JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2000; **13:** 757–764

Kinetics and mechanism of the gas-phase elimination of primary, secondary and tertiary 2-acetoxycarboxylic acids

Gabriel Chuchani,* Rosa M Dominguez, Armando Herize and Roman Romero

Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela

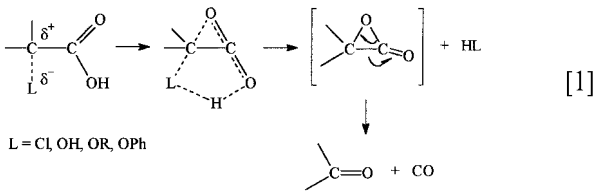
Received 25 May 2000; revised 31 July 2000; accepted 2 August 2000

ABSTRACT: The gas-phase elimination kinetics of the title compounds were examined over the temperature range 220.1 –349.0 °C and pressure range 19–120 Torr. These reactions proved to be homogeneous and unimolecular and to follow a first-order rate law. The overall rate coefficients are expressed by the following Arrhenius equations: for 2-acetoxyacetic acid, $\log k_1$ (s^{-1}) = (12.03 ± 0.28) − (170.8 ± 3.2) kJ mol^{-1} $(2.303RT)^{-1}$; for 2-acetoxypropionic acid, $\log k_1$ (s^{-1}) = (13.16 ± 0.24) − (174.2 ± 2.6) kJ mol^{-1} $(2.303RT)^{-1}$; for 2-acetoxy-2-methylpropionic acid, $\log k_1$ (s^{-1}) = (13.40 ± 0.72) − (160.9 ± 5.03) kJ mol^{-1} $(2.303RT)^{-1}$. The products of the acetoxyacids are acetic acid, the corresponding carbonyl compound and CO gas, except for 2-acetoxy-2-methylpropionic acid, which undergoes a parallel elimination to give methacrylic acid and acetic acid. The rates of elimination are found to increase from primary to tertiary carbon bearing the acetoxy group. The mechanism appears to proceed through a discrete polar five-membered cyclic transition state, where the acidic hydrogen of the COOH assists the leaving acetoxy group, followed by the participation of the carbonyl oxygen for α-lactone formation. The unstable α-lactone intermediate decomposes rapidly into the corresponding carbonyl compound and CO gas. The importance of the acidic H of the COOH assistance in the acetoxy acid mechanisms may be revealed in the elimination kinetics of methyl 2-acetoxypropionate. This substrate was studied in the ranges 370.0 –430.0 °C and 36–125 Torr. This reaction is homogeneous, unimolecular and follows a first-order rate law. The products are methyl acrylate and acetic acid. The rate coefficients is given by the equation $\log k_1$ (s^{-1}) = (12.63 ± 0.35) − (201.7 ± 4.4) kJ mol^{-1} $(2.303RT)^{-1}$.
Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: 2-acetoxycarboxylic acids; gas-phase elimination; kinetics; mechanism

INTRODUCTION

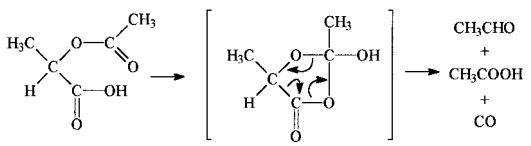
In recent years, experimental and theoretical studies on the gas-phase elimination kinetics of 2-substituted chloro-,[1] hydroxy-,[2,3] alkoxy-[4,5] and phenoxycarboxylic acids[6] implied that these reactions proceed through a mechanism according to Eqn. (1):



[1]

The polarization of the C—L bond, in the sense of $C^{\partial+}\cdots{}^{\partial-}L$, is the rate-determining step. In this respect, the elimination process proceeds through a moderately polar bicyclic (3.1.0) transition state, where the formation of the unstable α-lactone results through the assistance of the H of the COOH and the participation of the oxygen carbonyl. The α-lactone, which is unstable, decomposes into the corresponding carbonyl compound and carbon monoxide.

A qualitative pyrolysis study of 2-acetoxycarboxylic acids,[7] using the flow method for decomposition, did not give at 500 °C the expected propenoic acid but acetaldehyde, acetic acid and CO gas. The following mechanism was suggested:



[2]

Apparently, the acidic H of the COOH proceeds to protonate the oxygen carbonyl of the acetoxy group to form a five-membered cyclic intermediate, which then decomposes into acetic acid, acetaldehyde and CO gas.

The acetoxy group, CH_3COO, which is known to be a very good leaving group in gas-phase pyrolytic decompositions, suggests the examination of the gas-phase

**Correspondence to:* G. Chuchani, Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela.
Contract/grant sponsor: Consejo Nacional de Investigaciones Científicas y Tecnologicas (CONICIT); *Contract/grant number:* S1-97000005.

Copyright © 2000 John Wiley & Sons, Ltd.

elimination kinetics of primary, secondary and tertiary 2-acetoxycarboxylic acids. Moreover, in order to increase our knowledge of whether the mechanism proceeds as in Eqn. (1), it is intended to rationalize which of the steps is more important: the participation of the H of the COOH or the anchimeric assistance of the oxygen carbonyl for a three membered-structure. This idea implied the study of the elimination kinetics of methyl 2-acetoxypropionate.

RESULTS AND DISCUSSION

2-Acetoxyacetic acid

The elimination products of 2-acetoxyacetic acid (acetylglycolic acid), in the gas phase, are shown in reaction (3):

$$CH_3COOCH_2COOH \rightarrow CH_3COOH + CH_2O + CO \quad [3]$$

The stoichiometry of the reaction demands $P_f/P_0 = 3$, where P_f and P_0 are the final and initial pressures, respectively. The average experimental results at four different temperatures and 10 half-lives is 2.37 (Table 1). The departure of $P_f = 3P_0$ was found to be due to the polymerization of CH_2O. The stoichiometry of Eqn. (3) was verified by comparing up to 36% decomposition of the substrate from pressure measurements with those obtained from the quantitative chromatographic analyses of acetic acid formation (Table 2).

The elimination reaction (3) is homogeneous, since no significant variations in the rates were observed in these experiments when using either clean Pyrex or seasoned vessels with a surface-to-volume ratio of 6.0 relative to that of the normal vessel, which is equal to 1 (Table 3).

The effect of different proportions of the free radical suppressor cyclohexene in this reaction is shown in Table 4. The kinetic runs were always carried out with at least a twofold excess of cyclohexene in order to inhibit any possible free radical process of the substrate and/or products. No induction period was observed. The rate coefficients are reproducible with a relative standard deviation not greater than 5% at a given temperature.

The rate coefficient of 2-acetoxyacetic acid, calculated from $k_1 = (2.303/t)\log[2P_0/(3P_0 - P_t)]$, was found to be invariant with the initial pressure (Table 5). The temperature dependence of the rate coefficients is shown in Table 6. The data were fitted to the Arrhenius equation, where the rate coefficients at the 90% confidence level obtained with a least-squares method are given.

2-Acetoxypropionic acid

The gas-phase elimination of 2-acetoxypropionic acid (acetyllactic acid) leads to the products shown in reaction (4):

$$CH_3CH(OCCH_3{=}O)COOH \rightarrow CH_3COOH + CH_3CHO + CO$$
$$\searrow \; CH_2{=}CHCOOH + CH_3COOH \quad (\leq 3\%) \quad [4]$$

The stoichiometry of reaction (4) requires $P_f/P_0 \approx 3.0$. However, the average experimental P_f/P_0 at four different temperatures and 10 half-lives is 2.48 (Table 1). The observed $P_f/P_0 < 3$ of the overall elimination was due to a parallel decomposition to give, after 57% reaction, small amounts of acrylic acid and acetic acid [reaction (4)]. Moreover, some of the acetaldehyde and

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

Substrate	Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	Average
2-Acetoxyacetic acid	319.4	46	103.5	2.25	2.37
	329.8	73.5	166.5	2.27	
	340.7	62	152.5	2.46	
	349	56.5	141	2.50	
2-Acetoxypropionic acid	298.3	84	207.5	2.47	2.48
	309.9	37	90.5	2.45	
	316.1	42.5	106.5	2.51	
	324.8	48.5	121	2.49	
2-Acetoxy-2-methylpropionic acid	230.5	55	133	2.42	2.44
	240.3	31	76	2.48	
	250.7	55	135.6	2.46	
	260	32.5	79	2.43	
	269.4	50.5	123	2.44	
Methyl 2-acetoxypropionate	380.4	79	150	1.90	2.01
	389.6	71	147	2.07	
	399.5	78	157	2.05	
	410.1	87	171	1.97	
	420.2	86	180	2.09	

[a] Vessel seasoned with allyl bromide and in the presence of cyclohexene and/or toluene inhibitor. 1 Torr = 133.3 Pa.

Copyright © 2000 John Wiley & Sons, Ltd.

Table 2. Stoichiometry of the reaction[a]

Substrate	Temperature (°C)	Parameter	Value				
2-Acetoxyacetic acid	319.4	Time (min)	2.5	4	6	8	
		Reaction (%) (pressure)	13.8	20.6	28.0	36.3	
		Acetic acid (%) (GLC)[b]	13.6	21.0	28.5	36.7	
2-Acetoxypropionic acid	290.1	Time (min)	3	5	7	9	12
		Reaction (%) (pressure)	16.7	26.3	35.8	42.4	51.0
		Acetic acid (%) (GLC)	18.4	25.0	36.9	39.3	50.2
2-Acetoxy-2-methylpropionic acid	240.3	Time (min)	4	7	10	13	15
		Acetic acid (%) (GLC)	19.2	38.4	50.0	58.5	65.1
		Acetone (%) (GLC)	13.0	25.1	31.5	38.4	39.6
		Methacrylic acid (%) (GLC)	6.5	13.9	17.7	18.4	23.5
Methyl 2-acetoxypropionate	400.0	Time (min)	1	3	6	9	12
		Reaction (%) (pressure)	7.4	22.2	40.7	51.9	66.6
		Acetic acid (%) (titration)	6.5	24.6	42.9	50.9	62.1

[a] Seasoned with allyl bromide and in the presence of cyclohexene and/or toluene inhibitor.
[b] GLC = gas–liquid chromatography.

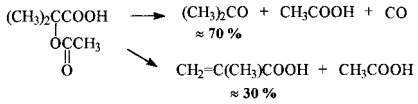
acrylic acid tend to polymerize. In order to check the stoichiometry described in reaction (4), up to 50% decomposition, the quantitative chromatographic analysis of acetic acid formation was in good agreement with the pressure increase (Table 2).

The homogeneity of this pyrolytic elimination was examined in a vessel with a surface-to-volume ratio six times greater than that of the normal vessel. The rates of elimination were unaffected in seasoned and clean Pyrex packed and unpacked vessels (Table 3). The free radical suppressor cyclohexene or toluene had no effect on the rates of elimination (Table 4). No induction period was observed and the rates were reproducible with a relative standard deviation not greater than 5% at a given temperature.

The rate coefficients were found to be independent of the initial pressure and the first-order plots are satisfactorily linear up to about 57% reaction (Table 5). The variation of the overall rate coefficients with temperature is shown in Table 6 (90% confidence coefficient).

2-Acetoxy-2-methylpropionic acid

The product formation in the gas-phase elimination of 2-acetoxy-2-methylpropionic acid (2-acetoxyisobutyric acid) is shown in reaction (5):



[5]

The stoichiometry is difficult to assess from the experimental pressure increase, since the theoretical P_f/P_0 ratio is <3. The average experimental P_f/P_0 at four different temperatures and 10 half-lives is 2.44 (Table 1). The above stoichiometry of reaction (5) was checked by comparing, up to 65% decomposition, the quantitative chromatographic analyses of the total amount of acetic acid formation with the sum of the amounts of products acetone and methacrylic acid (Table 2).

The effect of the surface on rates in a vessel with a surface-to-volume ratio of 6.0 relative to that of the normal vessel showed a significant heterogeneous effect in clean packed and unpacked Pyrex vessels (Table 3). This result may be due to the catalytic effect on the rate. However, the pyrolysis rates are not affected in a seasoned packed and unpacked vessel.

The presence of different proportions of the free radical inhibitor cyclohexene is shown in Table 4.

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-Acetoxyacetic acid	319.4	1	9.49	9.75
		6	9.55	9.68
2-Acetoxypropionic acid	298.3	1	17.23	17.30
		6	17.66	17.37
2-Acetoxy-2-methylpropionic acid	319.4	1	13.93	10.31
		6	26.11	10.52
Methyl 2-acetoxypropionate	400.0	1	9.29	9.16
		6	9.26	9.39

[a] S = surface area (cm^2); V = volume (cm^3).
[b] Clean Pyrex vessel.
[c] Vessel seasoned with allyl bromide.

Copyright © 2000 John Wiley & Sons, Ltd.

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

Substrate	Temperature (°C)	P_s (Torr)[b]	P_i (Torr)[b]	P_i/P_s	$10^4\ k_1$ (s^{-1})
2-Acetoxyacetic acid	329.8	70	—	—	16.86[c]
		40	36	0.8	17.52[c]
		42	58.5	1.4	17.52[c]
		73.5	157	2.1	17.60[c]
		61	188.5	3.1	17.58[c]
		47	240.5	5.1	17.54[c]
2-Acetoxypropionic acid	309.9	31	—	—	35.26
		52.5	28	0.5	35.12
		44	38.5	0.9	35.34
		57.5	82	1.4	35.02
		55	103.5	1.9	35.32
		46	112	2.5	35.37
2-Acetoxy-2-methylpropionic acid	250.4	55	—	—	20.80
		75	37.5	0.5	21.42
		54	68.5	1.3	21.13
		28.5	110	3.9	21.30
		18	91	5.0	21.40
Methyl 2-acetoxypropionate	410.4	36	—	—	15.06
		68	181	0.4	15.18
		92	99	1.1	15.22
		125	55	2.3	15.35

[a] Vessel seasoned with allyl bromide.
[b] P_S = pressure of the substrate; P_f = pressure of the inhibitor.
[c] Up to 35% reaction.

According to the results, cyclohexene does not affect the rate of elimination of 2-acetoxy-2-methylpropionic acid. However, in order to prevent any possible radical chain process, the kinetic experiments were always carried out in the presence of at least an equal amount of cyclohexene inhibitor. No induction period was observed and the *k*-values were reproducible with a relative standard deviation of less than 5% at any given temperature.

Tha rate coefficients were found to be invariant with the initial pressure (Table 5). The logarithmic plots are linear up to 65% decomposition. The temperature dependence of the overall rate coefficients and the corresponding Arrhenius equations are given in Table 6 (90% confidence coefficient from the least-squares procedure).

The partial rate coefficients of the product formation described in reaction (5) were determined, up to 65% decomposition of the acetoxyisobutyric acid, by quantitative gas chromatographic analyses of acetone and methacrylic acid. The variation of the rate coefficients for product formation with temperature (Table 7) gives, by the least-squares procedure and with 90% confidence limits, the following Arrhenius equations:

Acetone formation:

$$\log k_1(\mathrm{s}^{-1}) = (13.43 \pm 0.77) - (163.0 \pm 5.4)\ \mathrm{kJ\ mol}^{-1}(2.303RT)^{-1};\quad r = 0.99975$$

Methacrylic acid formation:

$$\log k_1(\mathrm{s}^{-1}) = (12.92 \pm 0.76) - (160.6 \pm 5.3)\ \mathrm{kJ\ mol}^{-1}(2.303RT)^{-1},\quad r = 0.99967$$

Table 5. Independence of the rate coefficients of initial pressure

Substrate	Temperature (°C)	Parameter	Value					
2-Acetoxyacetic acid	319.4	P_0 (Torr)	38	51	60	67	94	120
		$10^4\ k_1$ (s^{-1})	9.75	9.86	9.70	9.66	9.79	9.80
2-Acetoxypropionic acid	309.9	P_0 (Torr)	27	37	48	94.5		
		$10^4\ k_1$ (s^{-1})	17.35	17.47	17.37	17.66		
2-Acetoxy-2-methylpropionic acid	240.3	P_0 (Torr)	19	29	45	59	81	
		$10^4\ k_1$ (s^{-1})	10.40	10.16	10.34	10.48	10.20	
Methyl 2-acetoxypropionate	410.4	P_0 (Torr)	36	68	87	92	125	
		$10^4\ k_1$ (s^{-1})	15.06	15.18	15.28	15.22	15.35	

Copyright © 2000 John Wiley & Sons, Ltd.

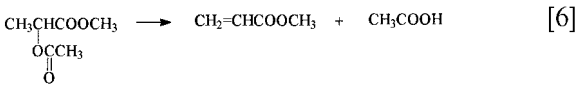
Table 6. Variation of rate coefficients with temperature[a]

Substrate	Parameter	Value						
2-Acetoxyacetic acid	Temperature (°C)	294.5	299.6	310.4	318.4	329.8	340.7	349.0
	$10^4\ k_1\ (s^{-1})$	2.01	2.93	5.59	9.75	17.55	30.48	49.87
Rate equation: $\log k_1\ (s^{-1}) = (12.03 \pm 0.28) - (170.8 \pm 3.2)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$; $r = 0.9998$								
2-Acetoxypropionic acid	Temperature (°C)	275.9	281.1	290.1	298.3	309.9	316.1	324.8
	$10^4\ k_1\ (s^{-1})$	3.70	5.48	10.08	17.30	35.24	51.30	84.95
Rate equation: $\log k_1\ (s^{-1}) = (13.16 \pm 0.24) - (174.2 \pm 2.6)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$; $r = 0.99991$								
2-Acetoxy-2-methylpropionic acid	Temperature (°C)	220.1	230.3	240.3	250.4	260.0	269.5	
	$10^4\ k_1\ (s^{-1})$	2.40	4.97	10.31	21.92	43.18	87.30	
Rate equation: $\log k_1\ (s^{-1}) = (13.40 \pm 0.72) - (160.9 \pm 5.0)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$; $r = 0.99958$								
Methyl 2-acetoxypropionate	Temperature (°C)	370.8	380.4	390.1	399.5	410.6	419.9	429.8
	$10^4\ k_1\ (s^{-1})$	1.81	3.31	5.53	9.40	15.06	26.23	45.32
Rate equation: $\log k_1\ (s^{-1}) = (12.63 \pm 0.35) - (201.7 \pm 4.4)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$; $r = 0.9996$								

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

Methyl 2-acetoxypropionate

The experimental stoichiometry for the gas-phase elimination of methyl 2-acetoxypropionate, as depicted in reaction (6), suggests $P_f = 2P_0$.



[6]

The average experimental value of P_f/P_0 at five different temperatures and 10 half-lives was 2.01 (Table 1). Confirmation of the stoichiometry of reaction (6), up to 65% reaction, showed that the percentage decompositon of the methyl acetoxypropionate calculated from pressure measurements was in good agreement with that obtained from the quantitative titration analyses of acetic acid with a 0.05 M NaOH solution (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 relative to that of the normal vessel, which is equal to 1 (Table 3).

The free radical inhibitor toluene has no effect on the rate of elimination (Table 4). No induction period was observed. The *k* values were reproducible with a relative standard deviation of 5% at any given temperature.

The rate coefficients were found to be invariant with the initial pressure (Table 5), and the first-order plots are satisfactorily linear up to 65% reaction. The variation of the rate coefficient with temperature is given in Table 6, where rate coefficients at the 90% confidence level obtained with a least-squares procedure are given.

The kinetic data obtained from the reactions leading to the decarbonylation process, i.e. loss of CO gas [reactions (3)–(5)] indicate an increase in the elimination rates from primary to tertiary carbons bearing the acetoxy substituent (Table 8). In view of the difficulties in determining the rate coefficients of 2-acetoxyacetic acid, up to 36% decomposition, the experimental mechanical errors led to the unexpected kinetic parameters shown in Table 8. However, the E_a values are always compensated by an increase or decrease in the frecuency factor *A*. In this respect, if we are assuming the transition states of the three acetoxy acids to be similar, then on scaling log *A*, to a reasonable value of 13.0 s^{-1}, the E_a value increases to 181.5 kJ mol^{-1}. Consequently, the sequence of rate increase from primary to tertiary acetoxy acids is reflected by the corresponding decrease in E_a (Table 8). In association with theoretical and experimental studies of the gas-phase elimination of 2-substituted carboxylic acids,[1–6] the mechanism may be assumed to proceed through a moderately semi-polar bicyclic (3.1.0) transition structure where an α-lactone is produced by the assistance of the acidic H of the COOH, followed by nucleophilic attack of the carbonyl oxygen [reaction (7)]. The unstable lactone intermediate decomposes into the corresponding carbonyl compound and carbon monoxide. This mechansim does not negate the proposed reaction (2).[7] However, calculations at the MP2 level with the 6–31G** basis set performed with the Gaussian

Table 7. Temperature dependence of rate coefficients for the formation of acetone and methacrylic acid

	$10^4\ k_1\ (s^{-1})$	
Temperature (°C)	Acetone	Methacrylic acid
220.1	1.45	0.95
230.3	3.42	1.55
240.3	6.80	3.51
250.4	14.20	7.72
260.0	28.21	14.97
269.5	56.21	31.06

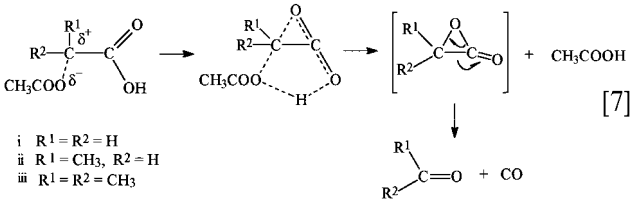
Copyright © 2000 John Wiley & Sons, Ltd.

Table 8. Kinetic parameters for α-lactone formation at 300 °C[a]

Substrate	$10^4\ k_1$ (s^{-1})	Relative rate	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})
2-Acetoxyacetic acid	2.88	1.0	170.8 ± 3.2	12.03 ± 0.28	−28.4	166.0	182.3
	(2.88)	(1.0)	(181.5)	(13.00)	(−2.53)	(176.7)	(178.2)
2-Acetoxypropionic acid	19.05	6.6	174.2 ± 2.6	13.16 ± 0.24	−6.8	169.4	173.3
2-Acetoxy-2-methylpropionic acid	371.54	129.0	163.0 ± 5.4	13.43 ± 0.77	−1.6	158.2	159.1

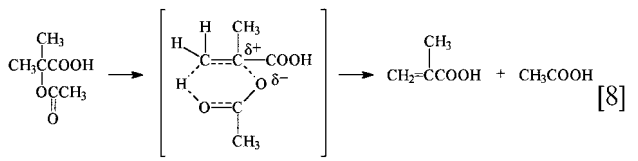
[a] Kinetic and thermodynamics parameters in parentheses have been scaled using log A = 13.0.

94 program for 2-substitued carboxylic acid pyrolyses[1–5] appear to support the mechanism described in reaction (7):



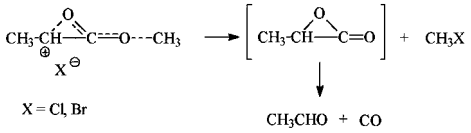
[7]

The mechanism for the parallel elimination pathway of 2-acetoxy-2-methylpropanoic acid may be associated with the gas-phase pyrolysis of carboxylic esters,[8,9] where the unimolecular elimination to acetic acid and methacrylic acid involves a semi-polar six-membered cyclic transition-state reaction. In this respect, the decomposition proceeds as described in reaction (8):

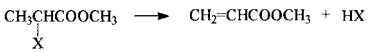


[8]

The pathway sequence in which the H of the COOH first assists the leaving $OOCCH_3$, followed by the nucleophilic participation of the oxygen carbonyl for lactone formation, may be associated with the results in the pyrolyses of 2-chloro- and 2-bromopropionic acid and their methyl esters.[10,11] Along this line, neighboring group participation of a three-membered structure in liquid media and in the gas phase has been reported.[12,13] Therefore, if the H of the COOH is replaced by a methyl group in the halo acid, the carbon–halogen bond polarization, in the direction of $C^{\partial+} \cdots X^{\partial-}$ may first be assisted anchimerically by the oxygen carbonyl. The leaving group, through intramolecular solvation or autosolvation, may take up the CH_3 to give CH_3X as described in reaction (9). However, the actual experimental results are shown in reaction (10). Therefore, the assistance of the H of the COOH to the leaving group is very important for elimination

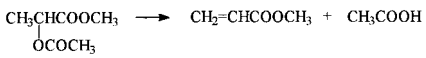


[9]



[10]

The explanation of the above suggestion is supported by the elimination kinetics of methyl 2-acetoxypropionate examined in the present work, where the idea of anchimeric assistance of the oxygen carbonyl in a three-membered structure does not give methyl acetate, propionaldehyde and CO gas; instead, methyl acrylate and acetic acid are actually formed [reaction (11)]:



[11]

As reported in previous work[14] and with the kinetic parameters given in Table 9, the order of leaving ability of substituents at the 2-position of carboxylic acids where their displacements are favoured by the acidic H of the COOH is as follows:

for LCH_2COOH: $CH_3COO > OH > C_6H_5O > CH_3CH_2O > CH_3O > Cl$

for $CH_3CHLCOOH$: $CH_3COO > C_6H_5O > Br > CH_3CH_2O > CH_3O > OH > Cl$

The difference in the two sequences is the leaving OH group in the LCH_2COOH series. The apparent fast dehydration rate of glycolic acid seems to be an exception in the bicyclic (3.1.0) transition structure type of mechanism. It is interesting that the rate difference in the elimination process between glycolic acid and lactic acid is small[15]. Therefore, the rate of decompostion of the

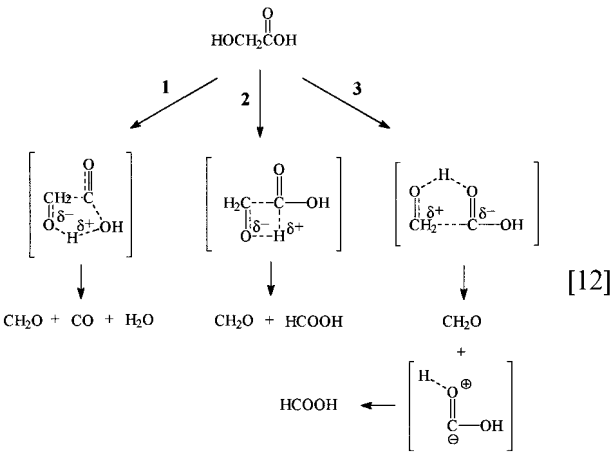
Copyright © 2000 John Wiley & Sons, Ltd.

Table 9. Comparative rates of the leaving group L in LCH_2COOH and $CH_3CHLCOOH$

	$10^4\ k_1$	(s^{-1})
L	LCH_2COOH (380°C)	$CH_3CHLCOOH$ (350°C)
Cl	1.20[14]	7.24[14]
Br	—	19.50[14]
OH	19.40[15]	8.19[15]
CH_3O	4.34[15]	15.64[5]
CH_3CH_2O	6.22[16]	20.48[5]
C_6H_5O	7.20[6]	60.76[6]
CH_3COO	234.4[a]	24547[a]

[a] This work.

former substrate appears to be faster than expected. Consequently, another process may be operating during pyrolysis. To rationalize this exception, an alternative mechanism may be considered, as described in reaction (12).



[12]

Path 1 suggests that the nucleophilicity of the hydroxyl alcohol is reduced by the electron-withdrawing effect of the COOH group. Because of this, the bond polarization of the OH group of the primary alcohol, in the sense $CO^{\delta-}\cdots H^{\delta+}$, may be rate determining. Therefore, this acidic hydrogen proceeds to dehydrate through a concerted fragmentation to give the obtained experimental products. However, if the acidic H assists the elimination process as in Path 2, HCOOH should be a primary product. The literature reports that HCOOH decomposes[17] from 435 to 530 °C, which is far above the pyrolysis temperature (340–390 °C) of glycolic acid. Finally, Path 3 requires C—C bond polarization as $CH_2(OH)^{\delta+}\cdots{}^{\delta-}COOH$ to be rate determining, which on decomposition may form an unstable zwitterionic intermediate. This species may isomerize to HCOOH. As mentioned above, formic acid is not isolated. Apparently, Path 1 may be a more probable mechanism than Paths 2 and 3.

The assumed reaction [(12), Path 1] differs from the mechanism derived from experimental examination[15] and theoretical calculations[2] related to glycolic acid transition state [reaction (1)] for elimination.[2,15]

EXPERIMENTAL

2-Acetoxyacetic acid. This acid was prepared by mixing and refluxing glycolic acid and acetyl chloride as reported.[18] The product was crystallized several times from benzene (m.p. 65–67 °C, lit.[18] 66–68 °C) with 99.0% purity as determined by GLC (10% SP 1200–1% H_3PO_4 on Chromosorb W AW, 80–100 mesh). The primary product acetic acid (Merck) was also analyzed quantitatively on the SP 1200 column.

2-Acetoxypropionic acid. This substrate was obtained when refluxing a mixture of lactic acid, acetic anhydride and HCl in glacial acetic acid as described.[19] The product was distilled several times (b.p. 157–158 °C 49 Torr; lit.[19] 85–100 °C 0.03 Torr) and the fraction of 98.1% purity as determined by GLC (10% SP 1200–1% H_3PO_4 on Chromosorb W AW, 80–100 mesh) was used. The products acetic acid (Merck) and acetaldehyde (Aldrich) were analyzed quantitatively on the SP 1200 column.

2-Acetoxyisobutyric acid. The synthesis of this substrate was carried out by mixing 2-hydroxyisobutyric acid and acetic anhydride as reported.[20] The acetoxyisobutyric acid was crystallized several times from CS_2 to 98.9% purity (GLC: 10% SP 1200–1% H_3PO_4 on Chromosorb W AW, 80–100 mesh) (m.p. 61–62 °C; lit.[20] 61 °C). The products acetone (Aldrich), methacrylic acid (Aldrich) and acetic acid (Merck) were analyzed quantitatively on the SP 1200 column.

Methyl 2-acetoxypropionate. Methyl lactate was acetylated with acetic acid–acetic anhydride with a few drops of HCl as described.[21] The reaction product was distilled several times to better than 99.0% purity (GLC: DB-5MS capillary column, 30 m × 0.25 mm i.d., 0.25 μm film thickness) (b.p. 120 °C 4 Torr). ^{1}H NMR ($CDCl_3$): δ 1.41–1.38 (d, 3H, CH_3), 2.04 (s, 3H, $COCH_3$), 3.66 (s, 3H, OCH_3), 4.98–5.00 (m, 1H, CH). MS: *m/z* 146 (M^+), 103 [$OCH(CH_3)COOCH_3^+$], 87 [$CH_3COOCH(CH_3)$], 59 (CH_3COO^+).

Further quantitative analyses and identifications of substrates and products were carried out by GC–MS (Saturn 2000, Varian) with a DB-5MS capillary column, 30 m × 0.250 mm i.d., 0.25 μm film thickness.

Kinetic procedure. The kinetic experiments were carried out in a static reaction apparatus[22,23] with several electronic and electrical modifications. The reaction vessel was seasoned with the product decomposition of allyl bromide and in the presence of the free radical chain suppressor cyclohexene and/or toluene. The temperature

Copyright © 2000 John Wiley & Sons, Ltd.

was controlled by a Shinko DC-PS 25RT resistance thermometer controller and an Omega Model SSR280 AC45 solid-state relay maintained within ±0.2 °C and measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was found along the reaction vessel. The solid substrates acetoxyacetic acid and acetoxyisobutyric acid disolved in dioxane and acetoxylactic acid and methyl 2-acetoxypropionate were injected directly into the reaction vessel through a silicone-rubber septum.

Acknowledgements

We are grateful to the Consejo Nacional de Investigaciones Cientificas y Tecnológicas (CONICIT) of Venezuela for financial support, project No. S1-97000005.

REFERENCES

1. Safont VS, Moliner V, Andres J, Domingo LR. *J. Phys. Chem.* 1997; **101**: 1859.
2. Domingo LR, Andres J, Moliner V, Safont VS. *J. Am. Chem. Soc.* 1997; **119**: 6415.
3. Domingo LR, Pitcher MT, Andres J, Safont VS, Chuchani G. *Chem. Phys. Lett.* 1997; **274**: 422.
4. Domingo LR, Pitcher MT, Safont VS, Andres J, Chuchani G. *J. Phys. Chem.* 1999; **103**: 3935.
5. Rotinov A, Chuchani G, Andres J, Domingo LR, Safont VS. *Chem. Phys.* 1999; **246**: 1.
6. Chuchani G, Domínguez RM, Rotinov A, Martin I. *J. Phys. Org. Chem.* 1999; **12**: 612.
7. Galoci J, Procházka M, Klitonová E. *Collect. Czech. Chem. Commun.* 1983; **48**: 1729.
8. Taylor R. In *The Chemistry of Functional Groups Supplement B. Acid Derivatives. Pyrolysis of Acids and Their Derivatives* Patai S (ed). Wiley: London, 1979; Chapt. 15, 859.
9. Hoolbrook KA. In *The Chemistry of Functional Groups. Supplement B. The Chemistry of Acid Derivatives*. Vol. 2. Vapour and Gas Phase Reactions of Carboxylic Acids and Their Derivatives, Patai S, (ed). Wiley: Chichester, 1992: Chapt. 12, 703.
10. Chuchani G, Rotinov A. *Int. J. Chem. Kinet.* 1989; **21**: 367.
11. Chuchani G, Domínguez RM, Rotinov A. *Int. J. Chem. Kinet.* 1991; **23**: 779.
12. Chuchani G. In *The Chemistry of Halides, Pseudo-Halides and Azides Supplement D2. Pyrolysis of Organic Halides*, Patai S, Rappoport Z. (eds). Wiley: Chichester, 1995: Chapt. 19, 1097.
13. Capon B, McManus SP. *Neighboring Group Participation*, vol. 1. Plenum Press: New York, 1976.
14. Chuchani G, Rotinov A, Domínguez RM, Martín I. *J. Phys. Org. Chem.* 1996; **9**: 348 and references cited therein.
15. Chuchani G, Martín I, Rotinov A, Domínguez RM. *J. Phys. Org. Chem.* 1993; **6**: 54.
16. Chuchani G, Rotinov A, Domínguez RM. *J. Phys. Org. Chem.* 1996; **9**: 787.
17. Hinshelwood C. *Proc. R. Soc. London, Ser. A* 1960; **255**: 444.
18. Anchutz R, Beltram W. *Chem. Ber.* 1903; **36**: 466.
19. Filachione EM, Fisher CH. US Patent 2 399 595, 1946; *Chem. Abstr.* 1946; **40**: 4394[4].
20. Anchutz R, Motschmann O. *Liebigs Ann.* 1912; **108**: 292.
21. Vogel A. *Practical Organic Chemistry*, (3rd edn), Longman: London, 1956; 367.
22. Maccoll A. *J. Chem. Soc* 1955; 965.
23. Swinbourne ES. *Aust. J. Chem.* 1958; **11**: 314.

Copyright © 2000 John Wiley & Sons, Ltd.