Mechanism and structure–reactivity correlation in the homogeneous, unimolecular elimination kinetics of 2-substituted ethyl methylcarbonates in the gas phase

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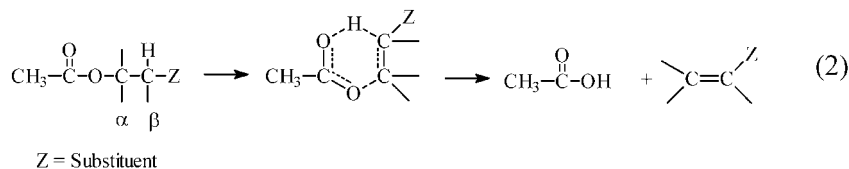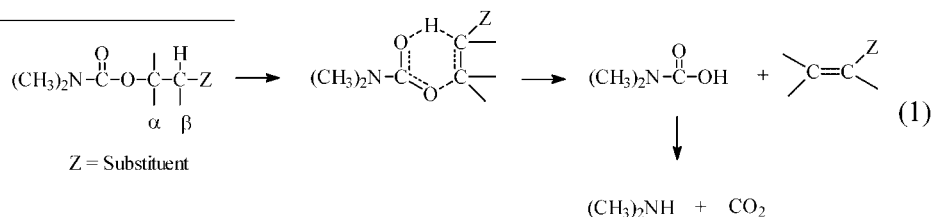
ABSTRACT: The gas-phase elimination kinetics of 2-substituted ethyl methylcarbonates were determined in a static reaction system over the temperature range of 323–435 °C and pressure range 28.5–242 Torr. The reactions are homogeneous, unimolecular and follow a first-order rate law. The kinetic and thermodynamic parameters are reported. The 2-substituents of the ethyl methylcarbonate ($CH_3OCOOCH_2CH_2Z$, Z = substituent) give an approximate linear correlation when using the Taft–Topsom method, $\log(k_Z/k_H) = -(0.57 \pm 0.19)\sigma_\alpha + (1.34 \pm 0.49)\sigma_R^-$ ($r = 0.9256$; SD $= 0.16$) at 400 °C. This result implies the elimination process to be sensitive to steric factors, while the electronic effect is unimportant. However, the resonance factor has the greatest influence for a favorable abstraction of the β-hydrogen of the C_β—H bond by the oxygen carbonyl. Because ρ_α is significant, a good correlation of the alkyl substituents of carbonates with Hancock's steric parameters was obtained: $\log(k_R/k_H)$ versus E_s^c for $CH_3OCOOCH_2CH_2R$ at 400 °C, R = alkyl, $\delta = -0.17$ ($r = 0.9993$, SD $= 0.01$). An approximate straight line was obtained on plotting these data with the reported Hancock's correlation of 2-alkyl ethylacetates. This result leads to evidence for the β-hydrogen abstraction by the oxygen carbonyl and not by the alkoxy oxygen at the opposite side of the carbonate. The carbonate decompostion is best described in terms of a concerted six-membered cyclic transition state type of mechanism. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: gas phase; elimination; pyrolysis; kinetics; 2-substituted ethyl methyl carbonates; Taft–Topsom correlation

INTRODUCTION

The kinetic and thermodynamic parameters for the gas-phase elimination of 2-substituted ethyl *N,N*-dimethylcarbamates [$(CH_3)_2NCOOCH_2CH_2Z$, Z = substituent] were recently reported[1] and the mechanism was described as in reaction (1). This process of decomposition was believed to be similar to the concerted six-membered cyclic transition state ascribed to the gas thermal decomposition of 2-substituted ethyl acetates[2,3] [reaction (2)].

$$Z = \text{Substituent} \tag{1}$$

$$Z = \text{Substituent} \tag{2}$$

Several correlation methods for substituent effects for these series of 2-substituted ethylcarbamates gave random points with no meanning for mechanistic interpretation. However, plotting $\log(k_Z/k_{CH_3})$ against the Taft

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original σ^* values[4] gave rise at the origin, $\sigma^*(CH_3) = 0.00$, three good straight lines. This result implied that small alterations in the polarity of the transition state may be due to changes in electronic transmission at the reaction center. This means that a simultaneous effect may be operating during the process of elimination, especially with the electron-withdrawing and multiple-bonded substituents at the 2-position of ethyl *N,N*-dimethylcarbamates. The Taft correlation was found to be as follows:

Alkyl groups: $\rho^* = -1.94 \pm 0.30$ at 360 °C ($r = 0.9768$, SD $= 0.0664$)

Electron-withdrawing groups: $\rho^* = -0.12 \pm 0.02$ at 360 °C ($r = 0.9364$, SD $= 0.0571$)

Multiple bonded substituents: $\rho^* = 0.49 \pm 0.03$ at 360 °C ($r = 0.9907$, SD $= 0.1036$)

However, the correlation analysis for 2-substituted ethylacetates [reaction (3)] was reported[5] as described below:

$$CH_3OCOOCH_2CH_2Z \rightarrow CH_3COOH + CH_2{=}CH_2Z$$

$$(3)$$
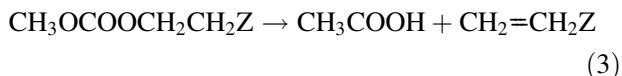
Alkyl groups: $\log(k/k_0) = \delta E_s^c$, $\delta = -0.12$ ($r = 0.916$ at 400 °C)

Polar groups: $\log(k/k_0) = \rho^*\sigma^*$, $\rho^* = -0.19$ ($r = 0.961$ at 400 °C)

Polar groups: $\log(k/k_0) = \rho_I\sigma_I$, $\rho_I = -1.03$ ($r = 0.960$ at 400 °C)

Alkyl and polar: $\log(k/k_0) = -(0.45 \pm 0.01)\sigma_\alpha - (1.29 \pm 0.11)\sigma_F$ ($r = 0.959$ at 400 °C)

Multiple bonds: $\log(k/k_0) = -(1.81 \pm 0.02)\sigma_\alpha - (0.38 \pm 0.03)\sigma_F + (7.34 \pm 0.17)\sigma_R^-$ ($r = 0.984$ at 400 °C)

In view of the several good correlations obtained by the application of different structure−reactivity relationship methods for 2-substituted carbamates and acetates, it was considered interest to examine the elimination kinetics of another type of organic ethyl ester. In this respect, the kinetic parameters and comparative rates of different substituents other than carbon at the acid side of an organic ethyl ester[6] were correlated by using the Taft–Topsom method. An approximate straight line, as shown in Fig. 1, was obtained.

The negative value of ρ_α suggested a modest participation of the polarizability or steric effect of the substituent Z. According to the greatest absolute value of ρ_F, the field or electronic effect has the most important influence in the process of elimination. The use of the value σ_R^-
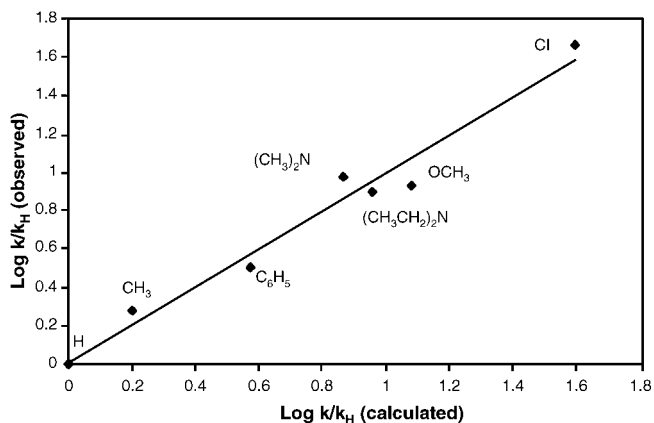

Figure 1. Taft-Topsom correlation for the pyrolysis of $ZCOOCH_2CH_3$: $\log(k/k_0) = -(0.68 \pm 0.12)\sigma_\alpha + (2.57 \pm 0.12)\sigma_F - (1.18 \pm 0.27)\sigma_R^-$ ($r = 0.984$, SD $= 0.119$) at 400 °C

confirms the interaction between the substituent Z and the incipient negative reaction center. The negative coefficient ρ_R^- implies a favorable effect for the abstraction of the β-hydrogen of the ethyl ester by the oxygen carbonyl in the transition state.

According to the linear correlation for $ZCOOCH_2CH_3$ (Fig. 1), and to the various correlations applied to aliphatic acetates and carbamates, it seemed of interest to examine esters of a more polar nature such as chloroformates or carbonates (Fig. 1). However, chloroformates are difficult to handle and unstable even at room temperature. For this reason, little research on the gas-phase elimination of these types of compounds has been reported. Consequently, the present work was aimed at examining the homogeneous molecular elimination of unsymmetrical 2-substituted ethyl methylcarbonates, $CH_3OCOOCH_2CH_2Z$, Z = substituent.

It has been reported that esters of carbonic acids containing at least one β-hydrogen atom at the alkyl side, when heated at high temperature, decompose to an alkene, alcohol (phenol) and CO_2.[7] O'Connor and Nace[8] suggested that symmetrical carbonates undergo a first-order rate law, give a negative entropy of activation and proceed through a unimolecular cyclic *cis*-elimination. In these sense, two mechanisms were proposed.

Mechanism A:
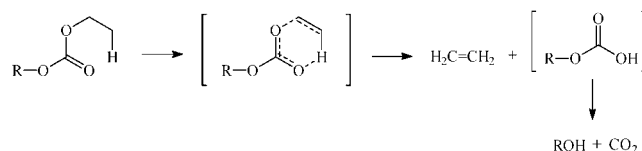
Mechanism B:
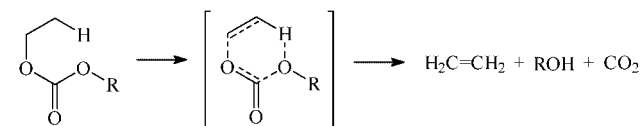
A symmetrical carbonate without a β-hydrogen atom, such as dimethyl carbonate, was reported to give dimethyl ether and CO_2 gas when pyrolyzed between 209 and 232 °C,[9] and also up to 250 °C[10] [reaction (4)]. However, further investigation on dimethyl carbonate[11] showed it to be extremely stable even up to 350 °C. The stability of this compound was later confirmed at temperatures as high as 390 °C.[12]
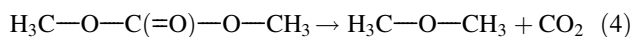
$$H_3C-O-C(=O)-O-CH_3 \rightarrow H_3C-O-CH_3 + CO_2 \quad (4)$$

In spite of the few studies on aliphatic carbonates in the gas phase, there is no evidennce for Mechanism B. Taylor[13] presented several arguments in favor of Mechanism A when describing the correlation of aryl ethylcarbonate pyrolysis,[14] $ArOCOOCH_2CH_3$, with $\rho° = 0.19$ (Scheme 1). This result suggested that the electron-withdrawing substituents in the benzene ring increased the rate, aiding the $C_\alpha-O$ polarization, exactly the opposite of what part would be obtained if Mechanism B was involved, since electron withdrawal would make the ethereal part less nucleophilic, thereby lowering the reaction rate. This suggested that Mechanism A applies.

Taylor and Thorne additionally pointed out that *tert*-butyl *N,N*-arylcarbamates[15] gave a good Hammett correlation of $\rho° = 0.63$. This value indicated a similar transition state of aryl ethylcarbonates, and that the abstraction of the β-hydrogen to the carbonyl group is very important. Hence both elimination reactions must undergo pyrolysis via Mechanism A. Moreover, methyl alkylcarbonates were believed to be less reactive than phenyl alkylcarbonates. In this sense, 1-phenylethyl phenylcarbonate[16] was found to react faster than 1-phenylethyl methylcarbonate,[17] with k values of 22.2×10^{-3} and 6.98×10^{-3} at 600 K, respectively (Scheme 1). Finally, the relative rates of Et : *i*-Pr : *t*-Bu are 1 : 29.6 : 2934, which was higher than expected when compared with other esters for which consideration of steric acceleration was not ruled out.

Even though these previous studies give to some extent reasonable arguments for Mechanism A, additional work may well be needed for a definite mechanistic elucidation of carbonate decomposition in the gas phase. For this reason and in association with the pyrolytic elimination of 2-substituted ethyl *N,N*-dimethylcarbamates[1] and acetates,[2,3] in this work the kinetics of the homogeneous, unimolecular elimination of 2-substituted ethyl methylcarbonates were examined.

RESULTS AND DISCUSSION

The products of elimination of 2-substituted ethyl methylcarbonates in the gas phase are the corresponding alkene, metanol and carbon dioxide [reaction (5)].

$$CH_3OCOOCH_2CH_2Z \rightarrow [CH_3OCOOH] + CH_2{=}CH_2Z$$
$$\downarrow$$
$$CH_3OH + CO_2$$
$$(5)$$
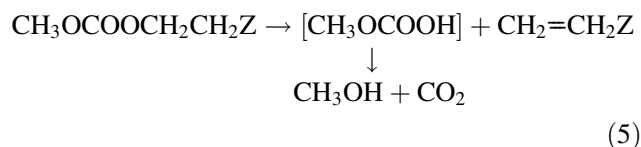
The theoretical stoichiometry for the gas-phase pyrolysis of the substrates, as described in reaction (5), requires $P_f/P_0 = 3.0$, where P_f and P_0 are the final and initial pressures, respectively. The average P_f/P_0 values at four different temperatures and 10 half-lives were, within experimental error, nearly 3.0 (Table 1). The departure of P_f/P_0 to <3.0 for 2-bromoethyl methylcarbonate, 2-chloroethyl methylcarbonate and 2-phenylethyl methyl carbonate was due to polymerization of the corresponding olefinic product. The pure unsaturated products of these substrates when introduced into the static reaction vessel show a decrease in pressure and formation of a solid polymer. The stoichiometry of reaction (5), up to 45–80% reaction, was satisfactorily verified by comparing the percentage decomposition of the substrate from pressure measurements with that obtained from the gas chromatographic (GC) analyses of the corresponding alkene formation (Table 2).

These elimination reactions can be said to be homogeneous since no significant effects on the rates were obtained when using both clean Pyrex and seasoned Pyrex vessels with a surface-to-volume ratio of 6.0 relative to the normal vessel, which is equal to 1.0. The effect of the addition of different proportions of the free radical inhibitor toluene or cyclohexene is described in Table 3. Nevertheless, the pyrolyses of these carbonates were carried out in the presence of at least twice the amount of the inhibitor in order to prevent any possible free radical chain reactions (Table 3). The k values are reproducible with a standard deviation not greater than 5% at a given temperature.

The rate coefficients for elimination, calculated from $k_1 = (2.303/t)\log[2P_0/(3P_0 - P_t)]$, are invariable to initial pressures (Table 4), and the first-order plots of log $(3P_0 - P_t)$ against time t gave a good straight lines up to 40–80% decomposition, suggesting that the elimination process is unimolecular in nature. The temperature dependence of the rate coefficients and the corresponding Arrhenius equation is shown in Table 5, where 90% confidence limits from a least-squares procedure are given.

$\rho^0 = +0.19$

$\rho^0 = +0.63$

$k_1 = 22.2 \times 10^{-3}$ at 600 K

$k_1 = 6.98 \times 10^{-3}$ at 600 K
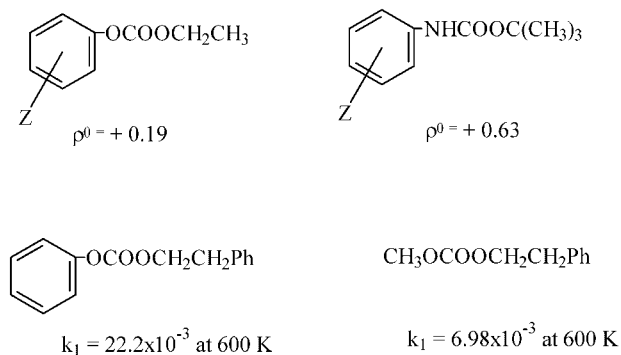
Scheme 1

Table 1. Ratio of final (P_f) to initial (P_0) pressures

Substrate	Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	Average
Ethyl	370.6	90	252	2.88	2.91 ± 0.03
methylcarbonate	380.2	105	298	2.83	
	389.8	107	318	2.96	
	399.8	80	238	2.98	
Propyl	360.0	118	350	2.97	2.89 ± 0.04
methylcarbonate	370.0	135	380	2.81	
	380.0	172	490	2.85	
	390.0	150	440	2.93	
1-Butyl	350.0	96	278	2.90	2.92 ± 0.01
methylcarbonate	360.0	118	344	2.92	
	370.0	88	258	2.93	
	380.0	92	270	2.93	
3-Methyl-1-butyl	350.0	126	300	2.94	2.94 ± 0.01
methylcarbonate	360.0	102	276	2.94	
	370.0	94	306	2.94	
	380.0	126	368	2.92	
3,3-Dimethyl-1-butyl	350.8	78	214.5	2.75	2.81 ± 0.03
methylcarbonate	360.4	28.5	78.5	2.75	
	370.9	50	143	2.86	
	379.5	50	144	2.88	
2-Bromoethyl	349.8	95	250	2.63	2.71 ± 0.06
methylcarbonate	359.3	35.5	92	2.59	
	370.2	122	351	2.87	
	380.4	120	332	2.77	
2-Chloroethyl	370.7	96	258	2.69	2.72 ± 0.02
methylcarbonate	380.0	108	288	2.67	
	389.3	90	248	2.76	
	398.8	105	290	2.76	
3-Chloropropyl	360.0	46	141	3.07	3.06 ± 0.07
methylcarbonate	370.0	49.5	154	3.11	
	380.0	69	212	3.07	
	390.0	106.5	320	3.00	
2-Methoxyethyl	400.0	84	239.5	2.85	2.95 ± 0.05
methylcarbonate	410.0	83	246	2.96	
	420.0	66.5	215	3.07	
	430.2	73	213	2.92	
2-Phenoxyethyl	405.7	136	372	2.73	2.91 ± 0.04
methylcarbonate	415.3	84	256	3.04	
	425.8	77	236	3.06	
	435.7	110	311	2.83	
2-Phenylethyl	344.5	88	231	2.68	2.56 ± 0.03
methylcarbonate	353.0	73	187	2.56	
	362.9	99.5	249.5	2.51	
	372.5	90	223.5	2.48	
3-Phenylpropyl	358.3	89	258	2.90	3.01 ± 0.09
methylcarbonate	370.2	30	94	3.10	
	380.3	41	122	2.98	
	390.4	25.5	78	3.07	

The kinetic and thermodynamic parameters for the gas-phase elimination of 2-substituted ethyl methylcarbonate, $CH_3OCOOCH_2CH_2Z$, Z = substituent, examined in this work are listed in Table 6. The negative entropy of activation, $\Delta S^{\neq}$, of these eliminations implies a symmetrical arrangement and possible planarity of the transition state. However, the substituents $(CH_3)_3C$ and CH_2Cl with a very small positive $\Delta S^{\neq}$ may be attributed to steric factors, which may hinder some approximation to a symmterical concerted transition state. The enthalpy of activation $\Delta H^{\neq}$, suggests endothermic processes. The values of the free energy of activation $\Delta G^{\neq}$, indicate that

the elimination of these carbonates is not spontaneous, unstable and endergonic. The application of several correlations of substituent effects, polar σ^*, inductive σ_I, steric E_S, E_S^C and ν values,[4] gave random points with no reasonable mechanistic interpretation for the carbonates. However, the data in Table 7 gave a relative good correlation by means of the Taft–Topsom equation (Fig. 2).

The size of the substituent described by ρ_α is sensitive to polarizability or steric effects. Since the standard error for the coefficient ρ_F is extremely high, the field/electronic effect appears to be unimportant and may be deleted from the above equation. However, the size and

Table 2. Stoichiometry of the reaction

Substrate	Temperature (°C)	Parameter	Value				
Ethyl methylcarbonate	371.0	Time (min)	5	8	13	15	21
		Reaction (%) (pressure)	20	30.6	44.8	50	62
		Ethylene (%) (GC)	19.8	29.5	45.5	51.7	60.7
Propyl methylcarbonate	370.0	Time (min)	5	7	10	13	18
		Reaction (%) (pressure)	24	30	40.7	49.3	61
		Propene (%) (GC)	23	29.8	39.4	51	62
1-Butyl methylcarbonate	375.0	Time (min)	5	7	9	12	15
		Reaction (%) (pressure)	26	34.4	42	52	60
		Butene (%) (GC)	26.1	33.1	42.7	51.8	60.3
3-Methyl-1-butyl methylcarbonate	350.0	Time (min)	10	15	20	25	30
		Reaction (%) (pressure)	20.8	29.5	37.3	44.2	50.4
		3-Methyl-1-butene (%) (GC)	21.3	30.0	38.2	44.1	52
3,3-Dimethyl-1-butyl methylcarbonate	350.8	Time (min)	10	16	21	26	
		Reaction (%) (pressure)	34.3	50	58.9	68.5	
		3,3-Dimethyl-1-butene	22.9	33.5	37.8	50.1	
		3,3-Dimethyl-1-butyl methyl ether (%) (GC)	7.6	2.1	3.0	2.0	
2-Bromoethyl methylcarbonate	360.3	Time (min)	2	4	5		
		Reaction (%) (pressure)	28.0	49.0	52.0		
		Vinyl bromide (%) (GC)	21.0	43.0	45.0		
2-Chloroethyl methylcarbonate	388.8	Time (min)	3	6	10	15	
		Reaction (%) (pressure)	18	32	56	80	
		Vinyl chloride (%) (GC)	20	30	51	77	
3-Chloropropyl methylcarbonate	370.0	Time (min)	6	11	16	23	31
		Reaction (%) (pressure)	31.1	49	59.2	70.5	78.1
		3-Chloropropene (%) (GC)	34.2	52.9	58.8	68.6	76.8
2-Methoxyethyl methylcarbonate	410.0	Time (min)	2	3	4	5	6
		Reaction (%) (pressure)	15	22.4	25.6	35.8	43.5
		Methyl vinyl ether (%) (GC)	16.8	21	27.8	33.6	45.1
2-Phenoxyethyl methylcarbonate	405.3	Time (min)	1.5	3	6	9	12
		Reaction (%) (pressure)	11.6	20.1	33.6	41.8	56.4
		Phenyl vinyl ether (%) (GC)	10.8	20.4	34.8	40.8	56.3
2-Phenylethyl methylcarbonate	353.4	Time (min)	1.5	3	4.5	6	7
		Reaction (%) (pressure)	11.1	20.8	31.4	36.6	47.1
		Styrene (%) (GC)	13.2	22.7	34.7	40.7	51.7
3-Phenylpropyl methylcarbonate	358.5	Time (min)	15.2	23.1	44.0	75.6	
		Reaction (%) (pressure)	31.6	43.1	53.9	64.7	
		Allylbenzene (%) (GC)	28.9	29.9	49.6	61.0	

the positive sign of ρ_R^- has the greatest influence in the elimination reaction, which implies that the C_α—O bond polarization in the transition state is the limiting factor. This result also suggests a favorable effect for the abstraction of the β-hydrogen of the C_β—H bond by the oxygen carbonyl in the elimination of these carbonates. This indicates that Mechanism A as the most probable process of decomposition.

Since $\rho_\alpha = -0.63$ is significant in the elimination reaction of these carbonates, the 2-substituted alkylethyl methylcarbonates may well give a good correlation with a steric parameter such as Hancock's E_S^C values. This is supported by the results shown in Table 8 and Fig. 3 ($\delta = -0.17$, $r = 0.9993$, SD = 0.0102 at 400 °C).

As described before, the 2-substituted alkylethyl acetates was reported to give an approximate straight line with Hancock steric parameter E_S^C values ($\delta = -0.12$, $r = 0.916$ at 400 °C). Any similarity of the transition state between carbonates and acetates is demonstrated by a linear correlation between $\log k_{\text{rel.}}$ of 2-substituted alkylethyl methylcarbonates and $\log k_{\text{rel.}}$ of 2-substituted alkylethyl acetates (Table 9).

Figure 4 shows a good straight line with a correlation coefficient $r = 0.9857$ and a standard deviation SD = 0.0457 at 400 °C.

The results obtained in this work appear to give additional support to Taylor's idea[13–17] that Mechanism A is the most reasonable transition-state type of mechanism

Table 3. Effect of the free radical inhibitor on rates

Substrate	Temperature (°C)	P_s [a] (Torr)	P_i [b] (Torr)	P_i/P_s	$10^4 k_1$ (s^{-1})
Ethyl	370.3	130	—	—	7.88
methylcarbonate		76	75	1.0	7.78
		80	120	1.5	7.80
		85	165	1.9	7.88
		60	180	3.0	7.79
Propyl	372.0	126	—	—	9.20
methylcarbonate		136	138	1.0	9.19
		81	160	2.0	9.18
		60	124	2.1	9.20
		88	260	3.0	9.17
1-Butyl	370.4	134	—	—	9.94
methylcarbonate		102	108	1.1	9.91
		80	120	1.5	9.96
		80	162	2.1	9.98
		90	200	2.2	9.98
3-Methyl-1-butyl	350.0	66	—	—	4.03
methylcarbonate		74	120	1.6	4.00
		80	160	2.0	4.02
		60	150	2.5	4.05
		48	136	2.8	3.96
3,3-Dimethyl-1-butyl	370.9	50	—	—	22.8
methylcarbonate		61	44	0.7	22.53
		72.5	71.5	1.0	22.34
		63	115	1.8	22.71
		36	106.5	3.0	22.69
2-Bromoethyl	359.1	101	—	—	25.36
methylcarbonate		242	91	0.3	7.77
		136	89	0.7	6.88
		63	77	1.2	7.76
		35.5	155	4.3	7.54
2-Chloroethyl	389.1	84	—	—	11.2
methylcarbonate		151	32	0.2	10.28
		91	55	0.6	10.50
		78	96	1.2	10.80
		61	129	2.1	10.15
3-Chloropropyl	360.0	60.5	—	—	6.34
methylcarbonate		52	47	0.9	5.37
		60	65	1.1	5.10
		52	176	3.4	5.10
2-Methoxyethyl	388.9	95.5	—	—	4.74
methylcarbonate		90	75.5	0.8	4.41
		86	155.5	1.8	4.50
		77	167.5	2.2	4.78
		64	183.5	2.9	4.52
2-Phenoxyethyl	405.7	122	—	—	11.31
methylcarbonate		125	77	0.6	11.72
		96	117	1.2	11.29
		73	153	2.1	11.11
		47	183	3.9	11.68
2-Phenylethyl	372.5	101.1	—	—	45.25
methylcarbonate		155	64	0.4	32.23
		84	110	1.3	33.12
		99.5	298.0	3.0	33.32
		42.5	277	6.6	33.08
3-Phenylpropyl	380.3	46.5	—	—	13.98
methylcarbonate		48.9	79	1.6	13.89
		45	110	2.4	13.98
		46.5	175	3.8	13.65
		45	234	5.2	14.24

[a] P_s = pressure of substrate.
[b] P_i = pressure of free radical inhibitor.

Table 4. Invariability of the rate coefficients from initial pressure

Substrate	Temperature (°C)	Parameter	Value				
Ethyl	370.3	P_0 (Torr)	80	95	115	125	170
methylcarbonate		$10^4 k_1$ (s^{-1})	7.98	7.80	7.80	7.88	7.84
Propyl	372.0	P_0 (Torr)	60	80	100	120	140
methylcarbonate		$10^4 k_1$ (s^{-1})	9.20	9.20	9.20	9.14	9.25
1-Butyl	370.4	P_0 (Torr)	80	90	100	122	140
methylcarbonate		$10^4 k_1$ (s^{-1})	9.92	9.92	9.91	9.90	9.90
3-Methyl-1-butyl	350.0	P_0 (Torr)	60	92	104	124	140
methylcarbonate		$10^4 k_1$ (s^{-1})	3.96	3.94	3.94	3.96	4.00
3,3-Dimethyl-1-butyl	360.4	P_0 (Torr)	28.5	46	78	117.5	
methylcarbonate		$10^4 k_1$ (s^{-1})	12.09	12.08	12.12	12.22	
2-Bromoethyl	359.6	P_0 (Torr)	35	63	74	242	
methylcarbonate		$10^4 k_1$ (s^{-1})	7.54	7.76	7.93	7.77	
2-Chloroethyl	389.3	P_0 (Torr)	30	55	90	129	219
methylcarbonate		$10^4 k_1$ (s^{-1})	9.99	10.38	10.86	10.15	10.37
3-Chloropropyl	360.0	P_0 (Torr)	46	54	68	77	90.5
methylcarbonate		$10^4 k_1$ (s^{-1})	5.42	5.45	5.60	5.30	5.32
2-Methoxyethyl	400.0	P_0 (Torr)	47.5	56	84	92.5	141
methylcarbonate		$10^4 k_1$ (s^{-1})	8.91	9.00	8.95	8.92	8.67
2-Phenoxyethyl	405.7	P_0 (Torr)	47	91	118	136	149
methylcarbonate		$10^4 k_1$ (s^{-1})	11.68	11.11	11.00	11.58	11.88
2-Phenylethyl	372.5	P_0 (Torr)	42.5	84	95	155	
methylcarbonate		$10^4 k_1$ (s^{-1})	33.08	33.12	32.67	32.93	
3-Phenylpropyl	358.3	P_0 (Torr)	27	39	50	78	89
methylcarbonate		$10^4 k_1$ (s^{-1})	4.47	4.57	4.67	4.52	4.44

Table 5. Temperature dependence of rate coefficients

Substrate	Parameter	Value						
Ethyl	Temperature (°C)	342.0	351.2	360.9	370.3	380.1	389.7	399.8
methylcarbonate	$10^4 k_1$ (s^{-1})	1.55	2.65	4.44	7.83	13.00	21.90	36.80
	Rate equation	$\log k_1$ (s^{-1}) = (12.21 ± 0.12) − (188.7 ± 1.5) kJ mol^{-1} (2.303 RT)$^{-1}$, r = 0.9998						
Propyl	Temperature (°C)	340.0	351.0	360.7	372.0	382.0	390.0	400.0
methylcarbonate	$10^4 k_1$ (s^{-1})	1.77	3.02	5.20	8.70	14.90	25.11	42.74
	Rate equation	$\log k_1$ (s^{-1}) = (11.72 ± 0.44) − (182.0 ± 2.3) kJ mol^{-1} (2.303 RT)$^{-1}$, r = 0.9987						
1-Butyl	Temperature (°C)	340.3	350.0	360.0	370.0	380.0	390.5	400.5
methylcarbonate	$10^4 k_1$ (s^{-1})	1.98	3.42	5.82	9.91	16.86	28.60	48.67
	Rate equation	$\log k_1$ (s^{-1}) = (11.77 ± 0.10) − (181.9 ± 0.5) kJ mol^{-1} (2.303 RT)$^{-1}$, r = 0.9998						
3-Methyl-1-butyl	Temperature (°C)	331.0	340.0	350.0	360.0	370.0	380.0	390.0
methylcarbonate	$10^4 k_1$ (s^{-1})	1.35	2.29	3.91	6.66	11.30	19.13	32.55
	Rate equation	$\log k_1$ (s^{-1}) = (11.60 ± 0.12) − (178.3 ± 1.2) kJ mol^{-1} (2.303 RT)$^{-1}$, r = 0.9990						
3,3 Dimethyl-1-butyl	Temperature (°C)	331.2	341.4	350.8	360.4	370.9	379.5	
methylcarbonate	$10^4 k_1$ (s^{-1})	1.80	3.42	6.26	11.74	20.93	34.10	
	Rate equation	$\log k_1$ (s^{-1}) = (13.60 ± 0.15) − (200.7 ± 1.8) kJ mol^{-1} (2.303 RT)$^{-1}$, r = 0.9998						
2-Bromoethyl	Temperature (°C)	329.0	338.6	348.7	359.6	370.5	380.4	
methylcarbonate	$10^4 k_1$ (s^{-1})	1.31	2.54	4.36	7.76	13.20	22.30	
	Rate equation	$\log k_1$ (s^{-1}) = (11.53 ± 0.28) − (177.3 ± 3.4) kJ mol^{-1} (2.303 RT)$^{-1}$, r = 0.9993						
2-Chloroethyl	Temperature (°C)	360.4	370.7	380.0	389.3	398.8		
methylcarbonate	$10^4 k_1$ (s^{-1})	1.97	3.69	6.02	10.33	17.20		
	Rate equation	$\log k_1$ (s^{-1}) = (12.71 ± 0.44) − (199.1 ± 5.5) kJ mol^{-1} (2.303 RT)$^{-1}$, r = 0.9999						
3-Chloropropyl	Temperature (°C)	340.6	350.6	360.4	370.1	380.5	390.3	
methylcarbonate	$10^4 k_1$ (s^{-1})	1.57	3.35	5.43	10.39	18.31	3.36	
	Rate equation	$\log k_1$ (s^{-1}) = (13.59 ± 0.07) − (204.3 ± 0.8) kJ mol^{-1} (2.303 RT)$^{-1}$, r = 0.9999						
2-Methoxyethyl	Temperature (°C)	380.0	388.9	396.3	400.0	410.0	420.0	430.2
methylcarbonate	$10^4 k_1$ (s^{-1})	2.87	4.60	7.03	8.84	14.30	23.74	38.36
	Rate equation	$\log k_1$ (s^{-1}) = (12.30 ± 0.14) − (198.0 ± 1.8) kJ mol^{-1} (2.303 RT)$^{-1}$, r = 0.9998						
2-Phenoxyethyl	Temperature (°C)	385.0	395.3	405.3	415.3	425.6	435.7	
methylcarbonate	$10^4 k_1$ (s^{-1})	3.73	6.25	10.40	16.74	30.40	45.47	
	Rate equation	$\log k_1$ (s^{-1}) = (11.92 ± 0.28) − (193.5 ± 3.6) kJ mol^{-1} (2.303 RT)$^{-1}$, r = 0.9993						
2-Phenylethyl	Temperature (°C)	323.9	332.5	344.5	353.5	363.5	372.5	
methylcarbonate	$10^4 k_1$ (s^{-1})	2.37	4.07	7.72	12.29	19.54	33.32	
	Rate equation	$\log k_1$ (s^{-1}) = (10.82 ± 0.23) − (164.9 ± 2.7) kJ mol^{-1} (2.303 RT)$^{-1}$, r = 0.9995						
3-Phenylpropyl	Temperature (°C)	340.3	358.3	370.2	380.3	390.4		
methylcarbonate	$10^4 k_1$ (s^{-1})	1.45	4.57	8.74	13.94	21.31		
	Rate equation	$\log k_1$ (s^{-1}) = (12.04 ± 0.10) − (186.5 ± 1.3) kJ mol^{-1} (2.303 RT)$^{-1}$, r = 0.9999						

Table 6. Kinetic and thermodynamic parameters for pyrolisis of $CH_3OCOOCH_2CH_2Z$ at 400 °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	36.65	12.22	188.7 ± 1.5	12.21 ± 0.12	−26.23	183.1	200.8
CH_3	39.27	19.63	182.0 ± 2.3	11.72 ± 0.44	−35.61	176.4	200.4
CH_2CH_3	44.86	22.43	181.9 ± 1.4	11.77 ± 0.10	−34.66	176.3	199.6
$CH(CH_3)_2$	57.71	28.85	178.3 ± 1.2	11.60 ± 0.22	−37.91	172.7	198.2
$C(CH_3)_3$	105.35	52.68	200.7 ± 1.8	13.60 ± 0.15	0.37	195.1	194.9
Br	58.73	29.36	177.3 ± 3.4	11.53 ± 0.28	−39.25	171.7	198.1
Cl	18.04	9.03	199.1 ± 5.5	12.71 ± 0.44	−16.66	193.5	204.7
CH_2Cl	54.10	27.05	204.3 ± 0.8	13.59 ± 0.07	0.18	198.7	198.6
OCH_3	8.55	4.28	198.0 ± 1.8	12.30 ± 0.14	−24.51	192.4	208.9
OC_6H_5	7.15	3.58	193.5 ± 3.6	11.92 ± 0.28	−31.78	187.9	209.3
C_6H_5	105.02	52.51	164.9 ± 2.7	10.82 ± 0.23	−52.84	159.3	194.9
$CH_2C_6H_5$	36.31	18.15	186.5 ± 1.3	12.04 ± 0.10	−29.49	180.9	200.8

Table 7. Parameters of substituents Z in $CH_3OCOOCH_2$-CH_2Z at 400 °C

Z	Log (k_Z/k_H)	σ_α	σ_F	σ_R^-
H	0.0000	0.00	0.00	0.00
CH_3	0.20	−0.35	0.00	0.03
CH_2CH_3	0.26	−0.49	0.00	0.02
$CH(CH_3)_2$	0.37	−0.62	0.00	0.01
$C(CH_3)_3$	0.63	−0.75	0.00	0.00
Br	0.38	−0.59	0.45	−0.10
Cl	−0.13	−0.43	0.45	−0.12
CH_2Cl	0.34	−0.54	0.23	0.02
OCH_3	−0.46	−0.17	0.25	−0.27
OC_6H_5	−0.54	−0.38	0.38	−0.26
C_6H_5	0.63	−0.81	0.10	0.22
$CH_2C_6H_5$	0.17	−0.70	0.05	0.02

Figure 3. Log(k_Z/k_H) versus E_s^c for $CH_3OCOOCH_2CH_2Z$ at 400 °C. $\delta = -0.17$, $r = 0.9993$, SD $= 0.0102$

Table 9. Logarithm of relative rates of carbonates and acetates [log(k_Z/k_H)] at 400 °C

Z	Carbonates	Acetates
H	0.00	0.00
CH_3	0.20	0.11
CH_2CH_3	0.26	0.20
$CH(CH_3)_2$	0.37	0.19
$C(CH_3)_3$	0.63	0.46

for the gas-phase elimination of carbonates with a C_β—H bond at the alkyl side of the ester.
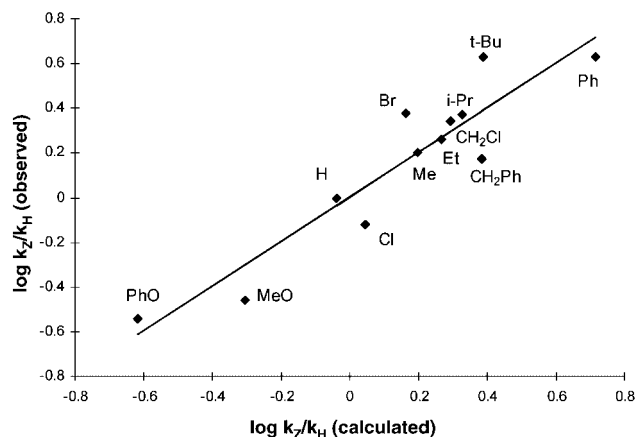
Figure 2. Taft–Tompson correlation for the pyrolysis of $CH_3OCOOCH_2CH_2Z$: log$(k_Z/k_H) = -(0.63 \pm 0.18)\sigma_\alpha + (1.29 \pm 0.45)\sigma_R^-$ ($r = 0.9447$; SD $= 0.14$) at 400 °C

Table 8. Log $k_{rel.}$ versus E_s^c at 400 °C

Z	Carbonates log (k_Z/k_H)	E_s^c
H	0.00	0.00
CH_3	0.20	−1.24
CH_2CH_3	0.26	−1.62
$CH(CH_3)_2$	0.37	−2.32
$C(CH_3)_3$	0.63	−3.70

EXPERIMENTAL

General procedure. The 2-substituted ethyl methyl-carbonates listed below were prepared by mixing 0.2 mol of methyl chloroformate (Aldrich) with 0.2 mol corresponding substituted alcohol in 40 ml of chloroform.
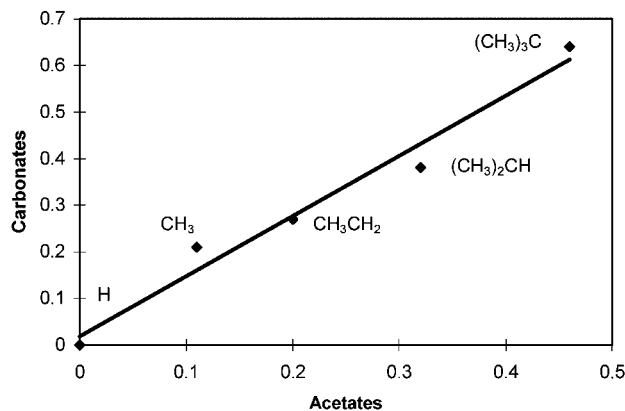
Figure 4. $\text{Log}(k_Z/k_H)$ (carbonates) versus $\text{log}(k_Z/k_H)$ (acetates) at $400\,^\circ\text{C}$. $r = 0.9857$, $\text{SD} = 0.045697$

The reaction mixture was refluxed until no more HCl was evolved. The product of the reaction was distilled several times to better than 98.8% purity as determined by GC–MS (Saturn 2000, Varian) with a DB-5MS capillary column, 30×0.53 mm i.d., $0.53\,\mu\text{m}$ film thickness.

Ethyl methylcarbonate. B.p. $108\,^\circ\text{C}$ at 630 Torr (1 Torr = 133.3 Pa), yield 46% (lit.,[13] 105–$107\,^\circ\text{C}$ at 760 Torr). ^1H NMR, δ 1.3 (t, 3H), 3.8 (s, 3H), 4.2 (m, 2H). MS, m/z 105 (M^+), 59 (CH_3OCO^+), 45 ($\text{OCH}_2\text{CH}_3^+$), 29 ($\text{CH}_2\text{CH}_3^+$).

Propyl methylcarbonate. B.p. $125\,^\circ\text{C}$ at 630 Torr, yield 90%. ^1H NMR, δ 0.9 (t, 3H), 1.6 (m, 2H), 3.9 (s, 3H), 4.0 (t, 2H). MS, m/z 119 (M^+), 75 (CH_3OCOO^+), 59 (CH_3OCO^+), 43 ($\text{CH}_3\text{CH}_2\text{CH}_2^+$).

1-Butyl methylcarbonate. B.p. 85–$87\,^\circ\text{C}$ at 61 Torr, yield 82%. ^1H NMR, δ 0.9 (t, 3H), 1.4 (m, 2H), 3.7 (s, 3H), 4.1 (t, 2H). MS, m/z 133 (M^+), 117 ($\text{OCOOCH}_2\text{CH}_2\text{CH}_2$ CH_3^+) 73 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3^+$), 59 ($\text{CH}_3\text{OCO}^+$), 43 ($\text{CH}_3\text{CH}_2\text{CH}_2^+$).

3-Methyl-1-butyl methylcarbonate. B.p. $149\,^\circ\text{C}$ at 630 Torr, yield 49%. ^1H NMR, δ 0.9 (d-d, 6H), 1.57 (m, 2H), 1.6 (m, 1H), 3.8 (s, 3H), 4.2 (t, 2H). MS, m/z 147 (M^+), 103 ($\text{CH}_3\text{OCOOCH}_2\text{CH}_2^+$), 87 [$\text{OCH}_2\text{CH}_2\text{CH}$ $(\text{CH}_3)_2^+$], 71 [$\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2^+$], 59 ($\text{CH}_3\text{OCO}^+$), 43 [$\text{CH}(\text{CH}_3)_2^+$].

3,3-Dimethyl-1-butyl methylcarbonate. B.p. $46\,^\circ\text{C}$ at 2 Torr, yield 99%. ^1H NMR, δ 0.9 (s, 9H), 1.6 (t, 2H), 3.8 (s, 3H), 4.2 (t, 2H). MS, m/z 160 (M^+), 103 ($\text{CH}_3\text{OCOOCH}_2\text{CH}_2^+$), 85 [$\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3^+$], 57 [$\text{C}(\text{CH}_3)_3^+$].

2-Bromoethyl methylcarbonate. B.p. $55\,^\circ\text{C}$ at 2 Torr, yield 81%. ^1H NMR, δ 3.8 (m, 2H), 4.0 (m, 2H). MS, m/z 183 (M^+), 103 ($\text{CH}_3\text{OCOOCH}_2\text{CH}_2^+$), 44 ($\text{CO}_2$).

2-Chloroethyl methylcarbonate. B.p. $95\,^\circ\text{C}$ at 82 Torr, yield 38%. ^1H NMR, δ 3.5 (m, 2H), 4.0 (m, 2H). MS, m/z 138 (M^+), 103 ($\text{CH}_3\text{OCOOCH}_2\text{CH}_2^+$), 59 ($\text{CH}_3\text{O}$ CO^+), 44 (CO_2).

3-Chloro-1-propyl methylcarbonate. B.p. $152\,^\circ\text{C}$ at 65 Torr, yield 54%. ^1H NMR, δ 2.1 (q, 2H), 3.6 (t, 2H), 3.8 (s, 3H), 4.3 (t, 2H). MS, m/z 153 (M^+), 117 (CH_3 $\text{OCOOCH}_2\text{CH}_2\text{CH}_2^+$), 103 ($\text{CH}_3\text{OCOOCH}_2\text{CH}_2^+$), 73 ($\text{COOCH}_2\text{CH}_2^+$), 59 ($\text{CH}_3\text{OCO}^+$), 44 ($\text{CO}_2$).

2-Methoxyethyl methylcarbonate. B.p. $95\,^\circ\text{C}$ at 82 Torr, yield 37%. ^1H NMR, δ 3.0 (s, 3H), 4.2 (t, 2H), 3.6 (s, 3H), 4.5 (t, 2H). MS, m/z 134 (M^+), 103 (CH_3 $\text{OCOOCH}_2\text{CH}_2^+$), 59 ($\text{CH}_3\text{OCO}^+$), 45 ($\text{CH}_3\text{OCH}_2^+$).

2-Phenoxyethyl methylcarbonate. B.p. $131\,^\circ\text{C}$ at 5 Torr, yield 49%. ^1H NMR, δ 3.8 (s, 3H), 4.2 (t, 2H), 4.5 (t, 2H), 6.9–7.3 (m, 5H). MS, m/z 196 (M^+), 121 (C_6H_5 $\text{OCH}_2\text{CH}_2^+$), 103 ($\text{CH}_3\text{OCOOCH}_2\text{CH}_2^+$), 77 ($\text{C}_6\text{H}_5^+$), 31 ($\text{CH}_3\text{O}^+$).

2-Phenylethyl methylcarbonate. B.p. $145\,^\circ\text{C}$ at 23 Torr, yield 45%. ^1H NMR, δ 2.8 (t, 2H), 3.7 (s, 3H), 4.5 (t, 2H), 7.1–7.2 (m, 5H). MS, m/z 180 (M^+), 104 (C_6H_5 CH_2CH_2^+), 59 (CH_3OCO^+).

3-Phenylpropyl methylcarbonate. B.p. $180\,^\circ\text{C}$ at 25 Torr, yield 58%. ^1H NMR, δ 2.0 (m, 2H), 2.7 (t, 2H), 3.8 (s, 3H), 4.2 (t, 2H), 7.2 (m, 5H). MS, m/z 195 (M^+), 117 ($\text{CH}_3\text{OCOOCH}_2\text{CH}_2\text{CH}_2^+$), 103 ($\text{CH}_3\text{OCOOCH}_2\text{CH}_2^+$), 91 ($\text{C}_6\text{H}_5\text{CH}_2^+$), 77 ($\text{C}_6\text{H}_5^+$).

Analyses. Quantitative analyses of the olefinic hydrocarbon products were carried out by GC with a Porapak Q column, 80–100 mesh. Quantitative analyses of the carbonate substrates, together with the identifications of products, were performed by GC–MS (Saturn 2000, Varian) with a DB-5MS capillary column, 30×0.53 mm. i.d., $0.53\,\mu\text{m}$ film thickness.

Kinetics. The kinetic determinations were carried out in a static system as reported[18,19] with an Omega DP41-TC/DP41-RTD high-performance digital temperature indicator. The rate coefficients were determined manometrically or by the quantitative analyses of the starting material and/or by the corresponding olefinic product. The temperature was controlled by a Shinko DC-PS resistance thermometer controller and an Omega SSR280A45 solid-state relay, maintained at $\pm 0.2\,^\circ\text{C}$ and measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was observed along the reaction vessel with a syringe through a silicone-rubber septum. The amount of substrate used for each reaction was ~ 0.05–0.2 ml.

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