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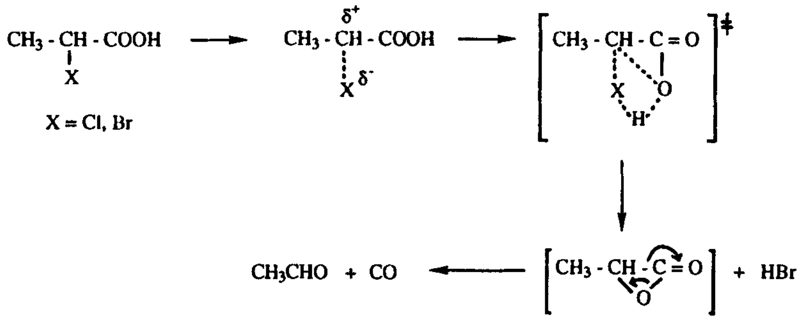
ELIMINATION KINETICS AND MECHANISM OF PRIMARY, SECONDARY AND TERTIARY α-HYDROXYCARBOXYLIC ACIDS IN THE GAS PHASE

GABRIEL CHUCHANI,* IGNACIO MARTIN, ALEXANDRA ROTINOV AND ROSA M. DOMINGUEZ
Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC) Apartado 21827, Caracas 1020-A, Venezuela

The rates of elimination of primary, secondary and tertiary α-hydroxycarboxylic acids were determined in a seasoned, static reaction vessel over the temperature range 280–390 °C and the pressure range 30–201 Torr. The reactions, in the presence of a free radical inhibitor, are homogeneous, unimolecular and follow a first-order rate law. The rate coefficients are given by the following equations: for glycolic acid, $\log k_1$ (s^{-1}) = (14·03 ± 0·24) − (209·3 ± 1·5) kJ mol^{-1} $(2\cdot303RT)^{-1}$; for lactic acid, $\log k_1$ (s^{-1}) = (12·24 ± 0·11) − (182·8 ± 1·3) kJ mol^{-1} $(2\cdot303RT)^{-1}$; and for 2-hydroxyisobutyric acid, $\log k_1$ (s^{-1}) = (12·91 ± 0·13) − (174·7 ± 1·5) kJ mol^{-1} $(2\cdot303RT)^{-1}$. The basicity and the ease with which the hydroxy group is removed from primary to tertiary α-hydroxycarboxylic acids are reflected in rate enhancement. The mechanism of these eliminations appears to proceed through a semi-polar five-membered cyclic transition state.

INTRODUCTION

The OH group of aliphatic alcohols has been found to be difficult and complicated as a leaving group in pyrolytic eliminations in the gas phase.[1] Because of this, very few alcohols have been pyrolysed since these reactions may undergo a radical chain to a molecular mechanism on changing from a primary to a tertiary structure.[1] However, intermolecular participation of acidic hydrogen occurs in the catalysed dehydration process with HCl and HBr, the molecular elimination is carried out at much lower temperatures and the activation energy is reduced by more than 100 kJ mol^{-1}.[1–3] In contrast to the intermolecular acid catalysis of alcohols, the intramolecular acidic hydrogen assistance may well be an interesting dehydration process. This line of thought is associated with recent results on the dehydrohalogenation of α-halocarboxylic acids by pyrolysis in the gas phase,[4,5] where the proton in the COOH group assists the leaving halogen atom in a polar five-membered cyclic transition state, as described in the equation



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[*] Author for correspondence.

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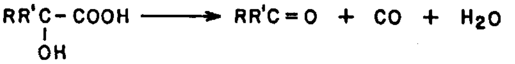
In order to assess the effect of the acidic hydrogen of the COOH group in the elimination of OH, this work was aimed at determining the gas-phase elimination kinetics of primary, secondary and tertiary α-hydroxycarboxylic acids, i.e. glycolic, lactic and 2-hydroxyisobutyric acid.

RESULTS AND DISCUSSION

The unimolecular elimination of the α-hydroxycarboxylic acids, in a seasoned static reaction vessel and in the presence of a free radical inhibitor, was examined in the temperature range 280·4–389·4 °C and pressure range 30·5–201·6 Torr (1 Torr = 133·3 Pa). The stoichiometry of the equation



$$RR'\underset{\displaystyle OH}{C}-COOH \longrightarrow RR'C{=}O + CO + H_2O \quad (2)$$

(i) $R, R' = H$
(ii) $R = H, R' = CH_3$
(iii) $R, R' = CH_3$

requires $P_f = 3P_0$, where P_f and P_0 are the final and initial pressure, respectively. The average experimental P_f/P_0 values measured after ten half-lives and at four different temperatures were 2·71 for glycolic acid, 2·88 for lactic acid and 2·93 for 2-hydroxyisobutyric acid. Only a small departure from the required stoichiometry was found with glycolic and lactic acids owing to the slight polymerization of the corresponding aldehyde. A further verification of the above stoichiometry, up to 50–60% decomposition, is that the acetaldehyde and acetone produced are equivalent to the pressure increase. However, the primary product CH_2O from glycolic acid could not be determined quantitatively owing to polymerization when collected out of the static system (Table 1).

The yields of pyrolysis products within the range of rate determination were as follows: glycolic acid gave up to 50% reaction, formaldehyde, CO and H_2O; lactic acid gave up to 60% reaction, acetaldehyde, CO, and H_2O; and 2-hydroxyisobutyric acid gave up to 50% decomposition, acetone, CO and H_2O and a very small amount of methacrylic acid (<5%).

The homogeneity of these pyrolytic eliminations was examined using reaction vessels with different surface-to-volume ratios (i.e. the packed vessel had a 6·0 times greater surface-to-volume ratio than the unpacked vessel). The packed and unpacked clean Pyrex vessels resulted in a marked heterogeneous effect. However, when the packed and unpacked vessels were seasoned with the product of decomposition of allyl bromide, no differences in the rate coefficients were obtained from these hydroxy acid substrates (Table 2). These compounds were always pyrolysed in seasoned vessels and in the presence of at least a threefold excess of the free chain radical inhibitor, propene, cyclohexene or toluene (Table 3). No induction period was observed and the rates were reproducible with a standard deviation not greater than 5% at a given temperature.

The first-order rate coefficients of these hydroxycarboxylic acids calculated from $k_1 = (2{\cdot}303/t)\log[2P_0/(3P_0 - P_t)]$ were independent of the initial pressure (Table 4). A plot of $\log(3P_0 - P_t)$ against time t gave a good straight line up to 50–60% decomposition. The temperature dependence of the rate coefficients is given in Table 5. The data were fitted to the Arrhenius equation shown where 90% confidence coefficients from a least-squares procedure are quoted.

It is evident from the data in Table 6 that the greater the basicity of the OH group of alcohols in the gas phase [6] the faster is its elimination through the assistance of the acidic hydrogen of the COOH group. Consequently, the sequence of rates increases from primary to tertiary α-hydroxycarboxylic acids. According to the product formation described in equation (2) and the results shown in Table 6, it is reasonable to consider the mechanism of elimination of lactic acid, as an example, in terms of a semi-polar five-membered cyclic transition state, where the C—OH bond polarization, in the direction of $C^{\delta+} \cdots OH^{\delta-}$ is

Table 1. Stoichiometry of the reaction[a]

Substrate	Temperature (°C)	Parameter	Values			
Lactic acid	360·0	Time (min)	2·5	5	10	15
		Reaction (%) (pressure)	20·5	34·5	54·1	62·8
		Decomposition (%) (chromatography)	19·0	34·0	53·9	59·8
2-Hydroxyisobutyric acid	300·0	Time (min)	5	7	10	12
		Reaction (%) (pressure)	24·6	31·3	41·5	48·5
		Decomposition (%) (chromatography)	26·0	32·0	44·0	52·5

[a] The product CH_2O from glycolic acid was difficult to determine owing to polymerization when collected out of the static system.

Table 2. Homogeneity of the reaction

Substrate	Temperature (°C)	S/V (cm^{-1})	10^4k_1 (s^{-1})[a]	10^4k_1 (s^{-1})[b]
Glycolic acid	371·0	1	25·40[c]	11·44
		6	27·35[c]	11·93
Lactic acid	360·0	1	50·12[c]	14·46
		6	55·92[c]	14·45
2-Hydroxyisobutyric acid	300·0	1	–[d]	9·67
		6	–[d]	9·62

[a] Clean Pyrex vessel.
[b] Seasoned with allyl bromide.
[c] Average k value.
[d] Starts with high k-value and then decreases rapidly.

Table 3. Effect of inhibitor on rates

Substrate	Temperature (°C)	P_s (Torr)[a]	Inhibitor	P_i (Torr)[a]	P_i/P_s	10^4k_1 (s^{-1})
Glycolic acid	371·0	47	Toluene	–	–	9·48
		58·2		94·5	1·6	10·21
		53·3		127	2·4	11·24
		51·1		163	3·1	11·44
		33·8		136·5	4·0	11·35
		33·7		158·5	5·2	11·28
Lactic acid	360·0	122·4	Propene	–	–	14·38
		153·9		128·5	0·8	14·74
		201·6		243·5	1·2	14·57
		162		266	1·6	14·20
		49·5		127·5	2·6	14·42
		83·2		358	4·3	14·84
2-Hydroxyisobutyric acid	300·0	103·5	Cyclohexene	–	–	9·41
		84·5		63·5	0·8	9·58
		43·5		82·5	1·9	9·65
		55·5		139·5	2·5	9·62
		50		154·5	3·1	9·71

[a] P_s = pressure of substrate; P_i = pressure of the inhibitor.

Table 4. Invariability of rate coefficient with initial pressure

Substrate	Temperature (°C)	Parameter	Values						
Lactic acid	371·0	P_0 (Torr)	30·5	47·0	58·2	80·3			
		10^4k_1 (s^{-1})	10·91	11·24	11·24	11·26			
Glycolic acid	360·0	P_0 (Torr)	49·5	67·0	83·2	117·0	152·1	162·0	201·6
		10^4k_1 (s^{-1})	14·42	14·32	14·84	14·47	14·28	14·20	14·57
2-Hydroxyisobutyric acid	300·0	P_0 (Torr)	33·0	43·5	59·0	69·5	84·5	104·0	
		10^4k_1 (s^{-1})	9·66	9·65	9·60	9·62	9·58	9·89	

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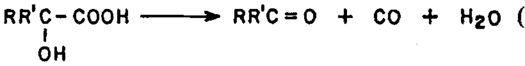

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pressor (propene, cyclohexene or toluene). The reaction vessels were seasoned with the products of decomposition of allyl bromide. The rate coefficients were determined manometrically. The temperature was controlled by a resistance thermometer temperature controller type RT 5/R MK2 of AEI or Shinko DIC-PS maintained within ±0·2 °C and measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient along the reaction vessel was found. The substrates glycolic acid and 2-hydroxyisobuyric acid, both dissolved in tetrahydrofuran, and pure lactic acid were injected directly into the reaction vessel with a syringe through a silicone-rubber septum.

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