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A structure–reactivity correlation with three slopes in the elimination kinetics of 2–substituted ethyl *N,N*-dimethylcarbamates in the gas phase

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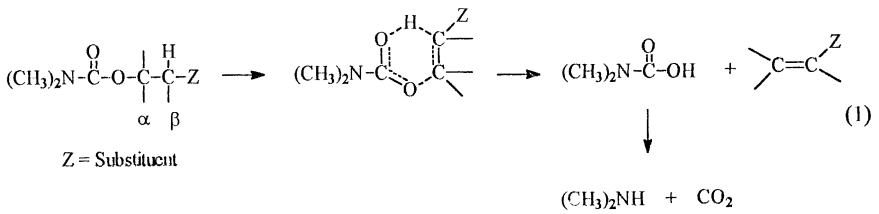
ABSTRACT: The elimination kinetics of 17 2-substituted ethyl *N,N*-dimethylcarbamates in the gas phase were determined in the temperature range of 269.5–420.2 °C and the pressure range of 24–186 Torr. The reactions in a static system and in the presence of a free radical inhibitor are homogeneous and unimolecular and follow a first-order rate law. The kinetics and thermodynamic parameters are described. The use of several structure-reactivity relationship methods meaningless results, except for Taft σ^* values. Three good slopes are originated at $\sigma^*(CH_3) = 0.00$. Slope a: the 2-substituted alkyl groups gave a good straight line when log (k/kCH_3) vs σ^* values ($\rho^* = -1.94 \pm 0.30$, $r = 0.977$ at 360 °C) were plotted. Slope b: Polar[2] substituents gave an approximate straight line with $\rho^* = -0.12 \pm 0.02$, $r = 0.936$ at 360 °C. Slope c: the correlation of multiple bonded and electron-withdrawing substituents interposed by a methylene group at the 2-position of ethyl *N,N*-dimethylcarbamate was found to give a very good straight line wirh $\rho^* = 0.49 \pm 0.02$, $r = 0.991$ at 360 °C. Mechanisms are suggested on the basis of these relationships. The point position of the substituents phenyl (C_6H_5) and isopropenyl [$CH_2{=}C(CH_3)$] at the 2-position was found to fall far above the three slopes of the lines. These results are interpreted in terms of neighboring group participation of these substituents in the elimination process of the carbamates. However, the acidity of the benzylic and allylic C_β-H bond for a six-membered cyclic transition state may not be ignored. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: 2-substituted ethyl *N*, *N*-dimethylcarbamates; gas-phase elimination kinetics; structure–reactivity correlation

INTRODUCTION

The first pyrolytic elimination of a carbamate at subatmospheric pressure was reported by Daly and Ziolkowski.[1] The substrate ethyl *N*-methyl-*N*-phenylcarbamate decomposed into *N*-methylaniline, ethylene and carbon dioxide Further investigations on *N,N*-dimethylcarbamate pyrolyses led to a general accepted mechanism of a six-membered cyclic transition state as described in reaction (1), which is similar to the transition states



Form A

designated for the thermal decomposition of acetates, carbonates and xanthates.[2–6]

In our most recent work, the branching of alkyl groups of *N,N*-dimethylcarbamates enhanced the rates of elimination in the order *tert*-butyl >isopropyl >ethyl.[7] In addition the presence of different substituents Z other

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Table 1. Ratio of final (P_f) to initial (P_0) pressure[a]

Substrate	Temperature (°)	P_o (Torr)	P_f (Torr)	P_f/P_o	Average
Ethyl *N*,*N*-dimethylcarbamate	359.6	73	215	2.95	2.96 ± 0.04
	370.4	88	257	2.92	
	380.8	118	254	3.02	
	390.1	97	285	2.94	
Propyl *N*,*N*-dimethylcarbamate	362.8	90	258	2.87	2.96 ± 0.06
	370.0	64	193	3.01	
	380.1	68	201	2.96	
	389.9	57.5	171	2.98	
1-Butyl *N*,*N*-dimethylcarbamate	361.0	68	179.5	2.64	2.41 ± 0.15
	371.0	71	169	2.38	
	379.0	78	181	2.32	
	400.0	72	167	2.30	
3-Methyl-1-butyl *N*,*N*-dimethylcarbamate	350.6	50	150	3.00	2.98 ± 0.02
	370.5	61	182	2.98	
	380.5	56	165	2.95	
	390.7	44	132	3.00	
3,3 Dimethyl-1-butyl *N*,*N*-dimethylcarbamate	339.7	44	130	2.96	2.93 ± 0.05
	350.7	48	142	2.96	
	370.2	38	112	2.95	
	390.3	37	106	2.85	
2-Chloroethyl *N*,*N*-dimethylcarbamate	379.6	27	80	2.96	2.95 ± 0.02
	390.6	79.5	232	2.92	
	400.5	92.5	275	2.97	
	420.2	89.5	265	2.96	
2-Bromoethyl *N*,*N*-dimethylcarbamate	360.8	94	277	2.95	2.95 ± 0.01
	370.7	95	279	2.94	
	400.6	92	271	2.95	
	410.4	98	288	2.94	
2-Methoxyethyl *N*,*N*-dimethylcarbamate	385.6	55	171	3.11	3.10 ± 0.04
	410.3	40	120.5	3.01	
	419.9	41	129	3.15	
	430.1	39	122	3.13	
2-Butoxyethyl *N*,*N*-dimethylcarbamate	389.6	56	172	3.07	3.04 ± 0.04
	401.1	43	130	3.02	
	410.0	47	145	3.08	
	420.5	67	201	3.00	
3-Phenylpropyl *N*,*N*-dimethylcarbamate	340.5	89	263	2.95	2.95 ± 0.02
	360.4	98	291	2.96	
	380.6	84	249	2.96	
	400.6	92	269	2.92	
3-Chloropropyl *N*,*N*-dimethylcarbamate	360.4	69	202	2.93	2.97 ± 0.03
	370.5	72	215	2.99	
	380.2	112	335	2.99	
	390.5	114.5	342	2.99	
3-Phenoxypropyl *N*,*N*-dimethylcarbamate	350.1	32.5	97	2.98	2.98 ± 0.10
	370.4	49.5	138	2.84	
	380.9	41	125	3.05	
	390.4	40	122	3.05	
2-Dimethylaminoethyl *N*,*N*-dimethylcarbamate	380.7	76	214	2.82	2.83 ± 0.03
	389.9	76	218	2.87	
	400.0	71.5	201.5	2.82	
	409.7	70	176	2.81	
3-Butyn-1-yl *N*,*N*-dimethylcarbamate	329.7	98	220	2.24	2.32 ± 0.07
	340.0	103	238.5	2.32	
	349.0	114.5	265.5	2.32	
	360.0	112	269	2.40	

Table 1 *continued.*

Substrate	Temperature (°)	P_o (Torr)	P_f (Torr)	P_f/P_o	Average
2-Cyanoethyl *N,N*-dimethylcarbamate	290.0	54.5	140	2.63	2.61 ± 0.08
	309.6	34	92	2.71	
	319.0	30.5	77.5	2.54	
	329.6	61	156	2.56	
2-Phenylethyl *N,N*-dimethylcarbamate	310.1	44	131	2.98	2.97 ± 0.03
	321.0	46	135	2.93	
	330.2	65	194	2.98	
	341.7	76	227	2.99	
3-Methyl-3-buten-1-yl *N,N*-dimethylcarbamate	339.6	63	159	2.52	2.26 ± 0.21
	349.6	67.5	157	2.33	
	360.9	67	138.5	2.07	
	370.1	70	147	2.10	

[a]Temperature <360 °C, cyclohexene inhibitor; >360 °C, toluene inhibitor.

than carbon in $ZCOOCH_2CH_3$ gave a good correlation when using the Taft–Topsom method.[7] In relation to this result, the field (inductive) effect of the substituent has the greatest influence on rate enhancement, whereas the polarizability (steric) and resonance factors favor the elimination process very little.

A considerable number of the database of substituents at the 2-position of ethyl acetates ($CH_3COOCH_2CH_2Z$) were examined in correlation studies [8]. The pyrolysis of the acetates with alkyl and polar substituents attached to the C_α—O bond by at least three methylene group was found to be affected by steric acceleration. The log (k/k_0) vs Hancock's steric parameter E_s^c gave a $\delta = -0.12$, $r = 0.916$ at 400 °C. However, electron-withdrawing substituents at the 2-position of ethyl acetates showed an approximate linear relationship with the Taft original inductive parameter σ^*.[9a,b] The ρ^* value was -0.19 ($r = 0.961$ at 400 °C). Likewise, plotting log k/k_0 against σ_1 value also gave a good straight line with slope $\rho_1 = -1.03$ ($r = 0.960$ at 400 °C). Further examination of the influence of these alkyls and a polar group separated by at least a three methylene chain in $CH_3COOCH_2CH_2Z$ was carried out by using the Taft–Topsom method of substituent effects. The result was log $(k/k_o) = -(0.450 \pm 0.004)\ \sigma_\alpha - (1.29 \pm 0.11)\ \sigma_F$ ($r = 0.959$ at 400 °C).[8] The negative value of ρ_α suggests that the elimination process is favored by the polarizability of the 2-substituent Z, while the size of the negative ρ_F implies the stabilization of the transition state by field/inductive effects. The influence of the resonance factor σ_R was found to be insignificant. Multiple bonded substituents Z at the 2-position of ethyl acetates led to a very good Taft–Topsom correlation log $(k/k_0) = -(1.81 \pm 0.02)\ \sigma_\alpha (0.38 \pm 0.03)\ \sigma_F + (7.34 \pm 0.12)\ \sigma_R^-$ (r = 0.999 at 400 °C). This result suggests significant polarizability and resonance effects on the elimination rates.

Because various correlations of substituent effects had to be used to obtain some reasonable explanation of the mechanisms of the gas-phase elimination of 2-substituted ethyl acetates, the present work was addressed at examining a considerable number of 2-substituted ethyl *N,N* dimethylcarbamates [$(CH_3)_2NCOOCH_2CH_2Z$, Z = substituent] in order to establish whether a similar or different linear relationships are obtained for the mechanistic considerations illustrated in reaction (1).

RESULTS AND DISCUSSION

The products of the gas-phase elimination of 2-substituted ethyl *N,N*-dimethylcarbamates are the corresponding olefin, dimethylamine and carbon dioxide [reaction (1)]. The stoichiometry based on reaction (1), demands that for long reaction times $P_f/P_0 = 3$, where P_f and P_0 are the final and initial pressure, respectively (Table 1). The average P_f/P_0 values at four temperatures and ten half-lives were, within the experimental errors, nearly 3.0. However, a departure of $P_f/P_0 < 3.0$ for 1-butyl, 2-dimethylaminoethyl, 3-butyn-1-yl, 2-cyanoethyl and 3-methyl-3-buten-1-yl *N,N*-dimethylcarbamates was due to polymerization of the corresponding olefinic product. These pure unsaturated products when introduced in the reaction vessel give rise to a decrease in pressure and formation of a solid polymer product. Further examination for the verification of the stroichiometry in reaction (1), up to 50–77% reaction, was made by comparing the extent of decomposition of the substrate from pressure measurements with that obtained from quantitative gas–liquid chromatographic (GLC) analyses of the corresponding olefin formation or from the unreacted amount of the carbamate (Table 2).

The pyrolytic elimination of reaction (1) was found to be homogeneous, since no significant variations in rates were obtained in these experiments when using both clean Pyrex and seasoned vessels with a surface-to-

Table 2. Stoichiometry of the reaction.[a]

Substrate	Temperature (C °C)	Parameter	Value				
Ethyl *N*,*N*-dimethylcarbamate	380.8	Time (min)	4	5	7	9	12
		Reaction (%) (pressure)	28	33.5	43.3	50.8	65.1
		Ethylene (%) (GLC)	28.2	33.5	44.7	50.2	64.1
Propyl *N*,*N*-dimethylcarbamate	370.0	Time (min)	8	12.5	20	46	300
		Reaction (%) (pressure)	20.6	30.8	41.2	60.8	72.5
		Propene (%) (GLC)	20.9	32.4	42.0	59.2	72.0
1-Butyl *N*,*N*-dimethylcarbamate	379.0	Time (min)	4	6	8	11	16
		Reaction (%) (pressure)	22.8	33.3	38.5	50.0	63.5
		Butene (%) (GLC)	22.9	33.5	37.8	50.1	63.9
3-Methyl-1-butyl *N*,*N*-dimethylcarbamate	370.0	Time (min)	4	6	10	12	16
		Reaction (%) (pressure)	21.9	34.2	45.5	52.0	62.5
		3-Methyl-1-butene (%) (GLC)	21.5	33.4	48.0	52.3	62.0
3,3 Dimethyl-1-butyl *N*,*N*-dimethylcarbamate	360.1	Time (min)	4	6	8	11	16
		Reaction (%) (pressure)	22.8	33.3	38.5	50.0	63.5
		3,3-Dimethyl-1-butene (%) (GLC)	22.9	33.5	37.8	50.1	63.9
2-Chloroethyl *N*,*N*-dimethylcarbamate	390.3	Time (min)	6	10	16	40	150
		Reaction (%) (pressure)	24.3	39.2	50.7	61.8	73
		Vinyl chloride (%) (GLC)	21.1	39.9	50	62.2	67.7
2-Bromoethyl *N*,*N*-dimethylcarbamate	400.0	Time (min)	4	6	8	10	13
		Reaction (%) (pressure)	21.4	30.6	39.6	49.7	64.9
		Vinyl bromide (%) (GLC)	20.3	30.2	40.2	51.1	65.1
2-Methoxyethyl *N*,*N*-dimethylcarbamate	380.3	Time (min)	10	20	30	40	60
		Reaction (%) (pressure)	22.1	31.9	41.9	54.6	69.6
		Methyl vinyl ether (%) (GLC)	21.1	34.5	44.4	53.8	66.6
2-Butoxyethyl *N*,*N*-dimethylcarbamate	390.0	Time (min)	6	12	18	25	35
		Reaction (%) (pressure)	15.3	29.7	36.3	45.1	73.4
		Butyl methyl ether (%) (GLC)	15.7	28.6	35.8	45.3	74.5
3-Phenylpropyl *N*,*N*-dimethylcarbamate	370.0	Time (min)	2	4	6	9	12
		Reaction (%) (pressure)	11.4	21.9	31.1	42.9	51.8
		3-Phenyl-1-propene (%) (GLC)	11.5	21.4	30.9	42.6	51.8
3-Chloropropyl *N*,*N*-dimethylcarbamate	350.3	Time (min)	6	10	18	22	30
		Reaction (%) (pressure)	19.2	28.5	37.8	72.6	60.6
		3-Chloro-1-propene (%) (GLC)	19.1	28.5	38.0	51.9	59.3
3-Phenoxypropyl *N*,*N*-dimethylcarbamate	360.8	Time (min)	2	5	10	14	22
		Reaction (%) (pressure)	10.7	22.1	37.8	47.4	63.0
		Allyl phenyl ether (%) (GLC)	10.6	24.3	37.2	48.0	61.5
2-Dimethylaminoethyl *N*,*N*-dimethylcarbamate	379.6	Time (min)	4	7	9	15	
		Reaction (%) (pressure)	18.7	32.7	41.7	50.4	
		Substrate (%) (GLC)	19.1	34.2	42.3	51.7	
3-Butyn-1-yl *N*,*N*-dimethylcarbamate	329.8	Time (min)	4	7	10	13	
		Reaction (%) (pressure)	19.4	31.7	41.6	56.0	
		Substrate (%) (GLC)	17.6	29.5	42.8	55.3	
2-Cyanoethyl *N*,*N*-dimethylcarbamate	300.3	Time (min)	4	7	12	19	
		Reaction (%) (pressure)	18.8	30.3	45.7	58.7	
		Acrylonitrile (%) (GLC)	18.6	28.1	43.1	55.8	
2-Phenylethyl *N*,*N*-dimethylcarbamate	300.0	Time (min)	5	15	20	28	35
		Reaction (%) (pressure)	14.6	34.2	44.8	53.5	75.4
		Styrene (%) (GLC)	14.8	34.6	45.1	53.2	76.8
3-Methyl-3-buten-1-yl *N*,*N*-dimethylcarbamate	339.6	Time (min)	6	8	10	12	15
		Reaction (%) (pressure)	23.2	28.6	40.4	47.4	57.1
		Substrate (%) (GLC)	22.2	30.6	38.4	49.2	59.1

[a]Temperature <360 °C, cyclohexene inhibitor; >360 °C, toluene inhibitor.

volume ratio of 6.0 relative to that of the normal vessel, which is equal to 1.0. The effect of the addition of different proportions of the free radical suppressor cyclohexene or toluene is shown in Table 3. Nevertheless, the pyrolysis experiments were carried out in the presence of at least twice the amount of the inhibitor in

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

Substrate	Temperature (°C)	P_S (Torr)	P_i (Torr)	P_i/P_S	$10^4\ k_1$ (s^{-1})
Ethyl *N*,*N*-dimethyl carbamate	370.4	93	—	—	8.11
		74	30	0.4	8.02
		66	86	1.3	7.98
		52	114	2.2	8.09
Propyl *N*,*N*-dimethylcarbamate	380.0	77	—	—	9.40
		98	89	0.9	9.39
		73	111	1.5	9.43
		47	129	2.7	9.38
1-Butyl *N*,*N*-dimethylcarbamate	379.0	72	—	—	9.92
		116	78	0.7	10.00
		78	103	1.3	10.24
		71	178	2.5	10.19
3-Methyl-1-butyl *N*,*N*-dimethylcarbamate	400.5	73	—	—	49.31
		56	100	1.8	49.81
		41	89	2.2	49.68
		28	86	3.1	48.85
3,3 Dimethyl-1-butyl *N*,*N*-dimethylcarbamate	360.1	44	—	—	11.11
		69.5	66	1.0	10.31
		75	164	2.2	10.99
		43.5	139	3.2	10.60
2-Chloroethyl *N*,*N*-dimethylcarbamate[b]	420.2	60	—	—	38.67
		37	38.5	1.0	37.19
		39	66.5	1.7	38.62
		32	84	2.6	37.95
2-Bromoethyl *N*,*N*-dimethylcarbamate	390.3	103	—	—	8.96
		88	52	0.6	8.85
		85	86	1.0	8.90
		84	165	2.0	8.88
2-Methoxyethyl *N*,*N*-dimethylcarbamate	410.4	49	—	—	14.61
		40	59.5	1.5	14.72
		33	81.5	2.1	14.63
		28	72.5	2.5	14.58
2-Butoxyethyl *N*,*N*-dimethylcarbamate	400.1	94	—	—	21.52
		92	64	0.7	21.65
		90	78	0.9	21.33
		91	118	1.3	21.50
3-Phenylpropyl *N*,*N*-dimethylcarbamate	350.8	85	—	—	3.32
		84	55	0.7	3.32
		68	101	1.5	3.33
		82	159	1.9	3.31
3-Chloropropyl *N*,*N*-dimethylcarbamate	360.4	62	—	—	9.36
		66.5	49	0.7	9.46
		69	107	1.6	9.30
		71	163	2.3	9.41
3-Phenoxypropyl *N*,*N*-dimethylcarbamate	360.6	49	—	—	7.05
		83.5	61	0.7	7.58
		46	87	1.9	7.50
		45	131	2.9	7.47
2-Dimethylaminoethyl *N*,*N*-dimethylcarbamate	379.6	62	—	—	9.42
		119	65	0.5	9.27
		76	105	1.4	9.44
		45	117	2.6	9.88
3-Butyn-1-yl *N*,*N*-dimethylcarbamate	340.0	95	—	—	15.53
		103	79.5	0.8	15.60
		66.5	72.5	1.1	15.49
		87	186.5	2.2	15.64

Table 3 *continued.*

Substrate	Temperature (°C)	P_S (Torr)	P_i (Torr)	P_i/P_S	$10^4\ k_1$ (s^{-1})
2-Cyanoethyl *N,N*-dimethylcarbamate	319.0	50	—	—	25.20
		74	73	1.0	25.23
		48	86	1.8	25.21
		30.5	98	3.2	25.53
2-Phenylethyl *N,N*-dimethylcarbamate	330.1	85	—	—	14.49
		65	58	0.9	14.62
		89	94	1.1	14.77
		94	115	1.2	14.54
3-Methyl-3-buten-1-yl *N,N*-dimethylcarbamate	339.6	60	—	—	8.98
		88	66.5	0.7	7.19
		72	101.5	1.4	7.31
		45	103	2.3	7.40

[a] Temperature <360 °C, cyclohexene inhibitor; >360 °C, toluene inhibitor.
P_S = pressure substrate, P_i = propene inhibitor.

order to prevent 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 these carbamates, calculated from $k_1 = (2.303/t)\log[2P_0/(3P_0 - P_t)]$, were independent of their initial pressure (Table 4). A plot of $\log(3P_0 - P_t)$ against time t gave good straight lines up to 50–75% reaction, indicating that the elimination process is unimolecular in nature. The variation of the rate coefficients with temperature and the corresponding Arrhenius equation is described in Table 5 (90% confidence coefficient from a least-squares procedure).

The kinetic and thermodynamic parameters of a significant number of 2-substituted ethyl *N,N*-dimethylcarbamates [$(CH_3)_2NCOOCH_2CH_2Z$, Z= substituent] are given in Table 6. 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 log of A values between 11.4 and 12.8 are reasonable for a six-membered cyclic transition mechanism.[9c] The indication that these carbamates eliminations are not spontaneous, unstable and endergonic are reflected by the free energy of activation $\Delta G^{\neq}$ values given in Table 6.

Table 7 lists a large number of pyrolyzed primary carbamates which makes it possible to estimate adequately the substituent effect of Z for the $(CH_3)_2NCOOCH_2CH_2Z$ compounds. The Taft–Topsom treatment of substituent effects [Eqn. (2)]:

$$\log(kk_o) = \rho_\alpha\sigma_\alpha + \rho_F\sigma_F + \rho_R^-\sigma_R^- \qquad (2)$$

where the contribution parameters are σ_α = polarizability effect, σ_F = field effect and σ_R^- = resonance effect, was satisfactorily applied to the gas-phase elimination kinetics of 2-substituted ethyl acetates, $CH_3COOCH_2CH_2Z$. However, employing this method of correlation for the carbamates given in Table 7 gave random points with no meaning, even when using one or two of the contribution parameters. Moreover, the application of various correlations[9a,b] such as the steric parameters Hancock's E_s^c, Taft's E_s, Charton's v and the inductive σ_I values also gave random points with no significance for mechanistic interpretations for these series of carbamates. However, plotting $\log k/k_{CH3}$) versus σ^* values gives rise at the origin of σ^* (CH_3) = 0.00 three good slopes (Fig 1), which, means that small alterations in the polarity of the transition state may be due to changes in electronic transmissions at the reaction center. This means that a simultaneous effect may be operating during the process of elimination, especially with electron-withdrawing and multiple-bonded substituents at the 2-position of ethyl *N,N*-dimethylcarbamates. The Taft correlation of alkyl groups gives an approximate straight line [Fig. 1, Eqn. (3)] Thus,

$$\rho^* = -1.94 \pm 0.30 \text{ at } 360^\circ\text{C } (r = 0.9768, \text{SD} = 0.0664) \qquad (3)$$

The negative ρ^* value suggests that a positively charged carbon is rate determining. The greater the electron release of the alkyl groups, the faster is the elimination process. The reaction of this series of carbamates appears to proceed through semi-polar six-membered cyclic transition state mechanims (**TS-1**).

Electron-withdrawing susbtituents give rise at $\sigma^*(CH_3) = 0.00$ to another approximate straight line [Fig 1, Eqn. (4)].

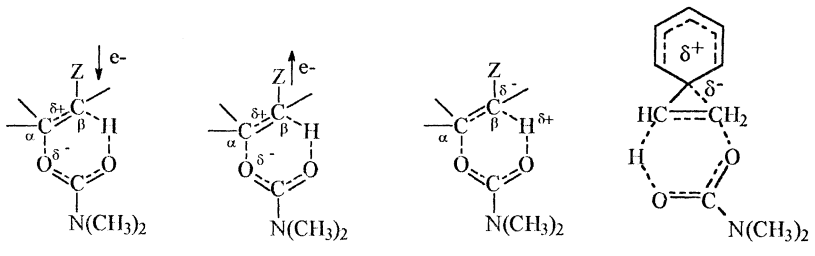
$$\rho^* = -0.12 \pm 0.02 \text{ at } 360^\circ\text{C } (r = 0.9364, \text{SD} = 0.0571) \qquad (4)$$

The smaller negative ρ^* value indicates some destabili-

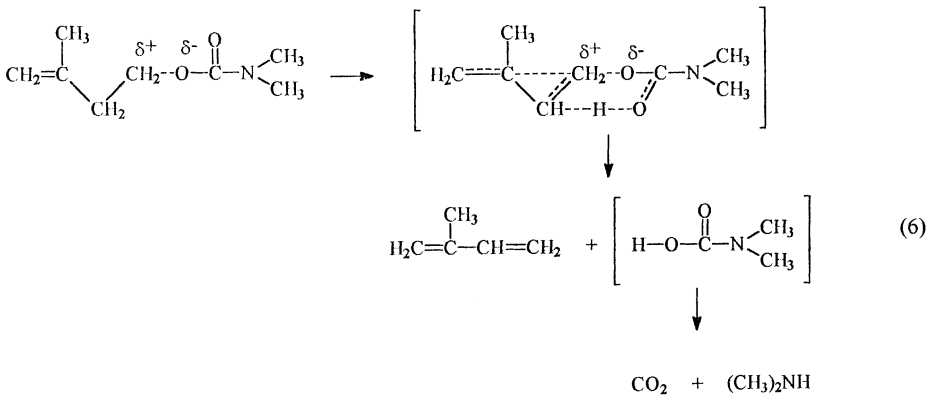
Table 4. Independence of the rate coefficients from initial pressure

Substrate	Temperature (°C)	Parameter	Value				
Ethyl *N*,*N*-dimethylcarbamate	380.5	P_o (Torr)	81.5	94	118	128	186
		$10^4\ k_1\ (s^{-1})$	13.94	13.10	13.97	13.78	13.46
Propyl *N*,*N*-dimethylcarbamate	380.0	P_o (Torr)	40	54	77	86	98
		$10^4\ k_1\ (s^{-1})$	9.45	9.33	9.40	9.34	9.39
1-Butyl *N*,*N*-dimethylcarbamate	379.0	P_o (Torr)	45	68	78.5	85	116
		$10^4\ k_1\ (s^{-1})$	9.83	10.34	10.24	10.19	10.00
3-Methyl-1-butyl *N*,*N*-dimethylcarbamate	400.0	P_o (Torr)	28	23.5	21	56	73.5
		$10^4\ k_1\ (s^{-1})$	49.85	50.21	49.68	49.81	49.32
3,3 Dimethyl-1-butyl *N*,*N*-dimethylcarbamate	360.1	P_o (Torr)	24	44.5	59.5	75	
		$10^4\ k_1\ (s^{-1})$	11.05	11.11	10.91	10.99	
2-Chloroethyl *N*,*N*-dimethylcarbamate	400.5	P_o (Torr)	31.5	43	53	67.5	89
		$10^4\ k_1\ (s^{-1})$	13.37	13.52	13.48	13.60	13.42
2-Bromoethyl *N*,*N*-dimethylcarbamate	400.4	P_o (Torr)	68	85	101	121	
		$10^4\ k_1\ (s^{-1})$	15.24	15.26	15.22	15.25	
2-Methoxyethyl *N*,*N*-dimethylcarbamate	390.2	P_o (Torr)	26	50.5	70	78.5	86
		$10^4\ k_1\ (s^{-1})$	8.53	8.64	8.55	8.53	8.48
2-Butoxyethyl *N*,*N*-dimethylcarbamate	400.1	P_o (Torr)	46	68	83	92	110
		$10^4\ k_1\ (s^{-1})$	21.45	21.58	21.42	21.75	21.52
3-Phenylpropyl *N*,*N*-dimethylcarbamate	380.2	P_o (Torr)	72	84	93	101	115
		$10^4\ k_1\ (s^{-1})$	16.24	16.67	16.33	16.53	16.46
3-Chloropropyl *N*,*N*-dimethylcarbamate	370.5	P_o (Torr)	42	71	119	142	171
		$10^4\ k_1\ (s^{-1})$	16.13	16.45	16.43	16.03	16.12
3-Phenoxypropyl *N*,*N*-dimethylcarbamate	350.2	P_o (Torr)	42	71	80.5	127	168
		$10^4\ k_1\ (s^{-1})$	4.45	4.44	4.23	4.80	4.24
2-Dimethylaminoethyl *N*,*N*-dimethylcarbamate	379.6	P_o (Torr)	45	57	76	97	119
		$10^4\ k_1\ (s^{-1})$	9.58	9.27	9.44	9.34	9.27
3-Butyn-1-yl *N*,*N*-dimethylcarbamate	340.0	P_o (Torr)	35.5	71	101.5	134	143
		$10^4\ k_1\ (s^{-1})$	9.25	8.90	9.00	8.80	9.07
2-Cyanoethyl *N*,*N*-dimethylcarbamate	309.6	P_o (Torr)	26.5	42.5	52.5	64.5	85
		$10^4\ k_1\ (s^{-1})$	14.26	14.51	14.87	14.51	14.47
2-Phenylethyl *N*,*N*-dimethylcarbamate	330.1	P_o (Torr)	34	59	63	72	89
		$10^4\ k_1\ (s^{-1})$	14.52	14.32	14.58	14.40	14.46
3-Methyl-3-buten-1-yl *N*,*N*-dimethylcarbamate	339.6	P_o (Torr)	45	52.5	72	88	147
		$10^4\ k_1\ (s^{-1})$	7.40	7.61	7.27	7.19	7.01

zation of the C_α—O bond polarization, while the C_β—H bond may increase in acidity and assist the O of the C=O in the transition state (**TS-2**). When Z is a multiple-bond substituent or an electron-withdrawing susbtituent interposed by a CH_2 at the 2-position of the ethyl ester there is another inflection point at $\sigma^*(CH_3) = 0.00$ with an



Form B



(6)

Form C

approximate straight line as described by Eqn. (5) (Fig 1).

$$\rho^* = 0.49 \pm 0.03 \text{ at } 360^\circ C \ (r = 0.9907, \text{SD} = 0.1036) \quad (5)$$

This result suggests that a negative carbon reaction center is being developed in the transition state. Apparently, the negative charge from the C_β—H bond polarization, in the sense of $C_\beta{}^{\delta-}...H^{\delta+}$, may be rate-determining step (**TS-3**).

The point position for Z = phenyl (C_6H_5, and isopropenyl [$CH_2{=}C(CH_3)$], falls far above the slopes of the lines (Fig.1) which leads to the consideration of neighboring group participation of these substituents for rate enhancement. According to the transition state TS-4. the π-electrons of the aromatic ring stabilize the bond polarization $C_\alpha{}^{\delta+}...O^{\delta-}$, thus causing a faster elimination process. This interpretation appears to find support from the gas-phase pyrolytic elimination of 2-phenylethyl chloride.[10] The presence of the OCH_3 at the 4-position of phenylethyl chloride confirms the participation of the aromatic nuclei by a significant increase in the rate of HCl elimination. Along this line of consideration, the phenyl substituent also assisted anchimerically in the gas-phase elimination of 2-phenylethyl methanesulfonate.[11] In addition to this reference, a classical study with convincing evidence neighboring double bond participation was described for the acetolysis of 4-methyl-3-pentenyl tosylate.[12] In association with this study, the influence of an olefinic double bond in alkenyl chloride pyrolyses has been assessed.[13,14] The vinyl substituent showed a significant rate enhancement effect in several 4-chloro-1-butene substrates. By analogy, the rate enhancement of 3-methyl-1-buten-1-yl *N,N*-dimethylcarbamate (Fig 1) may also be due to the anchimeric assistance of the neighboring double bond for elimination. The mechanism may be explained according to reaction (6). However, the acidity of the benzylic and allylic C_β—H bond for a six-membered cyclic transition state may not be ignored.

The mechanism of the formation of dimethylamine and CO_2 gas from the unstable *N,N*-dimethylcarbamic acid intemediate in the gas-phase elimination of 2-substituted ethyl *N,N*-dimethylcarbamates [reaction (1)] may be rationalized in terms of a four-membered cyclic transition state as described in reaction (7).

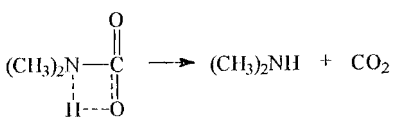
EXPERIMENTAL

General procedure. Method A: the 2-substituted ethyl esters of *N,N*-dimethylcarbamic acid were prepared by adding 0.15 mol of the corresponding alcohol to 0.15 mole of *N,N*-dimethylcarbamyl chloride (Aldrich) in 45 ml of anhydrous pyridine. The reaction mixture was heated in a 100 ml sealed vessel as described.[15]

Method B: the substituted alcohol (0.15 mol) was added to *N,N*-dimethylcarbamyl chloride (0.15 mol) in 50 ml of carbon tetrachloride until no more HCl gas was evolved.

Ethyl N,N-dimethylcarbamate. Method A was employed for the synthesis of this substrate (b.p. 38 °C at 10 Torr (1 Torr=133.3 Pa), lit.[16] 74 °C at 80 Torr, yield 71%). Several distillations gave 97.0% purity by GLC (Porapak Q, 80–100 mesh).

1-Butyl N,N-dimethylcarbamate. This substrate, obtained by Method A, was distilled several times to 90% purity by GLC (Porapak Q, 80–100 mesh). B.p. 48 °C at 10 Torr, yield 63%. ^{1}H NMR, δ 0.9 (t, 3H, δ), 1.3 (m, 2H, CH_2CH_2), 1.5 (m, 2H, CH_2CH_2), 2.8 (s, 6H, $2CH_3$), 4.0 (t, 2H, OCH_2). MS, *m/z* 145 (M^+), 88 [$(CH_3)_2NCOO^+$], 72 [$(CH_3)_2NCO^+$], 57 ($CH_3CH_2CH_2CH_2^+$),44 ($(CH_3)_2N^+$).



(7)

Form D

Table 5. Variation of rate coefficients with temperature[a]

Substrate	Parameter	Value						
Ethyl *N*,*N*-dimethylcarbamate	Temperature (°C)	340.6	350.5	359.6	370.4	380.8	390.1	
	$10^4\ k_1\ (s^{-1})$	1.43	2.68	4.57	8.07	13.97	23.28	
	Rate equation: $\log k_1\ (s^{-1}) = (12.23 \pm 0.30) - (188.8 \pm 3.3)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99981$, SD = 0.0097							
Propyl *N*,*N*-dimethylcarbamate	Temperature (°C)	349.5	362.8	370.0	380.0	390.0		
	$10^4\ k_1\ (s^{-1})$	1.64	3.66	5.67	9.63	16.67		
	Rate equation: $\log k_1\ (s^{-1}) = (12.68 \pm 0.30) - (192.2 \pm 3.7)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99989$, SD = 0.0067							
1-Butyl *N*,*N*-dimethylcarbamate	Temperature (°C)	351.6	361.2	371.6	379.0	390.3	400.2	
	$10^4\ k_1\ (s^{-1})$	2.23	4.08	6.80	10.03	17.44	31.31	
	Rate equation: $\log k_1\ (s^{-1}) = (11.91 \pm 0.29) - (186.0 \pm 3.6)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99926$, SD = 0.0179							
3-Methyl-1-butyl *N*,*N*-dimethylcarbamate	Temperature (°C)	340.2	350.2	360.5	370.0	380.2	390.6	400.5
	$10^4\ k_1\ (s^{-1})$	2.03	3.46	6.53	10.70	17.62	33.06	49.57
	Rate equation: $\log k_1\ (s^{-1}) = (12.16 \pm 0.15) - (186.1 \pm 1.8)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99954$, SD = 0.0169							
3,3 Dimethyl-1-butyl *N*,*N*-dimethylcarbamate	Temperature (°C)	330.2	339.7	350.7	360.1	370.2	380.6	390.3
	$10^4\ k_1\ (s^{-1})$	2.26	3.76	6.56	10.62	18.99	32.51	52.57
	Rate equation: $\log k_1\ (s^{-1}) = (11.48 \pm 0.20) - (174.9 \pm 3.2)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99950$, SD = 0.0172							
2-Chloroethyl *N*,*N*-dimethylcarbamate	Temperature (°C)	369.8	380.1	390.3	400.5	410.0	420.1	
	$10^4\ k_1\ (s^{-1})$	2.57	4.46	7.67	13.48	21.81	38.12	
	Rate equation: $\log k_1\ (s^{-1}) = (12.51 \pm 0.38) - (198.3 \pm 4.9)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99972$, SD = 0.0115							
2-Bromoethyl *N*,*N*-dimethylcarbamate	Temperature (°C)	360.8	370.7	380.4	390.3	400.5	410.5	420.2
	$10^4\ k_1\ (s^{-1})$	1.69	2.96	5.13	8.86	15.25	26.24	45.44
	Rate equation: $\log k_1\ (s^{-1}) = (12.83 \pm 0.15) - (201.6 \pm 1.9)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99978$, SD = 0.0119							
2-Methoxyethyl *N*,*N*-dimethylcarbamate	Temperature (°C)	360.1	370.0	380.2	385.3	390.0	400.5	
	$10^4\ k_1\ (s^{-1})$	1.62	2.82	5.00	6.75	8.52	14.66	
	Rate equation: $\log k_1\ (s^{-1}) = (12.23 \pm 0.20) - (194.2 \pm 2.5)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99992$, SD = 0.0050							
2-Butoxyethyl *N*,*N*-dimethylcarbamate	Temperature (°C)	370.0	380.2	390.1	401.0	410.1		
	$10^4\ k_1\ (s^{-1})$	4.40	7.49	12.78	21.73	37.26		
	Rate equation: $\log k_1\ (s^{-1}) = (12.30 \pm 0.69) - (192.9 \pm 8.7)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99933$, SD = 0.0156							
3-Phenylpropyl *N*,*N*-dimethylcarbamate	Temperature (°C)	340.4	350.8	360.7	370.0	380.1	390.3	400.5
	$10^4\ k_1\ (s^{-1})$	1.96	3.32	5.86	10.17	16.55	27.83	44.95
	Rate equation: $\log k_1\ (s^{-1}) = (11.71 \pm 0.26) - (181.2 \pm 3.2)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99974$, SD = 0.0124							
3-Chloropropyl *N*,*N*-dimethylcarbamate	Temperature (°C)	330.5	340.2	350.4	360.4	370.5	380.2	390.5
	$10^4\ k_1\ (s^{-1})$	1.59	3.20	5.30	9.37	16.28	27.07	46.09
	Rate equation: $\log k_1\ (s^{-1}) = (12.17 \pm 0.20) - (184.3 \pm 2.5)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99955$, SD = 0.0170							
3-Phenoxypropyl *N*,*N*-dimethylcarbamate	Temperature (°C)	330.5	340.1	350.1	360.5	370.5	380.5	390.5
	$10^4\ k_1\ (s^{-1})$	1.19	2.12	4.34	7.32	12.46	22.19	38.26
	Rate equation: $\log k_1\ (s^{-1}) = (12.60 \pm 0.23) - (190.8 \pm 2.8)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99951$, SD = 0.0186							
2-Dimethylaminoethyl *N*,*N*-dimethylcarbamate	Temperature (°C)	361.0	369.5	380.7	389.9	400.0	410.0	
	$10^4\ k_1\ (s^{-1})$	3.00	5.26	9.44	15.76	25.80	43.89	
	Rate equation: $\log k_1\ (s^{-1}) = (12.53 \pm 0.40) - (194.7 \pm 5.1)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99966$, SD = 0.0126							
3-Butyn-1-yl *N*,*N*-dimethylcarbamate	Temperature (°C)	310.3	319.5	329.8	340.0	349.7	360.0	
	$10^4\ k_1\ (s^{-1})$	2.61	4.67	8.81	15.64	26.79	47.15	
	Rate equation: $\log k_1\ (s^{-1}) = (12.39 \pm 0.14) - (178.3 \pm 1.6)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99996$, SD = 0.0047							

Table 5 *continued.*

Substrate	Parameter	Value						
2-Cyanoethyl *N,N*-dimethylcarbamate	Temperature (°C)	269.5	279.3	290.0	300.3	309.6	319.0	329.6
	$10^4\ k_1\ (s^{-1})$	1.32	2.44	4.94	8.39	14.52	25.28	44.36
	Rate equation: $\log\ k_1\ (s^{-1}) = (11.40 \pm 0.25) - (158.7 \pm 2.8)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99980$, SD = 0.0121							
2-Phenylethyl *N,N*-dimethylcarbamate	Temperature (°C)	291.1	300.2	310.5	321.1	330.1	341.8	
	$10^4\ k_1\ (s^{-1})$	1.39	2.54	4.79	9.03	15.29	29.51	
	Rate equation: $\log\ k_1\ (s^{-1}) = (12.21 \pm 0.24) - (173.5 \pm 3.1)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99999$, SD = 0.0025							
3-Methyl-3-buten-1-yl *N,N*-dimethylcarbamate	Temperature (°C)	320.8	329.8	339.6	349.6	360.9	370.1	
	$10^4\ k_1\ (s^{-1})$	2.52	4.57	7.61	13.12	23.99	40.18	
	Rate equation: $\log\ k_1\ (s^{-1}) = (11.87 \pm 0.38) - (175.8 \pm 4.5)$ kJ mol^{-1} $(2.303\ RT)^{-1}$ $r = 0.99968$, SD = 0.0127							

[a]Data for σ values obtained from Ref. 9.

3-Methyl-1-butyl N,N-dimethylcarbamate. This carbamate, prepared by Method A (b.p. 94 °C at 19 Torr, yield 51%) was distilled to 99% purity as determined by GLC (Penwalt 223). ^{1}H NMR, δ 0.9 (d, 6H, $2CH_3$), 1.5 (q, 2H, CH_2CH_2C), 1.6 (m, H, CH), 2.9 (s, 6H, $2CH_3$), 4.0 (t, 2H, OCH_2CH_2). MS, *m/z* 159 (M^+), 88[$(CH_3)_2NCOO^+$], 72[$(CH_3)_2NCO^+$], 43 [$(CH_3)_2C^+$].

3,3-Dimethyl-1-butyl N,N-dimethylcarbamate. This compound was prepared by Method B (b.p. 70 °C at 15 Torr, yield 58%). Several distillations gave a purity of 97% as determined by GLC (Carbopack C 80–100 mesh). 1H NMR, δ 0.9 (s, 9H, $3CH_3$), 1.5 (t, 2H, CH_2CH_2), 2.8 [s, 6H, $(CH_3)_2N$), 4.1 (t, 2H, OCH_2). MS, *m/z* 179 (M^+), 88 [$(CH_3)_2NCOO^+$], 72 [$(CH_3)_2NCO^+$], 69 [$(CH_3)_3CCH_2^+$], 57 [$(CH_3)_3C^+$].

n-Propyl N,N-dimethylcarbamate. This starting material was prepared by Method A. (b.p. 70 °C at 5 Torr, yield 66%). After several distillations the purity was 97.2% as detremined by GLC (Penwalt 223). ^{1}H NMR, δ 0,6 (t, 3H, CH_3), 1.3 (m, 2H, C—CH_2—C), 2.6 [s,6H, $(CH_3)_2N$], 3.7 (t, 3H, OCH_2). MS, *m/z* 131 (M^+), 102 [$(CH_3)_2NCOOCH_2^+$], 72 [$(CH_3)_2NCO^+$], 58 ($NCOO^+$), 43 ($CH_3CH_2CH_2^+$).

2-Methoxyethyl N,N-dimethylcarbamate. Method A was used for the preparation of this substrate (b.p. 70 °C at 9 Torr, yield 48%). Several distillations gave 98.7% purity by GLC (Porapak R 80–100 mesh). ^{1}H NMR, δ 2.5 [s, 6H, $(CH_3)_2N$], 3.1 (s, 3H, OCH_3), 3.3 (t, 2H, OCH_2—C), 3.9 (t, 2H, OCH_2). MS, *m/z* 147 (M^+), 116 [$(CH_3)_2NCOOCH_2CH_2^+$], 72 [$(CH_3)_2NCO^+$], 58 ($NCOO^+$), 45 ($CH_3OCH_2^+$).

Table 6. Kinetic parameters for pyrolysis of $(CH_3)_2NCOOCH_2CH_2Z$ at 360 °C

Z	$k_1 \times 10^{-4}$ (s^{-1})	$k_H \times 10^{-4}$ (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})
H	4.47	1.49	188.8 ± 3.3	12.23 ± 0.30	−25.30	194.1	210.1
CH_3	3.09	1.55	196.2 ± 3.7	12.68 ± 0.30	−16.70	201.5	212.1
CH_2CH_3	3.63	1.82	186.0 ± 3.6	11.91 ± 0.29	−31.46	191.3	211.2
$CH(CH_3)_2$	6.31	3.15	186.1 ± 1.8	12.16 ± 0.15	−26.65	191.4	208.3
$C(CH_3)_3$	12.22	5.61	174.9 ± 3.2	11.48 ± 0.20	−39.65	180.2	205.3
Cl	1.41	0.71	198.3 ± 4.9	12.51 ± 0.38	−19.95	203.6	204.3
Br	1.55	0.77	201.6 ± 1.9	12.83 ± 0.15	−14.01	206.9	215.8
OCH_3	1.62	0.81	194.2 ± 2.5	12.23 ± 0.20	−25.31	199.5	215.5
$O(CH_2)_3CH_3$	2.40	1.20	192.9 ± 8.7	12.30 ± 0.69	−23.97	198.2	213.4
$CH_2C_6H_5$	5.75	2.88	181.2 ± 3.2	11.71 ± 0.26	−35.26	186.5	208.8
CH_2Cl	9.12	4.56	184.3 ± 2.5	12.17 ± 0.20	−26.48	189.6	206.4
$CH_2OC_6H_5$	7.24	3.62	190.8 ± 2.8	12.60 ± 0.23	−18.24	196.1	207.6
$N(CH_3)_2$	2.88	1.44	194.7 ± 5.1	12.53 ± 0.40	−19.58	200.0	212.4
C≡CH	47.86	23.93	178.3 ± 1.6	12.39 ± 0.14	−22.25	183.6	197.7
C≡N	201.77	100.9	158.7 ± 2.8	11.40 ± 0.25	−41.20	164.0	190.1
C_6H_5	78.28	39.14	173.5 ± 3.1	12.21 ± 0.24	−25.62	178.8	195.1
$CH_2{=}C(CH_3)$	22.91	11.45	175.8 ± 4.5	11.87 ± 0.38	−32.21	181.1	201.5

Table 7. Parameters of substituents Z in $(CH_3)_2NCOOCH_2CH_2Z$ at 360 °C[a]

Z	Log (k_Z/k_o) (k_o = H)	(k_Z/k_o) (k_o = CH_3)	σ_α	σ_F	σ_{R+}	σ_{R-}	σ^*	σ_I
H	0.0000	−0.0171	0.00	0.00	0.00	0.00	0.49	0.00
CH_3	0.0171	0.0000	−0.35	0.00	−0.08	0.03	0.00	−0.046
CH_2CH_3	0.0868	0.0697	−0.49	0.00	−0.07	0.02	−0.10	−0.055
$CH(CH_3)_2$	0.3251	0.3079	−0.62	0.00	−0.07	0.01	−0.19	−0.064
$C(CH_3)_3$	0.5757	0.5586	−0.75	0.00	−0.06	0.00	−0.30	−0.074
Cl	−0.3219	−0.3397	−0.43	0.45	−0.17	−0.12	2.94	0.50
Br	−0.2867	−0.3038	−0.59	0.45	−0.15	−0.10	2.80	0.44
OCH_3	−0.2647	−0.2818	−0.17	0.25	−0.42	−0.27	1.67	0.27
$O(CH_2)_3CH_3$	−0.0940	−0.1111	−0.26	0.25	−0.46	−0.27	1.65	0.27
$CH_2C_6H_5$	0.2862	0.2690	−0.70	0.05	−0.05	0.02	0.215	−0.08
CH_2Cl	0.4857	0.4686	−0.54	0.23	−0.05	0.02	1.05	0.11
$CH_2OC_6H_5$	0.3855	0.3683	−0.94	0.05	−0.03	0.02	0.85	0.40
$N(CH_3)_2$	−0.0148	−0.0319	−0.44	0.10	−0.64	−0.26	0.62	0.06
C≡CH	1.2057	1.1886	−0.55	0.16	−0.16	0.16	2.13	0.35
C≡N	1.8307	1.8135	−0.46	0.60	0.00	0.10	3.64	0.56
C_6H_5	1.4194	1.4022	−0.81	0.10	−0.22	0.22	0.60	0.08
$CH_2=C(CH_3)$	0.8856	0.8684	—	—	—	—	0.36	0.058

[a] Data for σ values obtained from Ref. 9.

2-Chloroethyl N,N-dimethylcarbamate. Method A was used for this carbamatee, b.p. 110 °C at 13 Torr, yield 54%. Several distillations gave 97.0% purity by GLC, (Penwalt 223). ^{1}H NMR, δ 2.6 [s, 6H, $(CH_3)_2N$], 3.5 (t, 2H, Cl—CH_2—C), 4.1 (t, 2H, OCH_2). MS, *m/z* 152 (M^+), 116 [$(CH_3)_2NCOOCH_2CH_2^+$], 72 [$(CH_3)_2NCO^+$], 58 ($NCOO^+$), 49 (CH_2Cl^+), 44 [$(CH_3)_2N^+$].

2-Bromoethyl N,N-dimethylcarbamate. This compound obtained by Method B, was distilled several times to 99.8% purity by GLC (Penwalt 223) (b.p. 150 °C at 100 Torr, yield 49.8%). ^{1}H NMR, δ 2.8 [(s, 6H, $(CH_3)_2N$)], 3.5 (t, 2H, Br—CH_2—C), 4.3 (t, 2H, OCH_2). MS, *m/z* 196 (M^+), 152 ($COOCH_2CH_2Br^+$), 116 [$(CH_3)_2NCOOCH_2CH_2^+$], 72 [$(CH_3)_2NCO^+$], 44 [$(CH_3)_2N^+$].

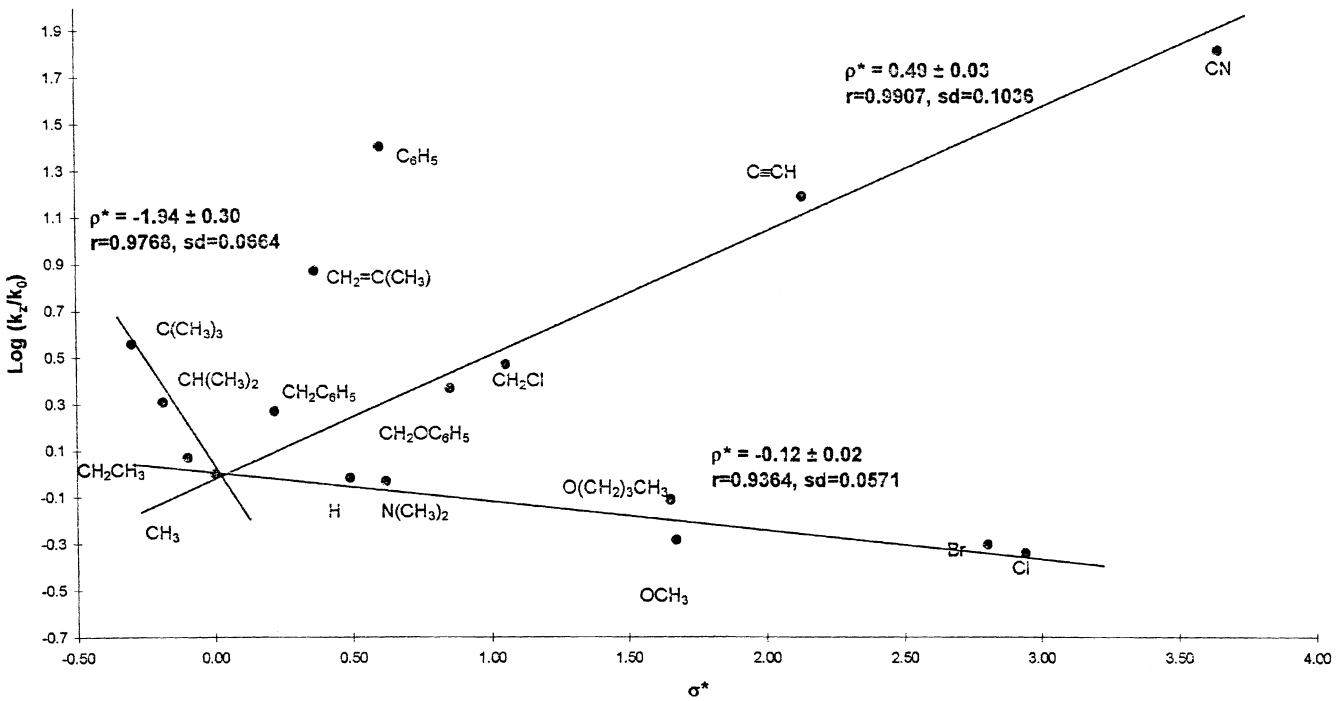


Figure 1. Log k_{rel} against Taft σ * values for $(CH_3)_2NCOOCH_2CH_2Z$ at 360 °C

3-Phenyl-I-propyl N,N-dimethylcarbamate. This carbamate was prepared by Method B (b.p. 175 °C at 20 Torr, yield 71.3%). Several distillations gave 99.8% purity by GLC (Penwalt 223). ^{1}H NMR, δ 1.9. (m, 2H, —CH_2—), 2.7 (t, 2H, $CH_2C_6H_5$), 2.9 [s, 6H, $(CH_3)_2N$], 4.1 (t, 2H, OCH_2), 7.1 (m, 5H, C_6H_5). MS, *m/z* 207 (M^+), 116 [$(CH_3)_2NCOOCH_2CH_2^+$], 102 [$(CH_3)_2NCOOCH_2^+$], 91 ($CH_2C_6H_5^+$), 77 ($C_6H_5^+$), 72 [$(CH_3)_2NCO^+$], 44 [$(CH_3)_2N^+$].

3-Chloro-1-propyl N,N-dimethylcarbamate. This substrate prepared according to Method B (b.p. 161 °C at 5 Torr, yield 75%) was distilled several times to 99% purity by GLC (Porapak Q, 80–100 mesh). ^{1}H NMR, δ 2.0 (m, 2H, C—CH_2—C), 2.8 [s, 6H, $(CH_3)_2N$], 3.6 (t, 2H, OCH_2), 4.1 (t, 2H, C—CH_2Cl). MS, *m/z* 165 (M^+), 130 [$(CH_3)_2NCOOCH_2CH_2CH_2^+$], 121 ($COOCH_2CH_2CH_2Cl^+$), 102 [$(CH_3)_2NCOOCH_2^+$], 72 [$(CH_3)_2NCO^+$], 58 ($COOCH_2CH_2^+$), 49 ($CH_2Cl^+$).

3-Phenoxy-I-propyl N,N-dimethylcarbamate. Using Method B, this starting material (b.p. 161 °C at 5 Torr, yield 70%) was distilled several times to 98.9% purity by GLC (Porapak Q, 80– 100 mesh). ^{1}H NMR, δ 2.1 (m, 2H, C—CH_2—C), 2.9 [s, 6H, $(CH_3)_2N$], 4.0 (t, 2H, OCH_2), 4.2 (t, 2H, OCH_2). MS, *m/z* 224 (M^+), 146 [$(CH_3)_2NCOOCH_2CH_2CH_2CH_2^+$], 130 [$(CH_3)_2NCOOCH_2CH_2CH_2^+$], 107 ($CH_2OC_6H_5^+$), 72 [$(CH_3)_2NCO^+$].

2-Phenylethyl N,N-dimethylcarbamate. This compound was prepared by Method B (b.p. 122 °C at 5 Torr, yield 75%). Several distillations gave a purity of 98% by GLC (Carbopack C 80–100 mesh). ^{1}H NMR, δ 2.8 [s, 6H, $(CH_3)_2N$], 3.4 (t, 2H, $CH_2C_6H_5$), 4.3 (t, 2H, OCH_2), 6.6 [t, 2H, $C_6H_3H_{2(ortho)}$], 6.7 [d, 1H, $C_6H_5H_{(para)}$], 7.2 [t, 2H, $C_6H_3H_{2(meta)}$]. MS, *m/z* 194 (M^+), 116 [$(CH_3)_2NCOOCH_2CH_2^+$], 102 [$(CH_3)_2NCOOCH_2^+$], 88 [$(CH_3)_2NCOO^+$], 72 [$(CH_3)_2NCO^+$], 44 [$(CH_3)_2N^+$].

2-Butoxyethyl N,N-dimethylcarbamate. This starting material obtained by Method B (b.p. 80 °C at 25 Torr, yield 70%), was distilled several times to 98.0% purity by GLC (Poparak Q 80–100 mesh). ^{1}H NMR, δ 1.3 (t, 3H, CH_3), 1.4 (m, 2H, OCH_2—C), 1.5 (m, 2H, C—CH_2—C), 2.8 [s, 6H, $(CH_3)_2N$], 3.4 (t, 2H, OCH_2—), 3.5 (t, 2H, CH_2—C), 4.1 (t, 2H, $COOCH_2$—C). MS, *m/z* 190 (M^+), 116 [$(CH_3)_2NCOOCH_2CH_2^+$], 102 [$(CH_3)_2NCOOCH_2^+$], 88 [$(CH_3)_2NCOO^+$], 72 [$(CH_3)_2NCO^+$], 44 [$(CH_3)_2N^+$].

I-Dimethylaminoethyl N,N-dimethylcarbamate. Dimethylcarbamyl chloride was added to 2-dimethylaminoethanol hydrochloride according to Method B (b.p. 106 °C at 693 Torr, yield 67%). Several distillation gave 98.4% purity by GLC (FFAP–Chromosorb W AW 80–100 mesh). MS, *m/z* 160 (M^+), 116 [$(CH_3)_2NCOOCH_2CH_2^+$], 102 [$(CH_3)_2NCOOCH_2^+$], 88 [$(CH_3)_2NCOO^+$], 72 [$(CH_3)_2NCO^+$], 44 [$(CH_3)_2N^+$].

3-Butyn-I-yl N,N-dimethylcarbamate. This carbamate prepared by Method B (b.p. 109 °C at 31 Torr, yield 63%) was distilled to 99.8% purity by GLC (FFAP–Chromosorb W AW 80–100 mesh). MS, *m/z* 141 (M^+), 97 ($COOCH_2CH_2C{\equiv}CH^+$), 72 [$(CH_3)_2NCO^+$], 53 ($CH_2CH_2C{\equiv}CH^+$),44 [$(CH_3)_2N^+$].

2-Cyanoethyl N,N-dimethylcarbamate. The preparation of this substrate was carried out by Method B (b.p. 133 °C at 13 Torr). Several distillations gave a purity of 99.1% by GLC (Porapak R, 80–100 mesh). MS, *m/z* 142 (M^+), 88 [$(CH_3)_2NCOO^+$], 72 [$(CH_3)_2NCO^+$], 54 ($CH_2CH_2C{\equiv}N^+$), 44 [$(CH_3)_2N^+$].

3-Methyl-3-buten-1-yl N,N,dimethylcarbamate. This carbamate was prepared by Method B (b.p. 92–94 °C at 14 Torr, yield 51%). Several distillations gave 99.9% purity by GLC (FFAP–Chromosorb W AW, 80–100 mesh). MS, *m/z* 157 (M^+), 88 [$(CH_3)_2NCOO^+$], 72 [$(CH_3)_2NCO^+$], 54 ($CH_2CH_2C{\equiv}N^+$), 40 ($CH_3C{\equiv}CH^+$).

Analyses. The quantitative chromatographic analyses of the olefinic products were performed using the same column as used for their corresponding carbamate substrates. The identifications of substrates and products were performed by GLC Film thickness–MS (Saturn 2000, Varian). With a DB-5MS capillary column 30 m x 0.250 mm i.d, 0.25 μm

Kinetics. The pyrolysis kinetics were studied in a static reaction system as described [17,18] with some modifications and additions of modern electronic and electrical devices. The temperature was controlled by a resistance thermometer controller, Shinko DIC-PS 25RT, and an Omega solid-state SSR240AC45, maintained within $\pm$ 0.2 °C and measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was found along the reaction vessel. The carbamate substrates were injected with a syringe through a silicone-rubber septum directly into the reaction vessel.

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