ELIMINATION KINETICS AND MECHANISMS FOR SEVERAL 2-ALKOXYACETIC ACIDS IN THE GAS PHASE

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The kinetics of the gas-phase elimination of three 2-alkoxyacetic acids were investigated in a static system, seasoned with allyl bromide, and in the presence of the free chain radical inhibitor cyclohexene. The working temperature and pressure range were 350·4–410·8 °C and 57–261·5 Torr, respectively. The reactions proved to be homogeneous and unimolecular and to follow a first-order rate law. The temperature dependence of the rate coefficients is given by the following equations: for 2-methoxyacetic acid, $\log k_1$ (s^{-1}) = $(12\cdot10\pm0\cdot22) - (193\cdot3\pm2\cdot8)$ kJ mol^{-1} $(2\cdot303RT)^{-1}$; for 2-ethoxyacetic acid, $\log k_1$ (s^{-1}) = $(12\cdot76\pm0\cdot29) - (199\cdot6\pm3\cdot7)$ kJ mol^{-1} $(2\cdot303RT)^{-1}$; and for 2-isopropoxyacetic acid, $\log k_1$ (s^{-1}) = $(12\cdot40\pm0\cdot32) - (193\cdot7\pm3\cdot9)$ kJ mol^{-1} $(2\cdot303RT)^{-1}$. The alkyl group R in $ROCH_2COOH$ does not seems to exert a significant effect on the rates. It is postulated that the predominant mechanism for the decomposition of the alkoxy acids involves a five-membered cyclic transition state, where the elimination of the RO substituents is assisted by the acidic proton of the COOH group.

INTRODUCTION

The gas-phase pyrolytic elimination reaction of linear dialkyl ethers have been found to proceed by a radical chain process.[1-11] However, unsymmetrical *tert*-butyl ethers such as *tert*-butyl methyl[12,13], *tert*-butyl ethyl[14], *tert*-butyl isopropyl[15], *tert*-butyl cyanomethyl[16], *tert*-butyl *p*-methoxyphenyl[17], *tert*-butyl *p*-aminophenyl[17] and *tert*-butyl *p*-nitrophenyl[17] undergo unimolecular elimination via a four-membered cyclic transition state to yield isobutene and the corresponding alcohol or phenol. The pyrolysis of ethers parallels that of alcohols, whereby primary and secondary alcohols decompose by radical chain reactions, whereas tertiary alcohols undergo unimolecular elimination of water[18] to give the corresponding alkenes.

Since the OR group of ethers is a slightly better leaving group than the OH function of alcohols, it is plausible by analogy with the postulate but forward to explain the kinetics of elimination of primary, secondary and tertiary 2-hydroxycarboxylic acids[19,20] [equation (1)], whereby the proposed involvement of an α-lactone or a similar intermediate is speculative. In other words, the elimination of the alkoxy substituents at the 2-position of carboxylic acids may be assisted by the acidic hydrogen of the COOH groups. Consequently, the purpose of this investigation was to examine the kinetics and mechanisms of several 2-alkoxyacetic acids in the gas phase, viz. methoxy-, ethoxy- and isopropoxyacetic acid.

(i) R, R' = H
(ii) R = H, R' = Alkyl
(iii) R = R' = Alkyl

CO + RR'C=O

(1)

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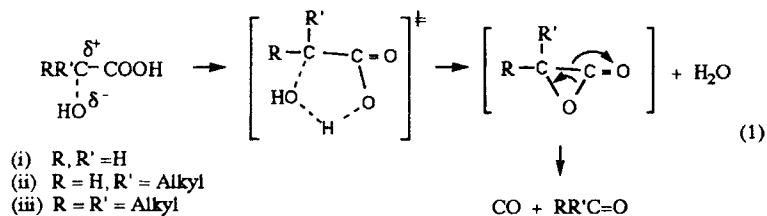
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RESULTS AND DISCUSSION

2-Methoxyacetic acid

The gas-phase pyrolysis of this carboxylic acid proceeds as follows:

$$CH_3OCH_2COOH \longrightarrow CH_3OH + CH_2O + CO \qquad (2)$$

The stoichiometry of the reaction requires $P_f/P_0 = 3$, 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 2·94 (Table 1). Additional verification of the stoichiometry of equation (2) was made by comparing, up to 50% decomposition, the pressure measurements with the results of quantitative gas chromatographic analyses of the unreacted substrate (Table 2).

The homogeneity of the reaction was investigated by using a packed reaction vessel with a surface-to-volume ratio six times greater than that of the unpacked reaction vessel (Table 3). The rate coefficients were the same in packed and unpacked vessels seasoned with allyl bromide. However, packed and unpacked clean Pyrex vessels had a marked effect on the rates.

The effect of different proportions of the free radical inhibitor cyclohexene in this reaction is shown in Table 4. The results indicate that cyclohexene does not affect the rates of elimination of methoxyacetic acid. However, in order to impede any possible radical chain process of this substrate, the kinetics were always determined in the presence of at least a twofold excess of cyclohexene inhibitor. No induction period was observed. The rate coefficients were reproducible with a relative standard deviation (RSD) of less than 5% at any given temperature.

The rate coefficient of methoxyacetic acid, calculated from $k_1 = (2·303/t)\log[2P_0/(3P_0 - P_t)]$ was found to be independent of the initial pressure (Table 5), and the first-order plots are satisfactorily linear up to 50% reaction. The temperature dependence of the rate coefficients, in seasoned vessels and in the presence of the inhibitor cyclohexene, is shown in Table 6. The data were fitted to the Arrhenius equation, where rate coefficients at the 90% confidence level obtained from a least-squares procedure are given.

In association with the mechanism described for 2-hydroxycarboxylic acids[19,20] [equation (1)], polarization of the C—OCH$_3$ bond, in the direction of $C^{\delta+} \cdots {}^{\delta-}OCH_3$, is rate determining. In this sense, the acidic hydrogen of the COOH group assists the leaving of the methoxy substituent through an intramolecular displacement reaction. Consequently, the process is postulated to take place via a semi-polar five-membered cyclic transition state as shown in equation (3).

2-Ethoxyacetic acid

According to the pyrolysis products of 2-ethoxyacetic acid described in equation (4), a threefold increase in

(3)
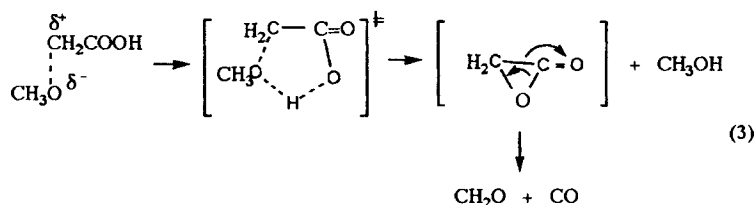
Table 1. Ratio of final to initial pressure[a,b]

Compound	Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0	Average
Methoxyacetic acid	379·9	139·0	395·5	2·85	2·94
	388·9	105·0	302·5	2·88	
	400·0	93·5	287·5	3·07	
	410·3	81·0	240·0	2·96	
Ethoxyacetic acid	379·9	128·0	387·0	3·02	3·02
	390·2	129·5	376·5	2·91	
	400·7	121·0	362·0	2·99	
	410·8	127·0	400·0	3·15	
Isopropoxyacetic acid	349·6	123·5	356·9	2·89	2·84
	360·0	101·5	289·3	2·85	
	370·1	121·0	340·5	2·82	
	379·7	112·0	312·5	2·79	

[a] P_0 = initial pressure; P_f = final pressure.
[b] Seasoned vessel with allyl bromide and in the presence of at least twice the amount of the free radical inhibitor cyclohexene.
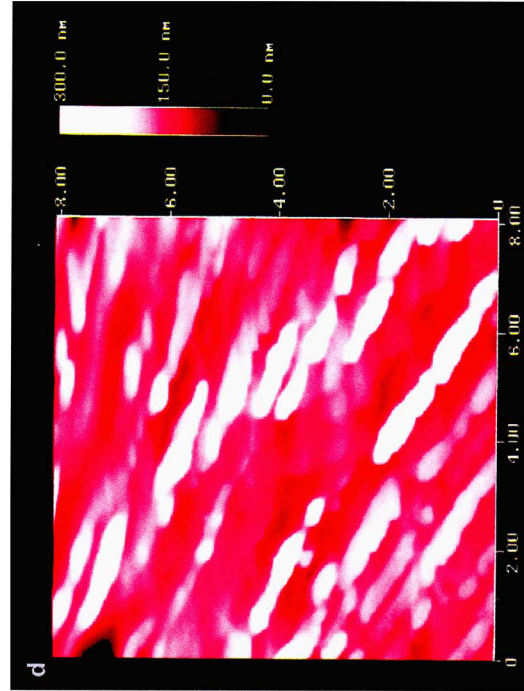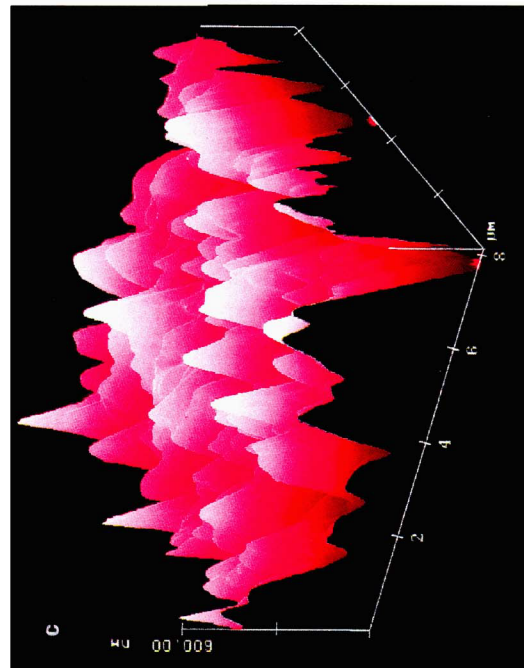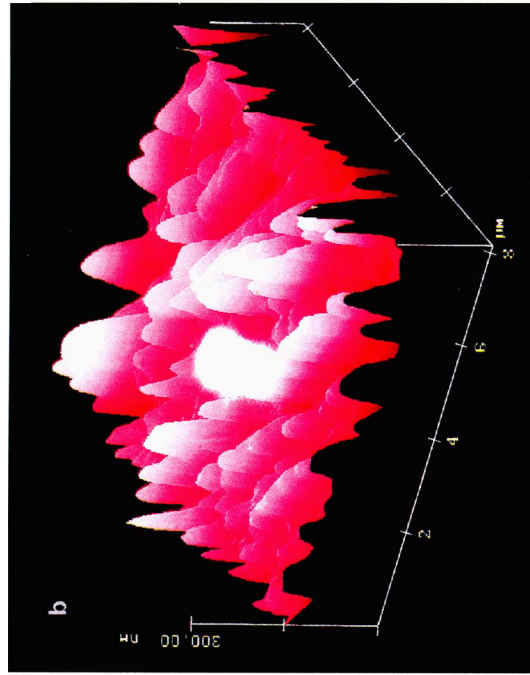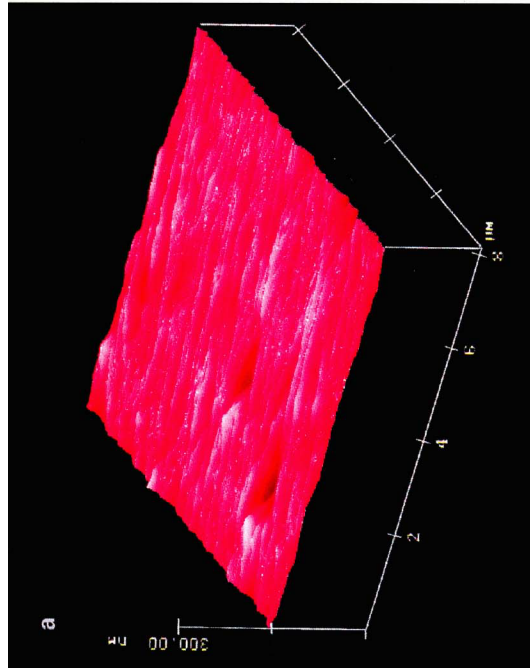
Plate 1. AFM surfaces of (*R,R*)-**2** on (001); (a) fresh; (b, d) after 3 h under a 0.15 mg dendritic polycrystal of (*S*)-**1** showing unidirectional floes; (c) after 3 days under 0.15 mg of (*S*)-**1** (when all non-imbibed material had sublimed off) showing random floes
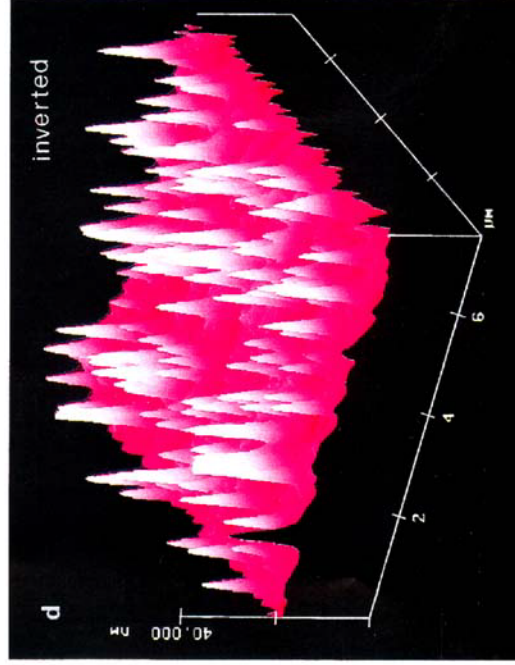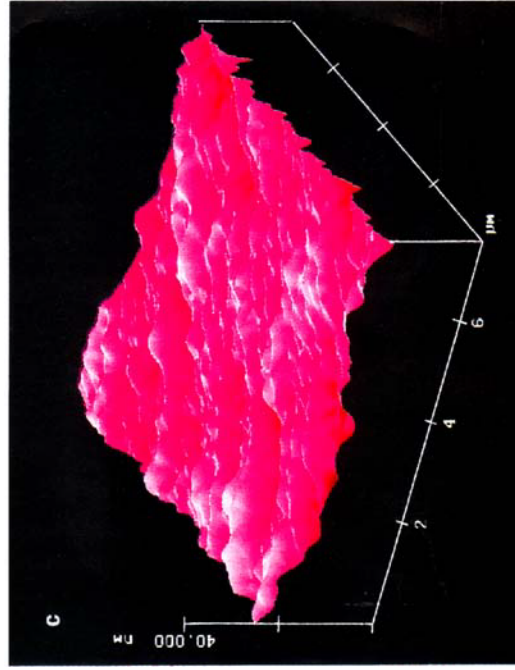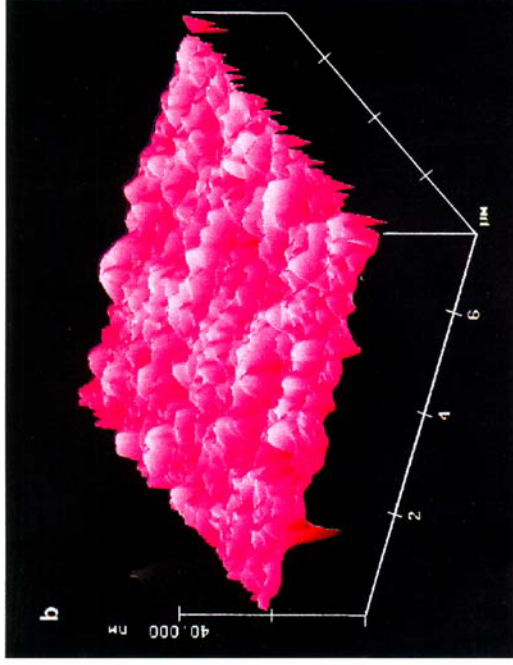
Plate 2. AFM surfaces of (*R,R*)-**3** on (010); (a) fresh, R^{ms} = 2.20 nm; (b, d) after 2 h under a 0.15 mg dendritic polycrystal of (*S*)-**1** showing changes of the surface corrugation and random craters all over the surface, the craters in (d) being imaged invertedly for a better view (upside down inversion of the image makes them appear in their inverse form as "volcanoes"); (c) after 3 days under 0.15 mg of (*S*)-1, when al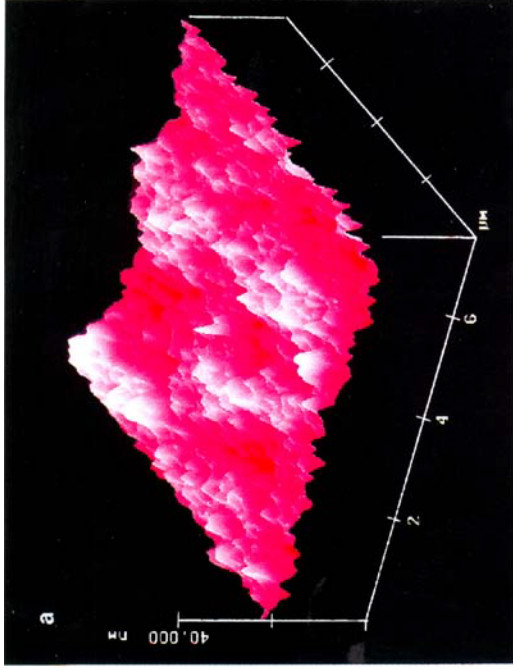l non-imbibed guest material had sublimed off, showing complete fill-up of the craters and another change of surface corrugation (R^{ms} = 2.10 nm). The crystal orientations and scan angles were the same in (a) – (c)

Table 2. Stoichiometry of the pyrolysis reactions[a]

Compound	Parameters	Values					
Methoxyacetic acid at 388·9 °C	Time (min)	2	4	8	10	14	18
	Reaction (%) (pressure)	8·3	16·1	28·7	36·4	44·4	51·9
	Substrate (%) (gas chromatography)	8·4	15·2	27·6	38·4	43·9	52·5
	Methanol (%) (gas chromatography)	2·7	5·0	8·9	12·2	14·3	17·1
Ethoxyacetic acid at 390·2 °C	Time (min)	5	8	10	15	20	
	Reaction (%) (pressure)	29·5	41·8	48·4	52·8	67·4	
	Substrate (%) (gas chromatography)	28·1	40·3	46·4	50·8	65·9	
	Ethanol (%) (gas chromatography)	9·1	12·9	15·2	16·6	21·4	
Isopropoxyacetic acid at 380·4 °C	Time (min)	5	8	10	12	15	
	Substrate (%) (gas chromatography)	26·1	32·7	44·6	54·0	61·2	
	Propan-2-ol (%) (gas chromatography)	17·3	25·0	32·3	38·4	43·4	
	Propene (%) (gas chromatography)	7·1	10·4	13·2	15·7	17·8	

[a] Vessel seasoned with allyl bromide, and in the presence of a twofold amount of cyclohexene.

Table 3. Homogeneity of the reactions

Compound	S/V (cm^{-1})[a]	$10^4 k_1$ (s^{-1})[b]	$10^4 k_1$ (s^{-1})[c]
Methoxyacetic acid at 380·3 °C	1	8·66[d]	4·43
	6	8·63[e]	4·36
Ethoxyacetic acid at 390·2 °C	1	11·94	11·10
	6	19·11	11·07
Isopropoxyacetic acid at 390·8 °C	1	14·89	16·09
	6	15·12	15·83

[a] S = surface area; V = volume.
[b] Clean Pyrex vessel.
[c] Vessel seasoned with allyl bromide.
[d] k value up to 35% reaction; it then decreases rapidly.
[e] k value up to 25% reaction; it then decreases rapidly.

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

Compound	P_0 (Torr)	P_i (Torr)	P_i/P_0	$10^4 k_1$ (s^{-1})
Methoxyacetic acid at 380·3 °C	95	—	—	4·60
	134	37	0·3	4·69
	136	167·5	1·2	4·67
	101·5	202	2·0	4·50
	78	200·5	2·6	4·37
	57	299·5	5·3	4·61
Ethoxyacetic acid at 390·2 °C	112	—	—	12·24
	183	81	0·4	12·40
	107·5	162	1·5	11·30
	74·5	176	2·4	11·67
	64·5	261·5	4·4	11·18
Isopropoxyacetic acid at 390·8 °C	100	—	—	18·39
	124	144	1·2	16·18
	91	198	2·2	15·82
	94	273	2·9	16·22
	99	364	3·7	16·09

[a] P_0 = pressure of the substrate; P_i = pressure of cyclohexene inhibitor. Vessel seasoned with allyl bromide.

Table 5. Invariability of rate coefficients with initial pressure

Methoxyacetic acid at 380·3 °C						
P_0 (Torr)	57	78	93	101·5	136	151
$10^4 k_1$ (s^{-1})	4·61	4·37	4·71	4·50	4·67	4·50
Ethoxyacetic acid at 390·2 °C						
P_0 (Torr)	64·5	107·5	183	212		
$10^4 k_1$ (s^{-1})	11·18	11·30	11·23	11·69		
Isopropoxyacetic acid at 390·8 °C						
P_0 (Torr)	70	91	124	261·5		
$10^4 k_1$ (s^{-1})	15·92	16·23	16·18	16·11		

the final pressure, P_f, is required, i.e. $P_f = 3P_0$. The average experimental P_f/P_0 values at four different temperatures and after 10 half-lives is 3·02 (Table 1). Further confirmation of the stoichiometry of equation (4), up to 65% decomposition, was obtained by comparing the pressure measurements with the quantitative gas chromatographic analyses of the amount of unreacted ethoxy acid substrate (Table 2).

$$CH_3CH_2OCH_2COOH \longrightarrow CH_3CH_2OH + CH_2O + CO \qquad (4)$$

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

Methoxyacetic acid

Temperature (°C)	360·1	370·8	380·3	388·9	400·0	410·3	
$10^4 k_1$ (s^{-1})	1·45	2·59	4·43	6·93	12·48	21·50	

Rate equation: $\log k_1(\mathrm{s}^{-1}) = (12\cdot10\pm0\cdot22) - (193\cdot3\pm2\cdot8)\ \mathrm{kJ\ mol}^{-1}\ (2\cdot303RT)^{-1}$

Ethoxyacetic acid

Temperature (°C)	350·8	359·7	370·0	379·9	390·2	400·7	410·8
$10^4 k_1$ (s^{-1})	1·11	1·94	3·54	6·23	11·10	18·34	33·79

Rate equation: $\log k_1(\mathrm{s}^{-1}) = (12\cdot76\pm0\cdot29) - (199\cdot6\pm3\cdot7)\ \mathrm{kJ\ mol}^{-1}\ (2\cdot303RT)^{-1}$

Isopropoxyacetic acid

Temperature (°C)	350·4	360·4	370·4	380·4	390·8	400·0	
$10^4 k_1$ (s^{-1})	1·68	3·04	5·29	8·95	16·09	26·86	

Rate equation: $\log k_1(\mathrm{s}^{-1}) = (12\cdot40\pm0\cdot32) - (193\cdot7\pm3\cdot9)\ \mathrm{kJ\ mol}^{-1}\ (2\cdot303RT)^{-1}$

[a] Seasoned vessel and in the presence of at least twice the amount of cyclohexene.

To examine the effect of the surface on the rate of elimination, several runs in the presence of at least twofold amount of cyclohexene inhibitor were carried out in a vessel with a surface-to-volume ratio six times greater than that of the normal vessel. The rates of elimination of ethoxyacetic acid were unaffected in a seasoned and clean unpacked vessel, but a significant heterogeneous effect was found in the clean packed Pyrex vessel (Table 3).

The effect of the addition of different proportions of cyclohexene suppressor is shown in Table 4. The pyrolysis experiments of the ethoxyacetic acid were always carried out in the presence of at least twice the amount of cyclohexene in order to prevent any possible radical chain reactions. No induction period was observed.
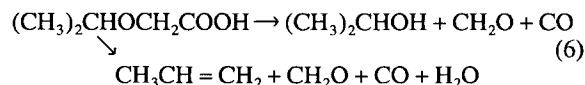
The first-order rate coefficients of this substrate calculated from $k_1 = (2\cdot303/t)\log[2P_0/(3P_0 - P_t)]$ were independent of the initial pressure (Table 5). A plot of $\log(3P_0 - P_t)$ vs time t gave a good straight line up to 60% decomposition. The rate coefficients are reproducible with an RSD not greater than 5% at a given temperature. The variation of the first-order rate coefficient with temperature is shown in Table 6, which gives rate coefficients at the 90% confidence level obtained from a least-squares procedure.

According to these results and by analogy with equation (3), the gas-phase elimination of ethoxyacetic acid may again be explained in terms of a semi-polar five centered cyclic transition state, where the acidic proton of the COOH group assists, through an intramolecular displacement, the leaving of the CH_3CH_2O group [equation (5)].
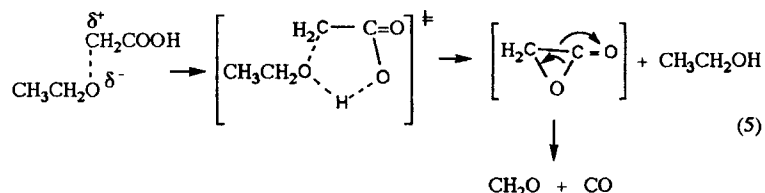
2-Isopropoxyacetic acid

The pyrolysis products of isopropoxyacetic acid shown in equation (6) make it difficult to assess the stoichiometry from experimental pressure increases, since the theoretical P_f/P_0 ratio is >3. The average experimental P_f/P_0 values at four different temperatures and 10 half-lives given in Table 1. The observed $P_f/P_0 < 3$ of the overall elimination was found to be due to a small degree of polymerization of the formaldehyde product. Verification of the stoichiometry [equation (6)] was possible by comparing, up to 60% reaction, the quantitative gas chromatographic analyses of the amount of unreacted substrate with the sum of the amounts of the products, propan-2-ol and propene (Table 2).

$$(CH_3)_2CHOCH_2COOH \rightarrow (CH_3)_2CHOH + CH_2O + CO$$
$$\searrow \qquad\qquad\qquad\qquad\qquad (6)$$
$$CH_3CH = CH_2 + CH_2O + CO + H_2O$$

The homogeneity of this pyrolytic elimination was examined, in the presence of the radical chain inhibitor cyclohexene, in a vessel with a surface-to-volume ratio six times greater than that of the normal vessel. The packed and unpacked clean Pyrex vessels showed a small effect on the rates. However, when the packed and unpacked vessels were seasoned with allyl bromide, no effect on the rate coefficients was observed (Table 3). Isopropoxyacetic acid was always pyrolysed in seasoned vessels and in the presence of at least a twofold excess of the free chain radical suppressor cyclohexene

$$(5)$$

(Table 4). No induction period was observed and the rates were reproducible with an RSD not greater an 5% at any given temperature.

The rate coefficients determined in seasoned vessels and in the presence of cyclohexene were found to be independent of the initial pressure of the substrate, and the first-order plots are satisfactorily linear to about 60% reaction with an RSD less than 5% at any given temperature (Table 5). The variation of the first-order rate coefficients with temperature is given in Table 6, where rate coefficients at the 90% confidence level obtained with a least-squares method are given.

The partial rates for the formation of the primary products, as described in equation (6) were determined up to 60% decomposition of the isopropoxyacetic acid by the quantitative gas chromatographic analyses of propan-2-ol and propene. The variation of the rate coefficients for the formation of these products with temperature (Table 7) gives, by the least-squares procedure and with 90% confidence limits, the following Arrhenius equations: for propan-2-ol formation

$$\log k_1(s^{-1}) = (12 \cdot 25 \pm 0 \cdot 36) - (193 \cdot 0 \pm 4 \cdot 4) \text{ kJ mol}^{-1} (2 \cdot 303RT)^{-1}$$

and for propene formation,

$$\log k_1(s^{-1}) = (12 \cdot 05 \pm 0 \cdot 36) - (195 \cdot 5 \pm 4 \cdot 5) \text{ kJ mol}^{-1} (2 \cdot 303RT)^{-1}$$

The nature of the products together with the kinetic parameters led to the consideration of two different parallel mechanisms [equation (7)]

Path 1 is analogous to the reactions described for methoxy- and ethoxyacetic acid, where the bond polarization $-O^{\delta-} \cdots {}^{\delta+}CH_2COOH$ is rate determining. The acidic proton of the COOH group is again thought to aid the intramolecular displacement to yield propan-2-ol and the postulated α-lactone. The latter decomposes to formaldehyde and CO. With regard to the mechanism of path 2, this may be rationalized in terms of isopropoxyacetic acid bond polarization. The isopropyl–oxygen bond, as a secondary ether, may be able to polarize as $(CH_3)_2CH^{\delta+} \cdots O^{\delta-}$-rather than $-O^{\delta-} \cdots {}^{\delta+}CH_2COOH$ of path 1. Since the β-hydrogen of the isopropyl group has been found to some extent assists the decomposition of tert-butyl isopropyl ether[15] to yield propene and tert-butanol as minor products (20%) together with isobutene and propan-2-ol, it seems reasonable to believe that propene and glycolic

Table 7. Temperature dependence of rate coefficient for formation of products from isopropoxyacetic acid pyrolysis

Temperature (°C)	$10^4 k_1$ (s⁻¹)	
	Propan-2-ol	Propene
350·4	1·20	0·48
360·4	2·20	0·84
370·4	3·82	1·47
380·4	6·35	2·60
390·8	11·52	4·57
400·0	19·10	7·76

(7)
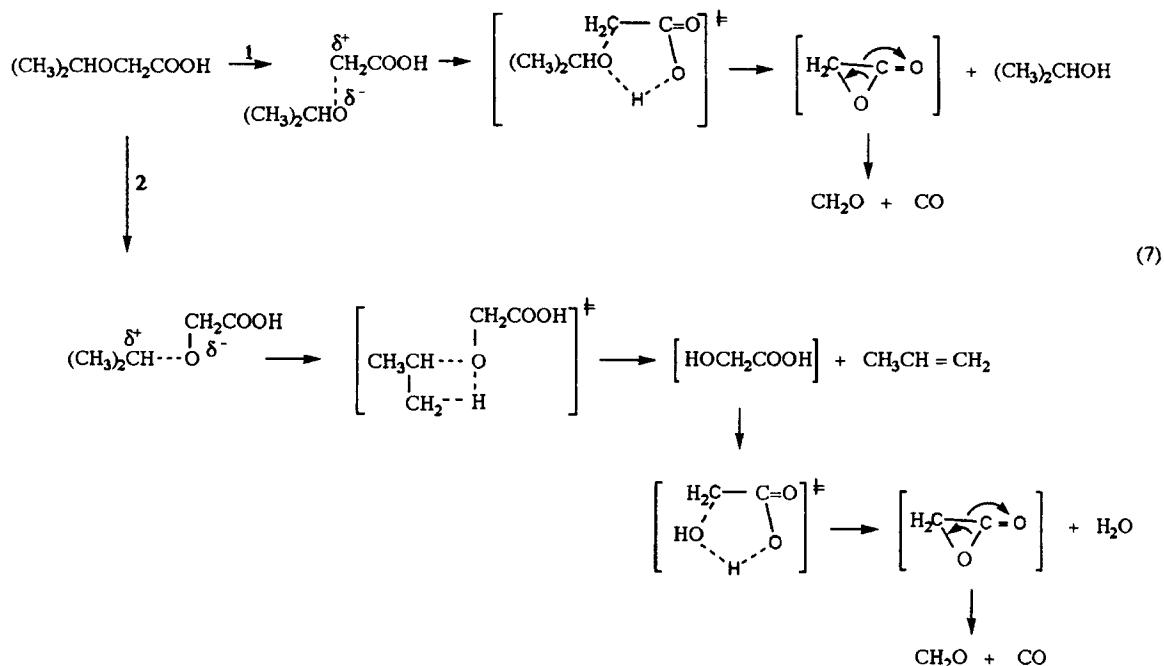
Table 8. Kinetic parameters for the postulated α-lactone formation at 380 °C

Substrate	$10^4 k_1$ (s^{-1})	Relative rate	E_a(kJ mol^{-1})	Log'A (s^{-1})	$\Delta S\ddagger$ (J mol^{-1} K^{-1})	$\Delta H\ddagger$ (kJ mol^{-1})
Methoxyacetic acid	4·37	1·0	193·3 ± 3·8	12·10 ± 0·22	−28·2	211·7
Ethoxyacetic acid	6·17	1·4	199·6 ± 3·7	12·76 ± 0·29	−15·5	209·8
Isopropoxyacetic acid	6·46[a]	1·5	193·0 ± 4·4	12·25 ± 0·36	−25·3	209·5

[a] Value of lactone formation from path 1 of equation (7).

acid may be produced via path 2. The working temperature for isopropoxyacetic acid pyrolysis is slightly higher than in the gas-phase elimination of glycolic acid.[19] Consequently, the latter acid, under the reaction conditions, must further decompose into formaldehyde, water and CO.

It appears from the Arrhenius parameters shown in Table 8 that the alkyl group R in ROCH$_2$COOH does not exert a significant effect on the rate. Isopropoxyacetic acid gives a similar rate to ethoxyacetic acid. This may well be because some amount of the former acid undergoes a parallel decomposition described in Path 2 of equation (7). This lack of a marked effect of R groups on rates is not surprising, since their influence in other types of organic molecules, such as alkyl halides[21] and acetates,[22] also showed a very small or nearly similar effect on gas elimination rates. Otherwise, the parameters log A and $\Delta S\ddagger$ are consistent with the assumed five-membered cyclic transition state unimolecular elimination mechanism.

EXPERIMENTAL

2-Methoxyacetic acid (Aldrich) of 98·6% purity and 2-ethoxyacetic acid (Aldrich) of 99·8% purity as determined by GLC (10% SP 1200 – 1% H$_3$PO$_4$ on Chromosorb W AW, 80–100 mesh) were used. The primary products methanol (Prolab) and ethanol (Aldrich) were quantitatively analysed on the same column (SP 1200).

2-Isopropoxyacetic acid was prepared by adding 2-bromoacetic acid to a mixture of sodium isopropoxide in propan-2-ol as reported.[23] The product was distilled several times (b.p. 100 °C at 1 Torr) and the fraction with 98·6% purity as determined by GLC (10% SP 1200 – 1% H$_3$PO$_4$ on Chromosorb W AW, 80–100 mesh) was used. The primary product propan-2-ol (Merck) was quantitatively analysed on the SP 1200 column, and the gas propene (Matheson) in a column of Porapak Q, 80–100 mesh. Formaldehyde could not be analysed quantitatively, because some amount of this compound polymerizes, thus giving erroneous values.

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

Kinetic experiments were carried out in a static system with the reaction vessels seasoned at all times

with allyl bromide and in the presence of the free radical inhibitor cyclohexene. The rate coefficients were determined manometrically and/or by quantitative gas chromatographic analyses of the substate and products. The temperature was controlled by a Shinko DIC-PS resistance thermometer controller and maintained within ±0·2 °C when measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was found in the reaction vessel. The substrates were injected direly into the reaction vessel with a syringe through a silicone-rubber septum.

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