JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 8, 133–138 (1995)

SEVERAL MECHANISMS IN THE ELIMINATION KINETICS OF ω-CHLOROCARBOXYLIC ACIDS IN THE GAS PHASE

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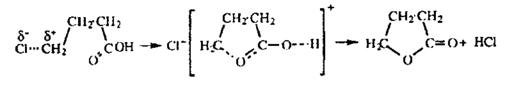
The kinetics of the gas-phase pyrolysis of ω-chlorocarboxylic acids were examined in a seasoned static reaction vessel and in the presence of at least twice the amount of the free radical inhibitor cyclohexene or toluene. In conformity with the available experimental data on rate determination, these reactions proved to be unimolecular and obeyed a first-order rate law. The presence of the primary chlorine leaving group in $Cl(CH_2)_nCOOH$ ($n = 1$–4) showed a change in mechanism from intramolecular displacement of the Cl leaving group by the acidic hydrogen of the COOH to anchimeric assistance of the carbonyl COOH to the C—Cl bond polarization in the transition state. This mechanistic consideration is nearly the same for the series of 2-, 3-, and 4-chlorobutyric acids. The chlorine atom at the 2-position of acetic, propionic and butyric acids is dehydrochlorinated through a prevailing reaction path involving a polar five-membered cyclic transition state.

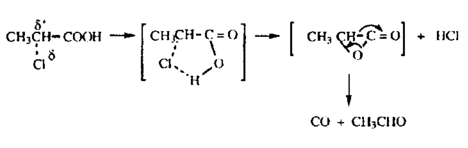
INTRODUCTION

An interesting elimination–cyclization process of an organic molecule in the gas phase occurs in the homogeneous, unimolecular pyrolysis of 4-chlorobutyric acid.[1] This reaction was described in terms of an intimate ion pair-type of mechanism through neighbouring group participation of the COOH group and by intramolecular solvation or autosolvation of the chloride ion [equation (1)].



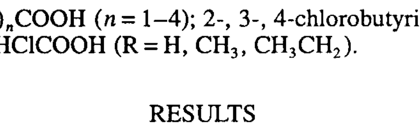
(1)

When the chlorine leaving group is adjacent to the COOH group, such as in 2-chloropropionic acid, a different mechanism takes place.[2] The hydrogen atom of the COOH group was considered to assist readily the leaving chloride ion (intramolecular displacement) in the transition state in terms of a polar five-membered cyclic transition state as described in equation (2).



(2)

It is interesting to note that prior to the above-mentioned studies, the pyrolysis kinetics of ethyl haloacetates[3–5] ($XCH_2COOCH_2CH_3$, X = F, Cl, Br) showed that the corresponding halocarboxylic acid product decomposed further to formaldehyde and hydrogen halide and little towards the formation of CH_3X and CO_2 [equation (3)].



(3)

In view of the different reaction paths described above,[1–5] in this study we examined the mechanisms of pyrolyses occurring when the chlorine leaving group is at different positions along the carbon chain of aliphatic carboxylic acids. The substrates examined were $Cl(CH_2)_nCOOH$ ($n = 1$–4); 2-, 3-, 4-chlorobutyric acids and $RCHClCOOH$ ($R = H, CH_3, CH_3CH_2$).

RESULTS

Chloroacetic acid

The pyrolytic elimination of chloroacetic acid, in the presence of at least twice the amount of the free-radical suppressor cyclohexene, obeys a first-order rate law to about 40% decomposition. The reaction products are described in equation (4).

$$ClCH_2COOH \rightarrow CH_2O + CO + HCl \qquad (4)$$

CCC 0894–3230/95/030133–06
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Received 10 May 1994
Revised 7 October 1994

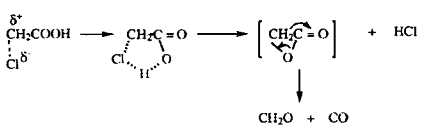
Table 1. Temperature dependence of the rate coefficient for the decomposition of $ClCH_2COOH$

Temperature (°C)	389·1	401·0	409·6	420·0
10^4k_1 (s^{-1})	2·10	3·45	5·39	9·54

The kinetic data are given in Table 1 and the resulting Arrhenius parameters are $\log A = 11{\cdot}21\ s^{-1}$ and $E_a = 189{\cdot}2$ kJ mol^{-1}. These values are within the range expected for unimolecular five-membered cyclic transition-state mechanism.

The rate coefficients are calculated from the pressure increase, which beyond 40% reaction tends to decrease owing to polymerization of the product formaldehyde. The ratio of the final pressure, P_f, to the initial pressure, P_o, with the stoichiometry of equation (4) should be 3. However, the experimental results at ten half-lives of P_f/P_o is 2·52. This result seems to derive, as described above, from the observation that in formaldehyde, under the same experimental conditions of pyrolysis, that is, in the presence of HCl gas and cyclohexene inhibitor, the pressure decreases owing to polymerization.

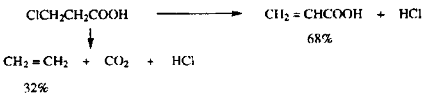
Apparently, and in association with the mechanism described for α-halopropionic acid pyrolyses,[1,6] the acidic hydrogen of the COOH group assists the leaving Cl substituent and the process undergoes a polar five-centered transition state as shown in equation (5).



(5)

3-Chloropropionic acid

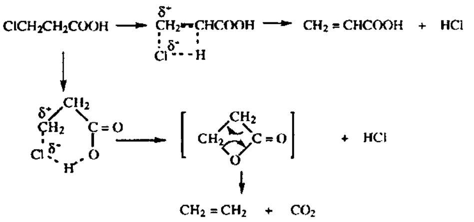
This substrate was found to be difficult for complete kinetic work. At 340·5 °C it showed a first-order parallel elimination [equation (6)] with an approximately overall rate $k = 4{\cdot}70 \times 10^{-4}\ s^{-1}$ (Table 2).



(6)

The overall rate coefficient was estimated by titration of HCl gas with 0·05 N NaOH solution. The major product acrylic acid (68%) suggested the normal dehydrochlorination process through a four-membered transition state. However, the yield of ethylene (32%) resulted from decomposition of the unstable β-propiolactone. This consideration is supported by the fact that working with pure acrylic acid in the presence of HCl gas at 340·5 °C, gave only traces of $CH_2{=}CH_2$. In addition, the gas-phase pyrolysis of β-propiolactone between 215 and 255 °C and 262 and 322 °C has been found to be a first-order reaction, yielding ethylene and carbon dioxide as the only products.[7,8]

Table 2 indicates that as the percentage decomposition of 3-chloropropionic acid in the reaction increased, the amount of product acrylic acid decreased and that of ethylene increased. In spite of our limited kinetic data and according to the above observations, the dehydrohalogenation mechanism proceeds in terms of a polar four-membered cyclic transition state for acrylic acid formation, whereas a very polar six-membered transition state leads to β-propiolactones which decomposes rapidly to ethylene and carbon dioxide [equation (7)].



(7)

It is interesting that the primary chloride of 3-chloropropionic acid eliminates HCl gas at much lower temperatures than do primary alkyl chlorides.[9]

2-Chlorobutyric acid

Acceptable first-order kinetics for this compound were difficult to obtain, but the dependence of the overall rate coefficient on temperature is given in Table 3.

Table 2. Rate coefficient for the pyrolysis of $ClCH_2CH_2COOH$ at 340·5 °C[a]

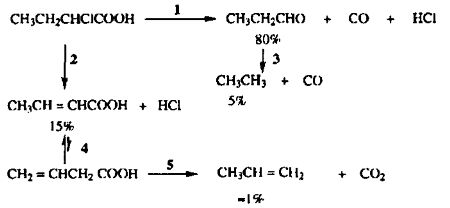
Time (min)	Reaction (%)	10^4k_{HCl} (k_T) (s^{-1})	10^4k_e (s^{-1})	10^4k_{ac} (s^{-1})
5	15	5·10	1·38	3·72
10	25	4·72	1·49	3·23
14	32	4·62	1·15	3·42
20	40	4·34	1·84	2·96

[a] $k_{HCl} = k_T$ = overall rate; k_e = rate towards ethylene formation; k_{ac} = rate towards acrylic acid formation.

Table 3. Variation of the rate coefficient with temperature for $CH_3CH_2CHClCOOH$

Temperature (°C)	319·5	329·0	340·1	351·0
10^4k_1 (s^{-1})	1·62	3·32	5·18	9·87

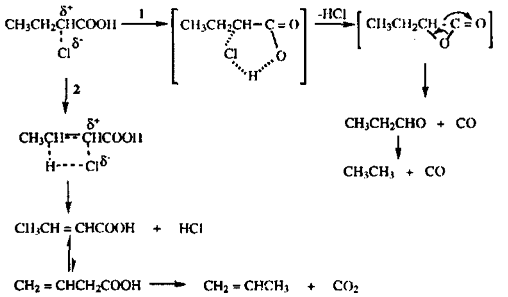
The Arrhenius parameters derived from Table 3 of $\log A = 11{\cdot}25\ s^{-1}$ and $E_a = 170{\cdot}4\ kJ\ mol^{-1}$ are very approximate values. The product decomposition of the chloroacid substrate is described by equation (8).



(8)

The overall rate (path 1 + path 2) was estimated by the quantitative titration of HCl gas with a solution of 0·05 N NaOH. Ethane (path 3) and propene (path 5) were quantitatively estimated by GLC (column: Porapak Q, 80–100 mesh). The major product propionaldehyde appears to be produced because aldehydes are formed from pyrolysis of α-halo-acids in the gas phase[2,6] through the unstable intermediate α-butyrolactone. This aldehyde under the present pyrolytic conditions gave a small amount of ethane (5%) and carbon monoxide. The 15% yield of but-2-enoic acid must evidently occur through the normal four-membered HCl elimination of alkyl halides.

On the basis of these results, two mechanistic pathways appear to take place during the pyrolytic elimination of 2-chlorobutyric acid. Path I seems to proceed through a polar five-membered cyclic transition state as pictured in equation (9). However, path 2 must occur via the normal four-membered transition state for dehydrochlorination of alkyl chlorides. The very small amounts of propene and carbon dioxide arise from the isomerization of but-2-enoic acid to but-3-enoic acid, which then decomposes through a six-centred transition state as reported.[10]



(9)

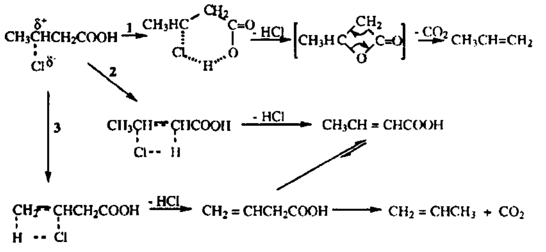
3-Chlorobutyric acid

The elimination of this substrate, with up to 60% decomposition, behaved well kinetically within a temperature range of 30 °C (Table 4), and the overall rate coefficients obey a first-order rate law. The Arrhenius parameters were $\log A = 14{\cdot}48\ s^{-1}$ and $E_a = 206{\cdot}0\ kJ\ mol^{-1}$. The reaction products are described in equation (10).

$$\begin{aligned}
CH_3CHClCH_2COOH \rightarrow\ & CH_3CH{=}CHCOOH \\
& 27.5\% \\
& + CH_2CHCH_2COOH \\
& 9.2\% \\
& + CH_3CH{=}CH_2 + CO_2 + HCl \\
& 63.3\%
\end{aligned} \qquad (10)$$

Titration of the HCl gas with 0·05 N $AgNO_3$ solution was employed for the overall rate determination. But-2-enoic acid (yield 27·5%) and but-3-enoic acid (yield 9.2%) are obtained through the four-centred dehydrochlorination process of the substrate. The high yield of propene (63·3%) apparently may arise both through a six-centred transition state decomposition of but-3-enoic acid[10,11] and from the decomposition of the unstable intermediate β-butyrolactone. This lactone was reported to pyrolyse (209–250 °C) with a first-order rate law to give only propene and carbon dioxide.[12]

Pure but-2-enoic acid in the presence of HCl gas does not isomerize or decompose. However, pure but-3-enoic acid in HCl gas, under similar pyrolysis conditions, gave a 17·5% yield of but-2-enoic acid and 50% yield of propene. Consequently, it appears that 14·2% of propene may be produced by decomposition of but-3-enoic acid and 49·1% may apparently be obtained through the unstable β-butyrolactone intermediate. According to this rationalization, a parallel pyrolytic elimination occurs whereby a polar four-membered cyclic transition state gives the corresponding unsaturated carboxylic acids and a very polar six-membered cyclic transition state forms the unstable β-butyrolactone, which rapidly decomposes to propene and carbon dioxide [equation (11)].



(11)

Table 4. Temperature dependence of the rate coefficient for pyrolysis of $CH_3CHClCH_2COOH$

Temperature (°C)	350·1	360·3	370·0
10^4k_1 (s^{-1})	16·40	30·10	55·24

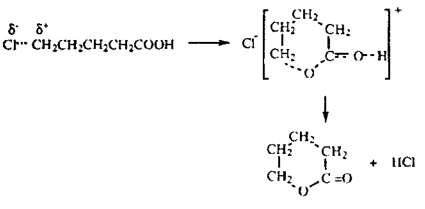
5-Chlorovaleric acid

Only at 349·5 °C was it possible to obtain good first-order kinetics up to 45% reaction with this substrate. The products of this elimination are δ-valerolactone and HCl gas [equation (12)].

(12)

This decomposition process, beyond 50% reaction and up to ten half-lives, showed some polymerization of the valerolactone and the formation of very small amounts of butadiene. The stoichiometry [equation (12)] was verified, up to 45% reaction, by comparing pressure measurements with titrimetric determination of HCl with a solution of 0·05 N NaOH (Table 5). Reproducible k-values were obtained whether by determination of the pressure increase or by quantitative titration of the HCl product (Table 6).

In association with the quantitative formation of γ-butyrolactone from the gas phase pyrolysis of 4-chlorobutyric acid,[1] the mechanism of this elimination was thought to require the participation of the neighbouring COOH group and the intramolecular solvation of the leaving chloride ion [equation (13)].



(13)

This result appears to confirm that cyclic product formation in the gas-phase reaction proceeds through an intimate ion-pair type of intermediate.

Table 5. Stoichiometry of 5-chlorovaleric acid pyrolysis at 349·5 °C

Time (min)	Reaction (%) (pressure)	HCl (%) (titration)
2	18·1	17·2
3	25·3	24·7
4	29·9	28·7
5	39·2	38·8
6	42·4	44·3

Table 6. Rate coefficient for pyrolysis of $ClCH_2CH_2CH_2CH_2COOH$

Reaction (%)	10^4k_1 (s^{-1}) (pressure)	10^4k_1 (s^{-1}) (HCl titration)
17·2	15·95	15·77
24·7	16·14	15·77
38·8	15·58	16·38
44·3	16·13	16·25
	Av. 15·95	Av. 16·04

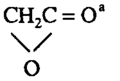
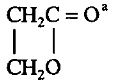
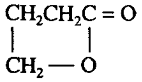
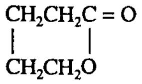
DISCUSSION

With most of the chlorocarboxylic acids examined in this work it was very difficult to carry out quantitative analyses for kinetic determinations in the gas phase. First, there was a lack of volatility of the halo acids and several reaction products. Moreover, quantitative titration of the HCl was interfered with by the presence of the COOH group of the unreacted substrate or by CO and CO_2 products. In addition to these effects, the unsaturated acids and lactone obtained in these eliminations tended to polymerize. In spite of these limitations, the available experimental data may lead to a reasonably comparative picture of the rate of the dehydrochlorination of ω-chlorocarboxylic acids in the gas phase. In the pyrolytic kinetic determination of each substrate, the k values are reproducible within a relative standard deviation of not greater than ±5% at a given temperature. The data, with the exception of those for 3-chloropropionic and 5-chlorovaleric acids, were fitted to the Arrhenius equations, where 90% confidence limits from a least-squares procedure are quoted.

The data in Table 7 suggest several types of mechanisms which change from intramolecular displacement of the chlorine leaving group by the acidic hydrogen of the COOH (chloroacetic acid and 3-chloropropionic acid) to the anchimeric assistance of the carbonyl COOH group to the C—Cl bond polarization of 4-chlorobutyric acid and 5-chlorovaleric acid. The five-membered conformation for chlorine displacement by the H of the COOH group for dehydrochlorination of chloroacetic acid [equation (5)] is less favourable than the six-membered conformation of 3-chloropropionic acid [equation (7)]. However, the five-membered conformation of neighbouring group participation in 4-chlorobutyric acid is more favoured in the rate of HCl elimination than the six-membered conformation in 5-chlorovaleric acid [equation (13)].

Consequently, the stabilization of the C—Cl bond polarization through anchimeric assistance of the

Table 7. Arrhenius parameters and comparative rates at 340·0 °C

Substrate	10^4k_l (s^{-1})	Relative rate of lactone formation		E_a (kJ mol^{-1})	Log A (s^{-1})	Ref.
$ClCH_2COOH$	0·12	1·0	 [a]	189·2	11·21	This work
$ClCH_2CH_2COOH$	1·47	12·3	 [a]	—	—	This work
$ClCH_2CH_2CH_2COOH$[b]	19·05	158·8		176·5	12·32	1
$ClCH_2CH_2CH_2CH_2COOH$	8·42[c]	70·2				This work

[a] Unstable intermediate.

[b] The Arrhenius parameters were recalculated from Ref. 1 and corrected.

[c] This k-value was estimated from Table 6, from the fact that 4-chlorobutyric acid increases or decreases the rates by a factor of 1·8–2·0 for every 10 °C change in temperature.

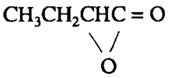
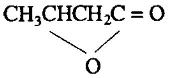
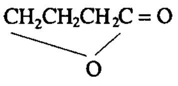
carbonyl group enhances the elimination rate of HCl more than intramolecular displacement by the acidic hydrogen. This consideration seems to be supported by the comparative results of the leaving chlorine from position 2 to position 4 in ω-chlorobutyric acids (Table 8). The neighbouring C═O group of 4-chlorobutyric acid[1] assists better the leaving Cl atom than direct participation of the acidic hydrogen of chloroacetic and 3-chloropropionic acids.

In the case of the leaving chlorine atom at the 2-position of several carboxylic acids (Table 9), it is evident that a secondary C—Cl bond is more readily displaced than a primary C—Cl bond. Consequently, both 2-chloropropionic and 2-chlorobutyric acids give a faster rate of elimination than chloroacetic acid.

In comparing the intramolecular displacement of the leaving chlorine by hydrogen, it appears that the normal four-centred transition state for HCl elimination is more favoured than the six-centered transition state as shown by the results of 3-chloropropionic acid and 3-chlorobutyric acid pyrolyses. Otherwise, the five-centred transition state is more facile in a dehydrochlorination process than the four-centred transition state described in the gas phase pyrolysis of 2-chlorobutyric acid [equation (9)].

In conclusion, it appears that the stabilization of the carbon containing a leaving group gives a faster rate of elimination than by intramolecular displacement of that group. In the present work, participation of the C═O of the COOH assisted the HCl elimination better

Table 8. Arrhenius parameters and comparative rates at 350·0 °C

Substrate	10^4k_T (s^{-1})[a]	10^4k_l (s^{-1})[a]	Lactone	E_a (kJ mol^{-1})	Log A (s^{-1})	Ref.
$CH_3CH_2CHClCOOH$	9·12	7·75		170·4	11·25	This work
$CH_3CHClCH_2COOH$	16·22	7·95		206·0	14·48	This work
$ClCH_2CH_2CH_2COOH$	33·11	33·11		176·5	12·32	1

[a] k_T = Overall rate, k_l = rate towards lactone formation.

Table 9. Arrhenius parameters and comparative rates at 370 °C

Substrate	10^4k_T (s^{-1})[a]	10^4k_i (s^{-1})[a] (α-lactone)	E_a (kJ mol^{-1})	Log A (s^{-1})	Ref.
$ClCH_2COOH$	0·69	0·69	189·2	11·21	This work
$CH_3CHClCOOH$	22·39	22·39	186·9	12·53	2
$CH_3CH_2CHClCOOH$	25·70	21·85	170·4	11·25	This work

[a] k_T = Overall rate; k_i = rate towards the intermediate lactone formation.

than intramolecular displacement by the acidic hydrogen of the COOH group.

EXPERIMENTAL

Chloroacetic acid. Chloroacetic acid of 99% purity was bought from Merck and the HCl gas was analysed with a solution of 0·05 N NaOH.

3-Chloropropionic acid. This substrate was prepared from ethyl 3-chloropropionate (Aldrich) as reported[13] and distilled until 99·7% purity [GLC: 10% SP-1200–1% H_3PO_4 on Chromosorb W AW (80–100 mesh)]. Acrylic acid (Merck) was analysed on the same column of 10% SP-1200, while ethylene (Matheson) was analysed on a column of Porapak Q (80–100 mesh). The HCl gas was determined quantitatively by titration with 0·05 N NaOH solution.

2-Chlorobutyric acid. This compound (Fluka) was distilled to 99·1% purity as determined by GLC [10% SP-1200–1% H_3PO_4 on Chromosorb W AW (80–100 mesh)]. The pyrolysis products propionaldehyde (Aldrich), propene (Matheson), and ethane (Matheson) were analysed using a column of Porapak Q (80–100 mesh) and but-2-enoic acid (Sigma) was analysed using the 10% SP-1200 column. The HCl gas was determined quantitatively by titration of 0·05 N NaOH solution.

3-Chlorobutyric acid. 3-Chlorobutyric acid (Pfaltz & Bauer) was distilled several times and the fraction over 97·1% purity [GLC: 10% SP-1200–1% H_3PO_4 on Chromosorb W AW (80–100 mesh)] was used. But-2-enoic acid (Sigma) and but-3-enoic acid (Koch-Light) were analysed on the 10% SP–1200 column, whereas propene (Matheson) was determined in a column of Porapak Q (80–100 mesh). The HCl gas analysis was determined by neutralizing the solution with calcium carbonate and then was titrated with a solution of 0·05 N $AgNO_3$ using fluorescein as indicator.

5-Chlorovaleric acid. After several distillations, the chlorovaleric acid was 98·0% pure [GLC: 10% SP-1200–1% H_3PO_4 on Chromosorb W AW (80–100 mesh)]. The columns used for quantitative analyses were Carbowax 20M–15% Chromosorb W AW DMCS (80–100 mesh) for δ-valerolactone (Aldrich) and 20% bis(2-methoxyethyl)adipate–Chromosorb P (80–100 mesh) for butadiene (Matheson). The HCl gas was determined quantitatively by titration with 0·05 N NaOH solution.

Kinetics. The pyrolysis experiments were carried out in a static reaction vessel, seasoned with allyl bromide and in the presence of at least twice the amount of cyclohexene or toluene inhibitors. The rate coefficients were determined by measurement of the pressure increase and/or by HCl titration with 0·05 N NaOH or $AgNO_3$ solution. The temperature was controlled by a Shinko DIC-PS 25RT resistance thermometer controller maintained within 0·02 °C and measured with a calibrated platinum–platinum–13% rhodium thermocouple. The reaction vessel showed no temperature gradient and the substrates were injected directly into the vessel through a silicone rubber septum.

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