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ELIMINATION KINETICS OF DL-MANDELIC ACID IN THE GAS PHASE

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DL-Mandelic acid was pyrolyzed in a static reaction vessel over the temperature range 300·1–340·0 °C and pressure range of the substrate 15·2–52·1 Torr. The reaction, in a seasoned vessel and in the presence of the free radical inhibitor cyclohexene, is homogeneous, unimolecular and obeys a first-order rate law. The reaction yielded benzaldehyde, CO, H_2O and small amounts of benzyl alcohol and CO_2. The rate coefficients followed the Arrhenius equation: log k_1 (s^{-1}) = (12·54 ± 0·12) − (171·3 ± 1·4) kJ mol^{-1} $(2{\cdot}303RT)^{-1}$. The present result may imply a unimolecular elimination involving a semi-polar five-membered cyclic transition-state mechanism. Steric factor appears not to be important in rate enhancement. © 1997 by John Wiley & Sons, Ltd.

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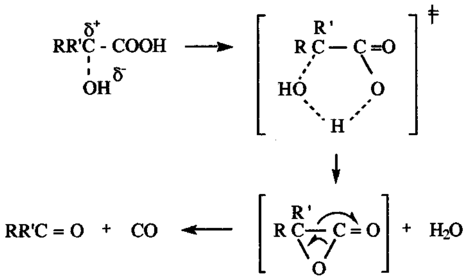
INTRODUCTION

In association with the results on the gas-phase elimination of 2-halocarboxylic acids,[1,2] where the acidic H of the COOH group assists the elimination of the halogen atom in a semi-polar five-membered cyclic transition state, several 2-hydroxycarboxylic acid pyrolyses were examined. In this respect, a correlation of rate increase in the homogeneous, unimolecular gas-phase dehydration process from primary to tertiary 2-hydroxycarboxylic acids was obtained.[3] Moreover, later work showed that an increase in the bulkiness of the alkyl group at the 2-position of the 2-hydroxycarboxylic acids gave a small but a significant increase in rate coefficients.[4] In this respect, the electronic transmission of the alkyl groups, without underestimating steric acceleration as a possible important factor, was believed to enhance the pyrolysis rate of these substrates. The mechanism of these reactions was suggested to proceed via a semi-polar five-membered cyclic transition state as shown in equation (1).

It is interesting to consider several earlier studies where high molecular weight aliphatic aldehydes were prepared by distillation following 2-hydroxy acid decomposition,[5,6] while degradation of disubstituted glycolic acids in the presence of lead tetraacetate led to the formation of the corresponding ketone.[7]

To obtain additional information about the extent of the nature of the transition state of these gas-phase eliminations, with the premise that the C—OH bond polarization is rate determining, the high stabilization of the C—OH bond by the benzylic part of a molecule, such as mandelic acid, may give rise to an effective assistance of the acidic hydrogen of the COOH group for a faster dehydration process. Consequently, this work was aimed at studying the homogeneous pyrolytic elimination kinetics of DL-mandelic acid in the gas phase.



(1)

Table 1. Stoichiometry based on the P_f/P_0 ratio[a]

Temperature (°C)	P_0 (Torr)	P_f (Torr)	P_f/P_0
310·0	26	71	2·73
320·1	27	73	2·67
330·1	32·5	91	2·80
340·0	25·3	68·3	2·70

[a] P_0 = initial pressure; P_f = final pressure

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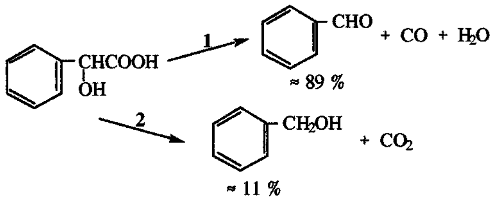
Table 2. Stoichiometry based on the pressure vs chromatographic analysis at 320·1 °C

Time (min)	1·5	3	6	9
Reaction (%) (pressure)	19·9	38·8	59·1	65·7
Benzaldehyde (%) (chromatography)	20·8	37·5	57·8	62·5

RESULTS AND DISCUSSION

The molecular elimination of DL-mandelic acid (α-hydroxyphenylacetic acid) in a seasoned static reaction vessel was studied in the temperature range 300·1–340·0 °C and pressure range 15·2–52·1 Torr. The reaction, after a very long period of time, can be described by equation (2).



(2)

The theoretical stochiometry based on the main reaction [equation (2), path **1**] demands $P_{\mathrm{f}}=3P_0$, where P_{f} and P_0 are the final and initial pressure of the substrate, respectively. The average experimental P_{f}/P_0, values measured after 10 half-lives and at four different temperatures was 2·72 (Table 1). The resulting departure from the required theoretical stoichiometry was due to the parallel decarboxylation process to give a small amount of benzyl alcohol in *ca* 11% yield [equation (2), path **2**]. Otherwise, the yields of pyrolysis products, within the range of rate determination and up to 60% decomposition, are only benzaldehyde, CO and H_2O.

The verification of the stoichiometry of equation (2), path **1**, was possible by comparing the percentage decomposition of the substrate mandelic acid as predicted from pressure measurements with the quantitative analysis of the product benzaldehyde (Table 2). The formation of a small amount of benzyl alcohol [equation (2), path **2**] was monitored by the quantitative chromatographic analysis of this product after 50% decomposition of the substrate (Table 3). The homogeneity of this reaction was examined by using a packed reaction vessel with a six times greater surface-to-volume ratio than the unpacked reaction vessel. The rate coefficients were unaffected in packed and unpacked vessels seasoned with the products of decomposition of allyl bromide. However, after several runs of the substrate in the packed and unpacked clean Pyrex vessels, no differences in the rate coefficients were obtained (Table 4). Apparently, the surface of the reaction was deactivated by pyrolyzing the substrate under study until reproducible *k* values were obtained.

The absence of a free radical process in this elimination process was examined by carrying out several runs in the presence of different proportions of cyclohexene as inhib-

Table 3. Formation of benzyl alcohol at 320·1 °C

Time (min)	5·2	10	40	51	83
Reaction (%) (pressure)	55·8	68·5	74·8	78·5	90·1
Benzyl alcohol (%) (chromatography)	0·6	1·2	4·5	5·7	9·2

Table 4. Homogeneity of the reaction

Temperature (°C)	S/V (cm^{-1})	10^4k_1 (s^{-1})	
		A[a]	B[b]
300	1	8·77	8·66
	6	8·89	8·55
320	1	28·18	28·39
	6	28·61	28·58
300	1	88·56	88·98
	6	88·98	88·28

[a] Clean Pyrex vessel and after several runs with the substrate.

[b] Seasoned vessel with allyl bromide.

Table 5. Effect of the inhibitor cyclohexene on rates at 320·1 °C

P_0 (substrate) (Torr)	P_0 (Inhibitor) (Torr)	P_i/P_0	10^4k_1 (s^{-1})[a]
33·3	–	–	28·55
41·2	145·3	1·2	28·37
43·0	101·5	2·3	28·47
52·1	159·0	3·1	28·07
15·2	65·5	4·3	28·23

[a] Rates determined up to 55% reaction.

Table 6. Invariability of the rate coefficients with initial pressure at 320·1 °C

P_0 (Torr)	15·2	26·4	40·1	43·0	52·1
10^4k_1 (s^{-1})	28·23	28·27	28·04	28·47	28·07

Table 7. Temperature dependence of rate coefficients

Temperature (°C)	300·1	310·0	320·1	330·1	340·0
10^4k_1 (s^{-1})	8·66	15·58	28·39	50·34	88·98

Log k_1 (s^{-1})$=(12{\cdot}54\pm0{\cdot}12)-(171{\cdot}3\pm1{\cdot}4)$ kJ mol^{-1} $(2{\cdot}303RT)^{-1}$ ($r=0{\cdot}999979$)

Table 8. Variation of rate coefficient with temperature for the benzyl alcohol formation

Temperature (°C)	310·0	320·1	330·1	340·0
10^4k_1 (s^{-1})	0·92	1·92	3·74	7·19

Log k_1 (s^{-1})$=(13{\cdot}15\pm0{\cdot}40)-(202{\cdot}7\pm4{\cdot}6)$ kJ mol^{-1} $(2{\cdot}303RT)^{-1}$ ($r=0{\cdot}999907$)

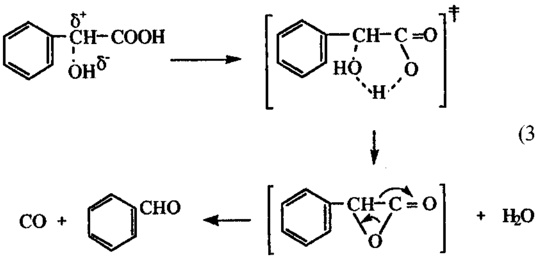
Table 9. Comparative rates at 340·0 °C

Substrate	10^4k_1 (s^{-1})	Rel· rate	E_a (kJ mol^{-1})	Log[A (s^{-1})]	Ref.
$CH_3CHOHCOOH$	4·57	1·0	182·8 ± 1·3	12·24 ± 0·22	3
$C_6H_5CHOHCOOH$	88·98	19·5	171·3 ± 1·4	12·54 ± 0·12	This work

itor (Table 5). This substrate was always pyrolyzed in seasoned vessels and in the presence of at least twice the amount of the free radical suppressor cyclohexene. No induction period was observed and the rates were reproducible with a standard deviation not greater than 5% at the working temperature.

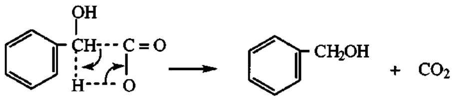
The rate coefficients of the hydroxy acid substrate, calculated from $k_1 = (2{\cdot}303/t)\log[2P_0/(3P_0 - P_t)]$, were found to be invariable with initial pressure (Table 6). Plotting $\log(3P_0 - P_t)$ against time t gave a good straight line up to 50–60% reaction. The variations of the rate coefficients with temperature are described in Table 7. The results given in Table 7 lead by using the least-squares procedure and 90% confidence limits, to the Arrhenius equation shown. The k values for the formation of benzyl alcohol were determined [equation (2), path **2**] from $k_1 = (2{\cdot}303/t)\log[(2P_0 - P_t)/P_0]$, while the variation of the rate coefficient with temperature is as given in Table 8 (with a confidence limit of 0.9).

The consideration that the decomposition of 2-hydroxycarboxylic acids may proceed through a mechanism where the C—OH bond polarization, in the sense of $C^{\delta+}\cdots OH^{\delta-}$ is rate determining,[3,4] appears to find support from the results shown in Table 9. In this respect, because of the greater stabilization of the benzylic C—OH bond polarization of mandelic acid in the transition state, the direct participation of the acidic H of the C=O of the COOH group leads to a faster dehydration rate compared with lactic acid. Apparently, the mechanism of this reaction, as in 2-hydroxycarboxylic acid decomposition,[3,4] appears to proceed through a semi-polar five-membered cyclic transition state as shown in equation (3).



(3)

In the case of the small amounts of benzyl alcohol obtained beyond the range of rate determination for 50% decomposition [equation (2), path **2**], the mechanism for the process is different and may be rationalized according to equation (4). This type of mechanism is nearly analogous to the pyrolysis of benzoylformic acid in the gas phase.[8]



(4)

The results of the present work suggest that the elimination processes of 2-hydroxy acids in the gas phase are polar in nature. Moreover, steric acceleration may not be an important factor for a faster elimination rate with increase in the bulkiness of the alkyl group at the 2-position of 2-hydroxycarboxylic acids.[4]

EXPERIMENTAL

The purity of better than 99·0% of the substrate DL-mandelic acid (Aldrich) was checked by GLC (10% SP 1200–1% H_3PO_4, Chromosorb W AW DMCS, 80–100 mesh) and titration with a solution of 0·05 M NaOH. The products benzaldehyde (Aldrich) and benzyl alcohol (Aldrich) were quantitatively analyzed with the above column. The analyses of CO and CO_2 were performed with a Carbosieve B (60–80 mesh) column. The identities of the substrate and products were further verified by NMR and mass spectrometry.

The hydroxy acid was pyrolyzed in a static reaction vessel, seasoned with allyl bromide, and in the presence of at least twice the amount with respect to pressure of the inhibitor cyclohexene (Table 4). The rate coefficients were determined manometrically up to 50–60% reaction. The temperature was controlled within ±0·2 °C by a Shinko DIC-PS resistance thermometer temperature controller and measured with a calibrated platinum/platinum–13% rhodium thermocouple. No temperature gradient was found in the reaction vessel when measured with a thermometer introduced around the heated aluminum block. The substrate mandelic acid, dissolved in dioxane (Merck, 99·5% pure), was injected directly into the reaction vessel with a syringe through a silicone-rubber septum.

REFERENCES

1. G. Chuchani and R. M. Dominguez, *Int. J. Chem. Kinet.* **21**, 367 (1989).
2. G. Chuchani, R. M. Dominguez and A. Rotinov, *Int. J. Chem. Kinet.* **23**, 779 (1991).

3. G. Chuchani, I. Martin, A. Rotinov and R. M. Domínguez, *J. Phys. Org. Chem*. **6**, 54 (1993).
4. G. Chuchani, I. Martín and A. Rotinov, *Int. J. Chem. Kinet*. **27**, 849 (1995).
5. E. E. Blaise, *Bull. Soc. Chim. Fr.* **31**, 483 (1904).
6. R. R. Davies and H. H. Hodgson, *J. Soc. Chem. Ind. (London)* **62**, 128 (1943).
7. E. Rohrmann, R. G. Jones and H. A. Shonle, *J. Am. Chem. Soc.* **66**, 1856 (1944).
8. R. Taylor, *Int. J. Chem. Kinet*. **23**, 247 (1991).