JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2002; **15:** 796–800
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/poc.525

Kinetics of elimination of several heterocyclic carbamates in the gas phase†

Yannely Brusco,[1] Rosa M. Domínguez,[2] Alexandra Rotinov,[2] Armando Herize,[2] Mary Cordova[1] and Gabriel Chuchani[2]*

[1]Departamento de Química, Universidad de Oriente, Cumana, Sucre, Venezuela
[2]Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela

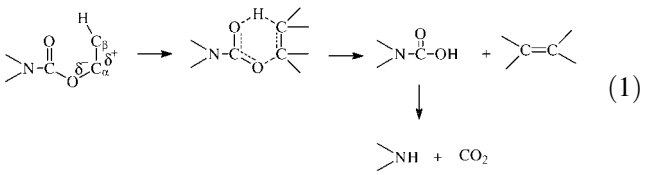
Received 18 February 2002; revised 27 March 2002; accepted 29 March 2002

ABSTRACT: The kinetics of the gas-phase elimination of several heterocyclic carbamates were determined in a static system over the temperature range 190.0–409.7 °C and the pressure range 26.5–125 Torr (1 Torr = 133.3 Pa). The reactions in seasoned vessels, with the free radical inhibitor cyclohexene and/or toluene always present, are homogeneous and unimolecular and obey a first-order rate law. The observed rate coefficients are represented by the following Arrhenius equations: for *tert*-butyl-1-pyrrolidine carboxylate, $\log k_1\ (s^{-1}) = (11.36 \pm 0.31) - (145.4 \pm 3.1)$ kJ mol^{-1} $(2.303RT)^{-1}$; for 1-(*tert*-butoxycarbonyl)-2-pyrrolidinone, $\log k_1\ (s^{-1}) = (11.54 \pm 0.29) - (140.8 \pm 2.8)$ kJ mol^{-1} $(2.303RT)^{-1}$; for *tert*-butyl-1-pyrrole carboxylate, $\log k_1\ (s^{-1}) = (12.12 \pm 0.05) - (145.2 \pm 1.0)$ kJ mol^{-1} $(2.303RT)^{-1}$; and for 1-ethylpiperazine carboxylate, $\log k_1\ (s^{-1}) = (12.05 \pm 0.19) - (188.2 \pm 4.6)$ kJ mol^{-1} $(2.303RT)^{-1}$. The saturated heterocyclic carbamates show a decrease in rates of elimination due to electronic factors. Heterocyclic carbamates with a nitrogen atom able to delocalize its electrons with π-bonds present in the ring were found to enhance the rates due to resonance interactions. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: elimination; kinetics; heterocyclic carbamates

INTRODUCTION

The gas-phase pyrolysis kinetics of 2-alkyl-substituted ethyl *N,N*-diethylcarbamates[1] have been shown to enhance the rate of ethylene elimination in the order *tert*-butyl > isopropyl > ethyl, which is consistent with the sequence of the comparative rates for the corresponding 2-alkyl-substituted ethyl *N,N*-dimethylcarbamates.[2] These reactions suggested that C_α—O bond polarization, in the direction $C_\alpha^{\delta+}$—$O^{\delta-}$, is the rate-determining step. The mechanism of these reactions was believed to proceed according to reaction (1).



(1)

The $(CH_3CH_2)_2N$ substituent at the acid side of the above-mentioned esters was found to decrease the rate slightly compared with $(CH_3)_2N$. This difference was explained in terms of the greater electron-releasing power of the CH_3CH_2 group to the N atom than CH_3. Along this line of work, the effect of a phenyl group at the N atom in ethyl *N*-methyl-*N*-phenylcarbamate[3] gave a small decrease in rate compared with $(CH_3)_2NCOOCH_2CH_3$. Moreover, when the remaining CH_3 at the N atom of ethyl *N*-methyl-*N*-phenylcarbamate was replaced by an additional phenyl group, i.e. ethyl *N,N*-diphenylcarbamate, the rate decreased significantly by a factor of 9.8. This result suggested that steric factors may well affect this process of elimination.

Further investigation of the factors which may affect the rate of elimination of carbamates involves considering heterocyclic nitrogen subtituents at the acid side of carbamates, where the nitrogen atom is part of a cyclic saturated or conjugated π-bond system. Therefore, the present work was aimed at examining the pyrolysis kinetics of *tert*-butyl-1-pyrrolidine carboxylate, 1-(*tert*-butoxycarbonyl)-2-pyrrolidinone, *tert*-butyl-1-pyrrole carboxylate and 1-ethylpiperazine carboxylate in the gas phase.

RESULTS AND DISCUSSION

The molecular elimination of the carbamates described by reaction (2): in a static system, with vessels seasoned

**Correspondence to:* G. Chuchani, Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela.
†Presented in part at the Sixth Latin American Conference on Physical Organic Chemistry (CLAFQO-6), held at Isla Margarita, Venezuela, during December 2001.
Contract/grant sponsor: Fondo Nacional de Ciencia, Tecnologíae Innovación (FONACIT); *Contract/grant number:* S1-97000005.

Copyright © 2002 John Wiley & Sons, Ltd.

with allyl bromide and in the presence of cyclohexene and/or toluene inhibitors, demands that $P_f/P_0 = 3.0$, where P_f and P_0 are the final and initial pressure, respectively (Table 1). The average experimental results for P_f/P_0 values at four different temperatures and 10 half-lives were 2.95 for *tert*-butyl-1-pyrrolidine carboxylate, 2.84 for 1-(*tert*-butoxycarbonyl)-2-pyrrolidinone, and 2.81 for *tert*-butyl-1-pyrrole carboxylate.

$$\begin{array}{l} ZCOOC(CH_3)_3 \rightarrow |\ ZCOOH\ | + CH_2=C(CH_3)_2 \\ \qquad\qquad\quad \downarrow \\ \qquad\qquad\quad ZH + CO_2 \end{array} \qquad (2)$$

$$Z = C_4H_8N,\ C_4H_6ON,\ \text{and}\ C_4H_4N$$

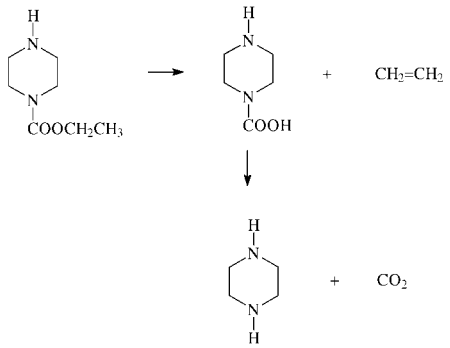
The departure from $P_f = 3P_0$ results mainly from a small extent of polymerization of an authentic sample of the olefinic product isobutene. Additional verification of the stoichiometry (2) was made by comparing the percentage decomposition of the substrate calculated from pressure measurements with that obtained from the chromatographic analyses of the olefin product isobutene (Table 2).

The homogeneity of these reactions was examined in the presence of the inhibitors cyclohexene and/or toluene in a vessel with a surface-to-volume ratio 6.0 times greater than normal, which is equal to 1.0 (Table 3). The packed and unpacked clean Pyrex vessels had a significant effect on the rates. However, when the packed and unpacked vessels were seasoned with allyl bromide, except 1-(*tert*-butoxycarbonyl)-2-pyrrolidinone, no marked effect on the rate coefficients of these carbamates occurred. The pyrolysis of these carbamates, in seasoned vessels, had to be carried out in the presence of at least twice the amount of the inhibitor cyclohexene and/or toluene (Table 4). No induction period was obtained. The rate coefficients are reproducible with a relative standard deviation not greater than 5% at a given temperature.

The rate coefficients of these eliminations were found to be invariable to initial pressures (Table 5), and the first-order rate was calculated from $k_1 = (2.303/t) \log [2P_0/(3P_0 - P_t)]$. A plot of $\log(3P_0 - P_t)$ against time t gave a good straight line up to 60–75% decomposition. The variation of the rate coefficient with temperature and the corresponding Arrhenius equations are given in Table 6 (90% confidence coefficient from the least-squares procedure).

1-Ethylpiperazine carboxylate

The elimination products of reaction (3):



(3)

suggest a theoretical $P_f/P_0 = 3.0$. The average experimental results for P_f/P_0 at four temperatures and 10 half-lives is 2.77 (Table 1). The small departure from stoichiometry was found to be due to a small extent of decomposition of an authentic sample of piperazine. Further verification of the stoichiometry of reaction (3), up to 45% decomposition, was obtained by comparing the pressure increase with the quantitative GLC analysis of ethylene formation (Table 2). The homogeneity of this pyrolytic elimination was examined by using a packed reaction vessel with a surface-to-volume ratio six times

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

Substrate	Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	Average
tert-Butyl-1-pyrrolidine carboxylate	230.2	18	54.5	3.03	2.95
	240.8	21	62.5	2.98	
	250.8	31	89.5	2.89	
	260.9	45	130.5	2.90	
1-(*tert*-Butoxycarbonyl)-2-pyrrolidinone	210.0	27	76	2.81	2.84
	219.6	34	97.5	2.87	
	229.3	26.5	75	2.83	
	239.8	59	164.5	2.83	
tert-Butyl-1-pyrrole carboxylate	213.7	96	281	2.93	2.81
	224.4	81	226	2.79	
	235.1	63	164	2.76	
	245.7	53	145	2.74	
1-Ethylpiperazine carboxylate	372.0	90	255	2.83	2.77
	380.5	92	259	2.82	
	389.0	80	217	2.71	
	399.0	67	181	2.70	

Copyright © 2002 John Wiley & Sons, Ltd.

Table 2. Stoichiometry of the reaction

Substrate	Temperature (°C)	Parameter			Value		
tert-Butyl-1-pyrrolidine carboxylate	260.9	Time (min)	5	6	8	10	12
		Reaction (%) (pressure)	31.6	39.3	44.7	57.1	64.9
		Isobutene (%) (GLC)	29.1	37.9	43.8	55.2	63.9
1-(*tert*-Butoxycarbonyl)-2-pyrrolidinone	239.8	Time (min)	3	5	7	10	15
		Reaction (%) (pressure)	25.6	38.3	47.1	61.8	71.0
		Isobutene (%) (GLC)	25.5	36.4	45.1	63.8	75.6
tert-Butyl-1-pyrrole carboxylate	235.1	Time (min)	1.5	3	6	9	11
		Reaction (%) (pressure)	15.5	24.3	42.0	53.3	62.1
		Isobutene (%) (GLC)	14.6	24.6	42.3	53.9	61.3
1-Ethylpiperazine carboxylate	372.0	Time (min)	1.5	3	7	10	16
		Reaction (%) (pressure)	8.3	16.1	33.3	40.6	43.9
		Ethylene (%) (GLC)	7.7	15.8	33.3	41.0	45.1

Table 3. Homogeneity of the reactions

Compound	S/V (cm^{-1})[a]	$10^4\ k_1$ (s^{-1})[b]	$10^4\ k_1$ (s^{-1})[c]
tert-Butyl-1-pyrrolidine carboxylate at 260.9 °C	1	7.90	13.85
	6	12.27	13.92
1-(*tert*-Butoxycarbonyl)-2-pyrrolidinone at 229.3 °C	1	47.05[d]	8.15
	6	50.0[d]	44.25[d]
tert-Butyl-1-pyrrole carboxylate at 235.1 °C	1	16.4	15.16
	6	20.98	15.58
1-Ethylpiperazine carboxylate at 369.9 °C	1	5.21	4.81
	6	5.60	4.83

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

Table 4. Effect of the free radical inhibitor on rates[a]

Substrate	Temperature (°C)	P_s (Torr)[b]	P_i (Torr)[c]	P_i/P_s	$10^4\ k_1$ (s^{-1})
tert-Butyl-1-pyrrolidine carboxylate	260.9	44	—	—	14.47
		24	16	0.7	13.91
		37	60	1.6	13.68
		45	122	2.7	13.72
		38.5	132	3.4	13.74
1-(*tert*-Butoxycarbonyl)-2-pyrrolidinone	229.3	33.5	—	—	—[d]
		43	35	0.8	7.07
		52.5	101.5	1.9	7.97
		43	109.5	2.6	8.34
		40	127.5	3.2	8.03
		26.5	111	4.2	8.35
tert-Butyl-1-pyrrole carboxylate	235.1	57	—	—	15.02
		66	50	0.7	15.20
		64	88	1.4	15.27
		55	161	2.9	15.29
		52	182	3.5	15.26
1-Ethylpiperazine carboxylate	380.5	103	—	—	13.29
		144	73	0.5	11.60
		98	114	1.2	11.64
		65	156	2.4	11.54
		75	204	2.7	11.69

[a] Cyclohexene or toluene inhibitor.
[b] P_s, pressure of the substrate.
[c] P_i, pressure of the inhibitor.
[d] k Value unreliable.

Copyright © 2002 John Wiley & Sons, Ltd.

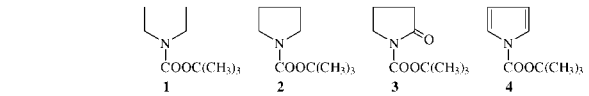
Table 5. Invariability of the rate coefficients with initial pressure

Substrate	Temperature (°C)	Parameter	Value				
tert-Butyl-1-pyrrolidine carboxylate	260.9	P_0 (Torr)	28	38.5	45	75	
		$10^4\ k_1\ (s^{-1})$	13.93	13.64	13.72	13.99	
1-(*tert*-Butoxycarbonyl)-2-pyrrolidinone	229.3	P_0 (Torr)	26.5	34.5	43	52.5	61
		$10^4\ k_1\ (s^{-1})$	8.35	8.05	8.34	7.97	8.00
tert-Butyl-1-pyrrole carboxylate	224.3	P_0 (Torr)	41	51	81	105	121
		$10^4\ k_1\ (s^{-1})$	7.32	7.45	7.51	7.46	7.41
1-Ethylpiperazine carboxylate	380.5	P_0 (Torr)	51	70	80	98	108
		$10^4\ k_1\ (s^{-1})$	11.54	11.62	11.57	11.60	11.59

greater than that of the unpacked vessel (Table 3). The packed and unpacked Pyrex vessels seasoned with allyl bromide had no effect on rates. However, the packed and unpacked clean Pyrex vessels gave a small but significant heterogeneous effect. The effect of addition of different proportions of toluene inhibitor is shown in Table 4. According to this result, the pyrolysis experiments had to be carried out in the presence of at least an equal amount of toluene 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 coefficients, in seasoned vessels and in the presence of toluene, were found to be independent of the initial pressure, and the first-order plots are satisfactorily linear up to about 45% reaction (Table 5). The temperature dependence of the rate coefficients, at the 90% confidence level with the least-squares method, is described in Table 6.

The kinetic and thermodynamic parameters of several heterocyclics containing the nitrogen atom at the acid side of esters are given in Table 7. The negative entropy of activation $\Delta S^{\neq}$ of these eliminations suggests a symmetrical arrangement and possible planarity of the transition state, while the enthalpy of activation $\Delta H^{\neq}$ implies endothermic processes. The values of log$A$ between 11.36 and 12.87 are reasonable for a six-membered cyclic transition-state mechanism. The fact that these carbamates are not spontaneous, unstable and endergonic is reflected by the free energy of activation $\Delta G^{\neq}$ given in Table 7.



	1	2	3	4
Relative rate, at 230°C	1.0	0.7	3.3	4.4

When the terminal CH_3 of the $(CH_3CH_2)N$ group of the *tert*-butyl ester **1** are bound together to form the heterocyclic substituent of the carbamate, i.e. *tert*-butyl-1-pyrrolidine carboxylate **2**, the rate of elimination of this substrate decreased compared with ethyl *N,N*-diethylcarbamate **1** (Table 7). Apparently, the electronic effect of the 1-pyrrolidine substituent may be operating during the process of decomposition. Moreover, when the pyrrolidine skeleton in **2** is modified by introducing a carbonyl group such as **3**, i.e. 1-(*tert*-butoxycarbonyl)-2-pyrrolidinone, or to a conjugated π-system such as **4**, i.e. 1-*tert*-butylpyrrole carboxylate, both substrates give a significant enhancement in the rate of isobutylene elimination with respect to **1** (Table 7). Consequently, an electronic effect seems to be the paramount factor in the decomposition process of these substrates. Delocalization of the nitrogen electrons to the carbonyl group in **3**, and to the

Table 6. Variation of rate coefficients with temperature

Substrate	Parameter	Value						
tert-Butyl-1-pyrrolidine carboxylate	Temperature (°C)	220.6	230.2	241.0	250.8	260.9	270.0	280.0
	$10^4\ k_1\ (s^{-1})$	0.99	1.82	3.63	7.48	13.72	23.82	42.88
Rate equation	$\text{Log}[k_1\ (s^{-1})] = (11.36 \pm 0.31) - (145.4 \pm 3.1)\ \text{kJ mol}^{-1}\ (2.303RT)^{-1}$; $r = 0.9997$							
1-(*tert*-Butoxycarbonyl)-2-pyrrolidinone	Temperature (°C)	209.5	219.3	229.3	239.8	250.1	260.0	
	$10^4\ k_1\ (s^{-1})$	2.03	3.85	8.15	15.83	29.78	56.00	
Rate equation	$\text{Log}[k_1\ (s^{-1})] = (11.54 \pm 0.29) - (140.8 \pm 2.8)\ \text{kJ mol}^{-1}\ (2.303RT)^{-1}$; $r = 0.9998$							
tert-Butyl-1-pyrrole carboxylate	Temperature (°C)	193.4	203.2	213.8	224.3	235.1	245.7	254.7
	$10^4\ k_1\ (s^{-1})$	0.72	1.53	3.49	7.39	15.15	31.23	56.14
Rate equation	$\text{Log}[k_1\ (s^{-1})] = (12.12 \pm 0.05) - (145.2 \pm 1.0)\ \text{kJ mol}^{-1}\ (2.303RT)^{-1}$; $r = 0.9999$							
1-Ethylpiperazine carboxylate	Temperature (°C)	353.4	369.9	372.0	380.5	389.0	399.0	409.7
	$10^4\ k_1\ (s^{-1})$	2.60	4.81	6.94	11.58	18.08	30.02	50.20
Rate equation	$\text{Log}[k_1\ (s^{-1})] = (12.05 \pm 0.19) - (188.2 \pm 4.6)\ \text{kJ mol}^{-1}\ (2.303RT)^{-1}$; $r = 0.9997$							

Copyright © 2002 John Wiley & Sons, Ltd.

Table 7. Kinetic and thermodynamic parameters for pyrolysis of $ZCOOC(CH_3)_3$ at 230 °C

Z	$k_1 \times 10^{-4}$ (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})	Ref.
$(CH_3CH_2)_2N$	2.52	158.6 ± 6.2	12.87 ± 0.62	−52.3	154.4	180.7	1
	1.83	145.4 ± 3.1	11.36 ± 0.31	−40.2	141.2	161.4	This work
	8.31	140.8 ± 2.8	11.54 ± 0.29	−36.8	136.6	155.1	This work
	11.03	145.2 ± 1.0	12.12 ± 0.05	−25.5	141.0	153.8	This work

Table 8. Comparative rates and kinetic parameters for pyrolysis of $ZCOOCH_2CH_3$ at 380 °C

Z	$k_1 \times 10^{-4}$ (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})	Ref.
$(CH_2CH_3)_2N$	15.83	178.4 ± 3.1	11.47 ± 0.25	−40.2	173.0	199.2	1
HNC_6H_8N	9.90	188.2 ± 4.6	12.05 ± 0.19	−29.1	182.8	201.8	This work

conjugated π-system in **4**, makes these substituents electron withdrawing in nature, thus favouring the C_α—O bond breaking, which is rate determining in the transition state [reaction (1)].

The small but significant decrease in rate of 1-ethylpiperazine carboxylate compared with ethyl *N,N*-diethylcarbamate (Table 8) leads us to believe that the piperazine substituent at the acid side of the ethyl ester affects the rate in terms of electronic effects.

EXPERIMENTAL

tert-Butyl-1-pyrrolidine carboxylate, 1-(*tert*-butoxycarbonyl)-2-pyrrolidinone, *tert*-butyl-1-pyrrole carboxylate and 1-ethylpiperazine carboxylate were acquired from Aldrich. Quantitative analyses of the substrates were performed by GLC (Pennwalt 223, KOH, 80–100 mesh). The olefin products ethylene and isobutylene were analyzed in a column of Porapak Q (80–100 mesh). The verification of the substrates and identifications of the products were carried out by GLC–MS (Saturn 2000, Varian) with a DB-5MS capillary column, 30 × 0.250 mm i.d., 0.25 μm film thickness.

Kinetics. The kinetic determinations were carried out in a static reaction system as described previously[4,5] with some additons and modifications of modern electronic and electrical devices. The reaction vessel was seasoned with the product of decomposition of allyl bromide. The rate coefficients were determined manometrically. The temperature was found to be constant within ±0.2 °C when controlled with a Shinko DIC-PS 23TR resistance thermometer controller, and measured with a calibrated platinum/platinum–13% rhodium thermocouple. The reaction vessel showed no temperature gradient at different points, and the substrate was injected directly into the reaction vessel through a silicone-rubber septum.

Acknowledgements

We are grateful for the financial support of FONACIT (Fondo Nacional de Ciencia, Tecnología e Innovación) of Venezuela, Project No. S1-97000005.

REFERENCES

1. Herize A, Dominguez RM, Rotinov A, Nuñez O, Chuchani G. *J. Phys. Org. Chem.* 1999; **12**: 201–206.
2. Daly NJ, Ziolkowsky F. *J. Chem. Soc., Chem. Commun.* 1972; 911–912.
3. Luiggi M, Dominguez RM, Rotinov A, Herize A, Cordova M, Chuchani G. *Int. J. Chem. Kinet.* 2002; **34**: 1–5.
4. Maccoll A. *J. Chem. Soc.* 1955; 965–973.
5. Swinbourne ES. *Aust. J. Chem.* 1958; **11**: 314–330.

Copyright © 2002 John Wiley & Sons, Ltd.