition is the field or electronic effect. This is demonstrated by the fact that the coefficient of greatest absolute value is ρ_F. The fact that the best correlation may be obtained by including σ_{R^-} values confirms the interaction between the substituent with an incipient negative reaction center. Moreover, the negative value of the coefficient ρ_{R^-} suggests a small favorable effect for the abstraction of the β-hydrogen of the ethyl ester by the oxygen of the carbonyl (Scheme 1).

EXPERIMENTAL

General preparations. The alkyl esters of *N,N*-diethylcarbamic acid were prepared by mixing 0.15 mol of the corresponding alcohol (Merck) with 0.15 mol of *N,N*-diethylcarbamyl chloride (Aldrich) in 45 ml of anhydrous pyridine. The reaction mixtures were heated in a 100 ml sealed glass tube as described.[18]

Ethyl N,N-diethylcarbamate. This product, obtained as described above, was distilled several times (b.p. 78–79 °C at 28 Torr; yield 55.1%) and the fraction with 97.8% purity as determined by GLC (Pennwalt 223/KOH, 80–100 mesh) was used. ^{1}H NMR, δ 0.99 (t, 6H), 1.13 (t, 3H), 3.1 (q, 4H), 4.0 (q, 2H). MS, *m/z* 145 (M$^+$), 130 (C$_6$H$_{12}$NO$_2^+$), 116 (M$^+$ – C$_2$H$_5$), 100 (M$^+$ – OCH$_2$CH$_3$), 86 (C$_3$H$_4$NO$_2^+$), 72 (C$_2$H$_2$NO$_2^+$), 58

(CON_2^+). The primary product ethylene (Matheson) was determined using a Porapak Q 80–100 mesh column.

Isopropyl N,N-diethylcarbamate. This carbamate substrate prepared according to the above general method[18] (b.p. 58 °C at 15 Torr; yield 63%) was distilled to 99.8% purity as determined by GLC (Pennwalt 223/KOH, 80–100 mesh). ^{1}H NMR, δ 0.98 (t, 6H), 1.11 (d, 6H), 3.1 (q, 4H), 4.80 (m, H). MS, *m/z* 159 (M^+), 144 ($M^+ - CH_3$), 116 [$M^+ - CH(CH_3)_2$], 102 ($C_4H_8NO_2^+$), 72 ($C_2H_2NO_2^+$), 58 (CON_2^+), 43 ($C_3H_7^+$). Propene (Air Products) was determined using a Porapak R 80–100 mesh column.

tert-Butyl N,N-diethylcarbamate. This compound was prepared as described[18] (b.p. 38 °C at 2 Torr; yield 31%). Several distillations gave a purity of 98.1% as determined by GLC (Porapak R, 80–100 mesh). ^{1}H NMR, δ 0.96 (t, 6H), 1.32 (s, 9H), 3.07 (q, 4H). MS, 173 (M^+), 100 [$M^+ - OC(CH_3)_3$], 72 ($C_2H_2NO_2^+$), 57 ($C_4H_9^+$). The olefin product isobutylene (Union Carbide) was determined using the same Porapak R column.

Kinetics. The kinetic determinations were carried out in a static system and the rate coefficients were followed by measuring the pressure increase. The temperature was controlled by a SHINKO DIC-PS 25 TR resistance thermometer controller maintaned within ±0.2 °C and measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was found in the reaction vessel and the carbamate substrates were injected with a syringe through a silicone-rubber septum directly into the reaction vessel.

Acknowledgements

We are grateful to Professor José L. Abbud for correlation calculations and the financial support of CONICIT (Consejo Nacional de Investigaciones Científicas y Tecnológicas) of Venezuela, Project No. S1-97000005.

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