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Pyrolysis kinetics of 2-phenoxycarboxylic acids in the gas phase

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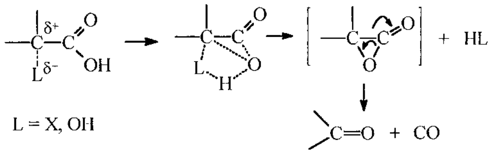
ABSTRACT: The gas-phase pyrolysis kinetics of primary, secondary and tertiary 2-phenoxycarboxylic acids were studied over the temperature range 240.1–409.9 °C and pressure range 16.3–67.8 Torr. The elimination reactions, carried out in seasoned vessels and in the presence of the free radical chain inhibitor cyclohexene, are homogeneous, unimolecular and follow a first-order rate law. The overall rate coefficients are expressed by the following equations: for 2-phenoxyacetic acid, $\log k_1(\mathrm{s}^{-1}) = (12.08 \pm 0.54) - (190.3 \pm 6.7)\mathrm{kJ\ mol}^{-1}(2.303RT)^{-1}$; for 2-phenoxypropionic acid, $\log k_1\ (\mathrm{s}^{-1}) = (12.21 \pm 0.31)\ - (172.9 \pm 3.6)\mathrm{kJ\ mol}^{-1}(2.303RT)^{-1}$; for 2-phenoxybutyric acid, $\log k_1(\mathrm{s}^{-1}) = (12.29 \pm 0.38) - (171.7 \pm 4.3)\mathrm{kJ\ mol}^{-1}(2.303RT)^{-1}$; and for 2-phenoxyisobutyric acid, $\log k_1(\mathrm{s}^{-1}) = (12.84 \pm 0.36) - (155.3 \pm 3.6)\mathrm{kJ\ mol}^{-1}(2.303RT)^{-1}$. The products of the phenoxyacids are phenol, the corresponding carbonyl compound and CO, except for 2-phenoxyisobutyric acid, which undergoes a parallel elimination into phenol and methylacrylic acid. The reaction rates increase from primary to tertiary carbon bearing the C_6H_5O group. The mechanism of these reactions appears to proceed through a semi-polar five-membered cyclic transition state, where the acidic H of the COOH group assists the leaving C_6H_5O substituent for phenol formation, followed by the participation of the oxygen carbonyl for lactone formation. Then the unstable lactone intermediate decomposes into the corresponding carbonyl compound and CO gas. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: 2-phenoxycarboxylic acids; pyrolysis kinetics; gas phase

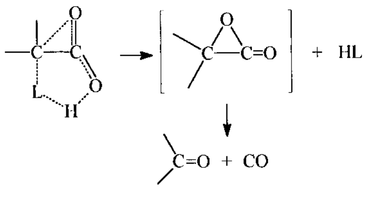
INTRODUCTION

In association with the elimination kinetics of 2-halocarboxylic acids,[1,2] the gas-phase pyrolyses of 2-hydroxycarboxylic acids have been examined.[3] A sequence of rate increase from primary to tertiary 2-hydroxycarboxylic acid acid was observed. The mechanism of these reactions was thought to proceed as follows:



(1)

The bond polarization of the C— L bond, in the direction of $C^{\delta+}\cdots L^{\delta-}$, was believed to be rate determining. The H of the COOH assisted the leaving group L for a five-membered cyclic transition state, while the hydroxy oxygen was assumed to participate in the stabilization of the positive carbon reaction center for lactone formation. However, recent quantum mechanical calculations on 2-chloropropionic acids,[4] glycolic, lactic and 2-hydroxyisobutyric acids[5] and mandelic acid,[6] using *ab initio* techniques at the MP2/6–31G** level, suggested that mechanism (1) proceeds by the nucleophilic attack of the carbonyl oxygen instead the hydroxylic oxygen for the formation of the α-lactone intermediate:



(2)

The OR group of ethers [$R = CH_3$, CH_3CH_2, $(CH_3)_2CH$] in the gas-phase pyrolyses of 2-alkoxyacetic acids[7] was shown to be faster in the elimination process than Cl and OH and the mechanism was pictured as in reaction (1). The alkyl group R in $ROCH_2COOH$ had no significant effect on rates. A recent examination of *ab initio* calculations of methoxy-, ethoxy- and isopro-

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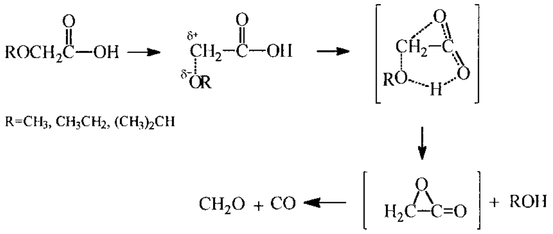
Table 1. Ratio of final (P_f) to initial (P_0) pressure[a,b]

Compound	Temperature (°C)	P_f (Torr)	P_0 (Torr)	P_f/P_0	Average
2-Phenoxyacetic acid	369.4	30.5	83.0	2.72	2.91
	389.2	29.9	87.4	2.92	
	400.2	40.0	117.6	2.94	
	409.9	23.0	70.0	3.04	
2-Phenoxypropionic acid	315.8	24.8	70.3	2.83	2.83
	329.8	37.6	100.6	2.87	
	340.2	34.0	91.5	2.80	
	351.0	30.0	85.5	2.85	
2-Phenoxybutyric acid	314.9	36.2	99.7	2.75	2.78
	320.1	45.0	125.5	2.79	
	328.7	51.6	144.0	2.79	
	338.5	34.6	202.0	2.78	
2-Phenoxyisobutyric acid	260.4	15.5	35.5	2.29	2.30
	270.1	44.0	97.0	2.20	
	280.0	22.5	54.0	2.40	

[a] Vessel seasoned with allyl bromide.
[b] In the presence of the inhibitor cyclohexene.

poxyacetic acids molecular eliminations at the MP2/6–31G** level[8] implied the mechanism to be as described as



(3)

To increase our understanding of the nature of the transition state in the gas-phase pyrolyses of 2-substituted carboxylic acids, the investigation of a better leaving group such as phenoxy, C_6H_5O, was thought to be of interest. Therefore, the molecular elimination kinetics of 2-phenoxyacetic acid, 2-phenoxypropionic acid, 2-phenoxybutyric acid and 2-phenoxyisobutyric acid were examined.

RESULTS AND DISCUSSION

2-Phenoxyacetic acid

The gas-phase elimination of this substrate proceeds according to the reaction

$$C_6H_5OCH_2COOH \rightarrow C_6H_5OH + CH_2O + CO \qquad (4)$$

The stoichiometry of the reaction demands $P_f/P_0 = 3$, where P_f and P_0 are the final and initial pressure, respectively. The average experimental results at four different temperatures and 10 half-lives is 2.91 (Table 1).

Table 2. Stoichiometry of the reactions[a]

Substrate	Temperature (°C)	Parameter	Value					
Phenylacetic acid	389	Time (min)	4	6	8	10	13	
		Reaction (%) (pressure)	20.5	33.5	48.2	56.9	78.2	
		Phenol (%) (GLC)[b]	21.1	31.2	45.7	54.1	76.2	
2-Phenoxypropionic acid	320.0	Time (min)	3	5	8	12	17	
		Reaction (%) (pressure)	25.0	39.7	44.8	59.8	72.7	
		Acetaldehyde (%) (GLC)	28.5	42.2	47.1	61.5	75.0	
2-Phenoxybutyric acid	320.1	Time (min)	2.5	4	6	8	10	12
		Reaction (%) (pressure)	20.4	30.4	41.8	51.5	58.8	65.3
		Propionaldehyde (%) (GLC)	20.9	28.6	41.3	51.0	59.4	64.3
2-Phenoxyisobutyric acid	250	Time (min)	3	6	9	12		
		Phenol (%) (GLC)	35.5	57.3	72.2	83.8		
		Acetone (%) (GLC)	19.3	33.1	40.2	46.5		
		Methylacrylic acid (%) (GLC)	15.5	24.8	31.3	34.5		

[a] Vessel seasoned with allyl bromide, and in the presence of cyclohexene inhibitor.
[b] GLC = gas-liquid chromatography.

Table 3. Homogeneity of the reaction

Substrate	Temperature (°C)	S/V (cm^{-1})[a]	$10^4 k_1$ (s^{-1})[b]	$10^4 k_1$ (s^{-1})[c]
2-Phenoxyacetic acid	389.2	1	15.94	12.08
		6	20.46	11.94
2-Phenoxypropionic acid	320.0	1	11.65	11.13
		6	11.70	11.25
2-Phenoxybutyric acid	320.2	1	15.57	15.19
		6	15.53	15.24
2-Phenoxyisobutyric acid	250.0	1	9.88[d]	(12.30[e] + 9.15[f]) = 21.45
		6	4.01[d]	(12.07[e] + 9.74[f]) = 21.81

[a] S = surface area (cm^2); V = volume (cm^3).
[b] Clean Pyrex vessel.
[c] Vessel seasoned with allyl bromide.
[d] Average overall k values.
[e] k Value of acetone formation.
[f] k Value of methylacrylic acid formation.

Further verification of the stoichiometry of reaction (4) was made by comparing, up to 75% decomposition, the pressure measurements with the results of quantitative gas chromatographic analysis of phenol (Table 2).

The homogeneity of the reaction was examined by carrying out several runs in a vessel with a surface-to-volume ratio of 6.0 relative to that of the normal vessel, which is equal to 1.0. A packed and unpacked Pyrex vessel, seasoned with allyl bromide, had no effect on rates. However, the packed and unpacked clean Pyrex vessel had a significant heterogeneous effect on the rate coefficient (Table 3). The effect of a free radical inhibitor is shown in Table 4. The kinetic runs had to be carried with at least a threefold excess of cyclohexene in order to suppress any possible free radical processes of the reactant and/or products. No induction was observed. The rate coefficients were reproducible with a relative standard deviation of $\leq$5% at any given temperature.

The first-order rate coefficients of phenoxyacetic acid, calculated from $k_1 = (2.303/t)\ \log[2P_0/(3P_0 - P_t)]$, were independent of the initial pressure (Table 5). A plot of log $(3P_0 - P_t)$ against time t gave a good straight line up to 75% decomposition. The variation of the rate coefficient, in a seasoned vessel and in the presence of the inhibitor cyclohexene, with temperature is shown in Table 6. The data were fitted to the Arrhenius equation, where the rate

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

Substrate	Temperature (°C)	P_s (Torr)	P_i (Torr)	P_i/P_s	$10^4 k_1$ (s^{-1})
Phenoxyacetic acid	389.9	55.6	—	—	18.83
		67.8	97.5	1.4	13.08
		62.8	108.6	1.7	12.82
		53.0	106.0	2.0	12.81
		34.0	99.6	2.9	12.91
		21.7	67.5	3.1	12.77
2-Phenoxypropionic acid	320.0	38.1	—	—	12.05
		37.9	58.0	1.5	11.63
		43.0	89.5	2.1	10.75
		34.3	110.5	3.2	11.17
		35.9	146.5	4.1	11.17
2-Phenoxybutyric acid	329.1	20.0	—	—	25.20
		49.6	32.0	0.7	25.11
		51.6	62.0	1.2	25.00
		21.7	67.0	2.3	25.08
		26.1	117.5	4.5	25.09
2-Phenoxyisobutyric acid	260.0	23.0	—	—	(24.81[b] + 18.96[c]) = 43.77
		44.0	44.5	1.0	(24.69[b] + 18.12[c]) = 42.81
		22.8	29.0	1.3	(24.88[b] + 18.33[c]) = 43.21
		16.3	70.0	4.3	(24.82[b] + 18.36[c]) = 43.18
		16.7	84.5	5.1	(24.84[b] + 18.32[c]) = 43.16

[a] P_s = pressure of the substrate; P_i = pressure of the inhibitor. Vessel seasoned with allyl bromide.
[b] k Value of acetone formation.
[c] k Value of methylacrylic acid formation.

Table 5. Invariability of rate coefficients with initial pressure

Compound	Temperature (°C)	Parameter	Values				
2-Phenoxyacetic acid	389.9	P_0 (Torr)	21.7	34.0	53.0	67.8	
		$10^4\ k_1$ (s^{-1})	12.91	12.81	12.82	12.77	
2-Phenoxypropionic acid	320.0	P_0 (Torr)	22.0	34.3	43.0	50.7	
		$10^4\ k_1$ (s^{-1})	11.53	11.17	10.75	11.33	
2-Phenoxybutyric acid	320.1	P_0 (Torr)	22.1	27.4	34.6	37.6	44.0
		$10^4\ k_1$ (s^{-1})	15.06	15.17	15.13	15.22	15.29
2-Phenoxyisobutyric acid	260.4	P_0 (Torr)	16.3	23.0	31.0	44.0	
		$10^4\ k_1$ (s^{-1})	($24.82^a + 18.36^b$)	($24.81^a + 18.96^b$)	($24.90^a + 18.83^b$)	($24.69^a + 18.12^b$)	

[a] k Value of acetone formation.

[b] k Value of methylacrylic acid formation.

Table 6. Variation of rate coefficients with temperature[a]

Compound	Parameter	Values						
2-Phenoxyacetic acid	Temperature (°C)	349.8	359.9	369.4	380.3	389.2	400.5	409.9
	$10^4\ k_1$(s^{-1})	1.41	2.24	4.21	6.94	12.08	21.20	34.42
	Rate equation	Log k_1 (s^{-1}) = (12.04 ± 0.54) $-$(190.3 ± 6.7)kJ mol^{-1} (2.303RT)$^{-1}$; r = 0.9992						
2-Phenoxypropionic acid	Temperature (°C)	310.0	315.8	320.0	329.8	340.2	351.0	
	$10^4\ k_1$ (s^{-1})	6.39	8.72	11.13	18.97	37.77	63.93	
	Rate equation	Log k_1(s^{-1}) = (12.28 ± 0.31) $-$(172.9 ± 3.6)kJ mol^{-1}(2.303RT)$^{-1}$; r = 0.99915						
2-Phenoxybutyric acid	Temperature (°C)	300.2	309.3	314.9	320.2	329.1	338.5	
	$10^4\ k_1$ (s^{-1})	4.34	8.05	11.18	15.19	25.10	42.10	
	Rate equation	Log k_1(s^{-1}) = (12.29 ± 0.38) $-$(171.7 ± 4.3)kJ mol^{-1}(2.303RT)$^{-1}$; r = 0.9997						
2-Phenoxyisobutyric acid	Temperature (°C)	240.1	250.5	260.4	270.1	280.0		
	$10^4\ k_1$ (s^{-1})	10.48	22.66	43.49	79.23	147.0		
	Rate equation	Log k_1(s^{-1}) = (12.84 ± 0.36) $-$(155.3 ± 3.6)kJ mol^{-1}(2.303RT)$^{-1}$; r = 0.9996						

[a] Vessel seasoned with allyl bromide and in the presence of cyclohexene inhibitor.

coefficient at the 90% confidence level obtained from least-squares procedures are given.

2-Phenoxypropionic acid

The experimental stoichiometry for the gas-phase elimination of 2-phenoxypropionic acid, as described in reaction (5), implies $P_f = 3P_0$.

$$CH_3(C_6H_5O)CHCOOH \rightarrow C_6H_5OH + CH_3CHO + CO \qquad (5)$$

The average P_f/P_0 at four different temperatures and 10 half-lives was 2.83 (Table 1). The small departure from the theoretical stoichiometry was due to a parallel path, where less than 1% of phenol and acrylic acid are formed. Verification of the stochiometry of reaction (5), up to 75% reaction, was possible, considering that the acetaldehyde produced is equivalent to the pressure increase (Table 2).

The pyrolysis reaction (5) is homogeneous, since no significant variations in rates were obtained in these experiments when using both clean Pyrex and seasoned vessels with a surface-to-volume ratio of 6.0 relative to that of the normal vessel, which is equal to 1.0 (Table 3). This substrate was always pyrolyzed in the presence of at least a twofold excess of the free radical chain inhibitor cyclohexene (Table 4). No induction period was observed and the rates were reproducible with a relative standard deviation of $\leq$5% at any given temperature.

The rate coefficients were found to be invariant of their initial pressure (Table 5). The logarithmic plots are linear up to 75% decomposition. The temperature dependence of the first-order rate coefficients is shown in Table 6, where rate coefficients at the 90% confidence level obtained with a least-squares method are given.

2-Phenoxybutyric acid

The stoichiometry for the gas-phase elimination of 2-phenoxybutyric acid as represented in reaction (5) suggests $P_f = 3P_0$. The average P_f/P_0 at four different temperatures and 10 half-lives was 2.78 (Table 1). The small departure from stoichiometry in the reaction

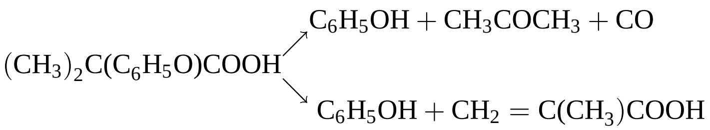
$$CH_3CH_2CH(OC_6H_5)COOH \rightarrow C_6H_5OH + CH_3CH_2CHO + CO \qquad (6)$$

was due to a parallel decomposition to give, after 68% reaction, small amounts of phenol, vinylacetic acid and crotonic acid. Additional examination of the stoichiometry of reaction (6), up to 65% reaction, showed that the percentage decomposition of the phenoxybutyric acid calculated from pressure measurements was in good agreement with that obtained from the chromatographic analysis of the product propionaldehyde (Table 2). Reaction (6) was found to be homogeneous since no significant variations in rates were obtained when using both clean Pyrex and seasoned vessels with a surface-to-volume ratio of 6.0 relative to that of the normal vessel, which is equal to 1.0 (Table 3). The free radical inhibitor cyclohexene had no effect on the rate of elimination (Table 4). No induction period was observed. The rate coefficients were reproducible with a relative standard deviation of <5% at any given temperature.

The rate coefficients were shown to be independent of the initial pressure of this substrate (Table 5), and the first-order plots are satisfactorily linear up to about 65% reaction. The variation of the rate coefficient with temperature is described in Table 6, which gives rate coefficients at the 90% confidence limits obtained from a least-squares procedure.

2-Phenoxyisobutyric acid

The pyrolysis products of 2-phenoxyisobutyric acid according to the reaction



$$(CH_3)_2C(C_6H_5O)COOH \begin{array}{l} \nearrow C_6H_5OH + CH_3COCH_3 + CO \\ \searrow C_6H_5OH + CH_2 = C(CH_3)COOH \end{array} \qquad (7)$$

make it difficult to determine the stoichiometry from the pressure increase. The average experimental P_f/P_0 at three different temperatures and 10 half-lives is 2.30 (Table 1). However, to verify the stoichiometry of reaction (7), up to 84% decomposition, quantitative chromatographic analyses of total phenol formation were compared with the sum of acetone and methacrylic acid products (Table 2). The effect of the surface on the rate in a vessel with a surface-to-volume ratio six times greater than that of the normal vessel showed a significant heterogeneous effect in a clean packed and unpacked Pyrex vessel (Table 3). This result appears to be due to

Table 7. Variation of rate coefficient with temperature for formation of acetone and methylacrylic acid

	$10^4\ k_1$ (s^{-1})	
Temperature (°C)	Acetone	Methacrylic acid
240.1	6.12	4.36
250.5	13.03	9.63
260.4	24.94	18.55
270.1	43.03	36.20
280.0	81.17	65.87

some polymerization of methacrylic acid. However, the rate of elimination was unaffected in a seasoned packed and unpacked vessel. 2-Phenoxyisobutyric acid was always pyrolyzed in seasoned vessels and in the presence of at least a twofold excess of the free radical inhibitor cyclohexene (Table 4). No induction period was observed and the rates were reproducible with a relative standard deviation of $\leq 5\%$ at any given temperature.

The rate coefficients, in seasoned vessels and in the presence of cyclohexene, were found to be independent of the initial pressure, and the first-order plots are satisfactorily linear up to about 80% reaction (Table 5). The variation of the rate coefficients with temperature is described in Table 6 (90% confidence coefficient).

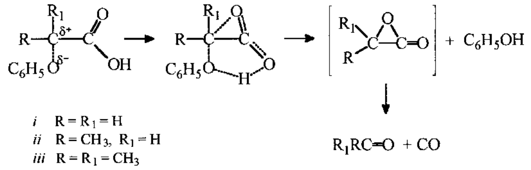
The partial rates of primary product formation, described in reaction (7), were determined, up to 80% decomposition of the phenoxyisobutyric acid, by quantitative gas chromatographic analyses of acetone and methacrylic acid. The variation of the rate coefficients for the formation of these products with temperature (Table 7) gives, by a least-squares procedure and with a 90% confidence coefficient, the following Arrhenius equations: for acetone formation

$$\begin{aligned}\log k_1(\mathrm{s}^{-1}) &= (12.20 \pm 0.52) - (151.3 \\ &\quad \pm 5.2)\mathrm{kJ\ mol}^{-1}(2.303RT)^{-1}; r \\ &= 0.9996\end{aligned}$$

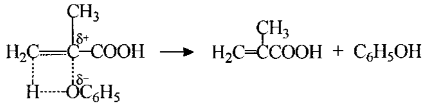
and for methacrylic acid:

$$\begin{aligned}\log k_1(\mathrm{s}^{-1}) &= (12.99 \pm 0.38) - (160.5 \\ &\quad \pm 3.9)\mathrm{kJ\ mol}^{-1}(2.303RT)^{-1}; r \\ &= 0.9998\end{aligned}$$

According to the kinetic parameters described in Table 8, the elimination rates of the phenoxy acids increase from primary to tertiary carbon bearing the C_6H_5O susbtituent. Moreover, with the support of theoretical studies on the reaction pathways of 2-substituted chloro[4] and hydroxy[5,6] carboxylic acids, the mechanism may be rationalized in terms of a moderately polar bicyclic (3,1,0) transition structure, where an α-lactone intermediate is achieved by the assistance of acidic hydrogen of the COOH, followed by nucleophilic attack of the carbonyl oxygen. The unstable lactone proceeds to decompose into the corresponding carbonyl compound and carbon monoxide:



With respect to the parallel elimination pathway of 2-phenoxyisobutyric acid in the formation of phenol and methacrylic acid, the mechanism may be associated with the gas-phase pyrolysis of *tert*-butyl phenyl ether,[9,10] where the unimolecular elimination of phenol involves a polar four-centered cyclic transition-state reaction. Consequently, reaction of this phenoxy acid appears to proceed through a semi-polar four-membered cyclic transition state:



EXPERIMENTAL

2-Phenoxyacetic acid. 2-Phenoxyacetic acid was prepared by treating bromoacetic acid with phenol as reported.[11] The product was recrystallized several times from water, m.p. 97 °C. The primary product phenol (Aldrich) was analyzed using GLC: 10% SP-1200–1% H_3PO_4 on Chromosorb W AW DMCS, 80–100 mesh.

Table 8. Kinetic parameters for the assumed α-lactone formation at 300.0 °C

Substrate	$10^4\ k_1$ (s^{-1})	Relative rate	E_a (kJ mol^{-1})	Log*A* (s^{-1})	ΔS‡ (J mol^{-1} K^{-1})	ΔH‡ (kJ mol^{-1})
2-Phenoxyacetic acid	0.054	1.0	190.3 ± 6.7	12.08 ± 0.54	−6.55	195.1
2-Phenoxypropionic acid	3.31	61.3	172.9 ± 3.6	12.28 ± 0.31	−5.64	177.7
2-Phenoxybutyric acid	4.37	80.9	171.7 ± 4.3	12.29 ± 0.38	−5.59	176.5
2-Phenoxyisobutyric acid	257.04	4760.0	151.3 ± 5.3	12.20 ± 0.52	−6.01	156.1

2-Phenoxypropionic acid. This substrate (Aldrich) was found to be of >98.8% purity (GLC: Porapak R, 80–100 mesh). The pyrolysis products acetaldehyde (Aldrich) and phenol (Aldrich) were quantitatively analyzed in the same column.

2-Phenoxybutyric acid. Phenoxybutyric acid (Aldrich) of 99.9% purity determined by GLC (10% SP-1200–1% H_3PO_4 on Chromosorb W AW DMCS, 80–100 mesh) was used. The product propionaldehyde (Aldrich) was quantitatively analyzed in a column of Porapak Q, 60–80 mesh.

2-Phenoxyisobutyric acid. The synthesis of this substrate was carried out by mixing phenol (Aldrich), 1,1,1-trichloro-2-methyl-2-propanol (Aldrich) in NaOH and acetone (Merck) as described[12] (m.p. 99–100 °C). NMR: δ 2.55 (s, 6H), 7.1 (m, 5H), 9.4 (s, 1H). MS: *m/z* 180 (M^+), 135 [$M^+ - C_6H_5OC(CH_3)_2$], 94 ($M^+ - C_6H_5O$), 77 ($M^+ - C_6H_5$). The pyrolysis product acetone (Merck) was quantitatively analyzed in a column of diisodecyl phthalate 5%–Chromosorb G AW DMCS, 60–80 mesh, and the methacrylic acid (Aldrich) in a column of 10% SP-1200–1% H_3PO_4 on Chromosorb W AW DMCS, 80–100 mesh.

The identities of the substrates and products were further verified by mass and NMR spectrometry.

Kinetic experiments. The phenoxy acids were pyrolyzed in a static reaction system, seasoned with allyl bromide, and in the presence of cyclohexene as a free-radical chain suppressor. The rate coefficients were determined by pressure increase and by quantitative GLC analyses of the products. The temperature was controlled by a Shinko DIC-PS resistance thermometer controller maintained within ±0.2 °C and measured with a calibrated platinum–platinum 13% rhodium thermocouple. The substrates 2-phenoxyacetic acid, 2-phenoxypropionic acid and 2-phenoxybutyric acid dissolved in dioxane (Merck) and 2-phenoxyisobutyric acid dissolved in chlorobenzene (Aldrich) were injected directly into the reaction vessel through a silicone-rubber septum.

Acknowledgements

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