

Kinetics of the Gas-Phase Elimination of α -Bromophenylacetic Acid Under Maximum Inhibition

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ABSTRACT: The gas phase elimination kinetics of the title compound was studied over the temperature range of 260.1–315.0°C and pressure range of 20–70 Torr. This elimination, in seasoned static reaction system and in the presence of at least fourfold of the free radical inhibitor toluene, is homogeneous, unimolecular and follows a first-order rate law. The reaction yielded mainly benzaldehyde, CO, and HBr, and small amounts of benzylbromide and CO₂. The observed rate coefficients are expressed by the following Arrhenius equations:

For benzaldehyde formation:

$$\log k_1 (\text{s}^{-1}) = (12.23 \pm 0.26) - (164.9 \pm 2.7) \text{ kJ mol}^{-1} (2.303 RT)^{-1}$$

For benzylbromide formation:

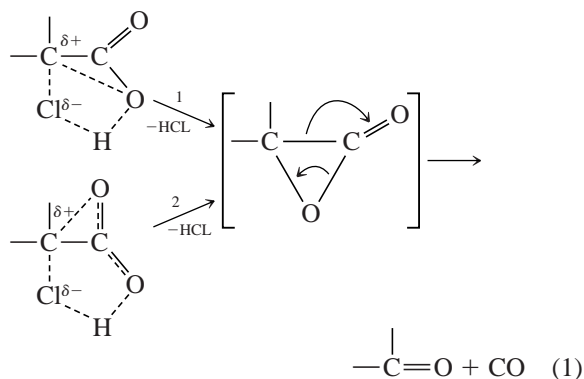
$$\log k_2 (\text{s}^{-1}) = (13.82 \pm 0.50) - (192.8 \pm 5.5) \text{ kJ mol}^{-1} (2.303 RT)^{-1}$$

The mechanisms are believed to proceed through a semi-polar five-membered cyclic transition state for the benzaldehyde formation, while a four-centered cyclic transition state for benzylbromide formation. © 1999 John Wiley & Sons, Inc. *Int J Chem Kinet* 31: 725–728, 1999

INTRODUCTION

The mechanism for the gas-phase elimination of 2-substituted chlorocarboxylic acids [1,2] was described in terms of a semi-polar five-membered cyclic transition state, where the acidic H of the COOH assisted the leaving Cl atom, followed by the carboxylic oxygen participation in the stabilization of the incipient positive carbon atom (reaction 1, Path 1) to give the corresponding α -lactone. This unstable lactone intermediate decomposed into the corresponding carbonyl compound and CO gas [reaction (1)]. To verify the

result of 2-chloropropionic acid pyrolysis, the decomposition of 2-bromopropionic acid [3] showed to have a similar mechanistic process.



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Along this line of work, the theoretical ab initio calculations for the gas phase elimination of 2-chloropropionic acid at the MP2/6-31G** level [4] have suggested the formation of α -propiolactone intermediate through a semi-polar five-membered cyclic transition structure by the assistance of the acidic H of the COOH group, but followed by the participation of the oxygen carbonyl as described in reaction (1), Path 2. The unstable lactone then proceeded to yield CH_3CHO and CO molecules. Good agreement with the experimental values were obtained.

To obtain additional information about the extent of the nature of the transition state of 2-halocarboxylic acids decomposition, the present work aimed at studying the pyrolysis kinetics of α -bromophenylacetic acid. This purpose arises from the fact that the C—Br bond polarization may be rate determining. Therefore, the higher stabilization of the C—Br bond by the benzylic carbocation of this molecule may cause an effective participation of the oxygen carbonyl for a faster elimination rate.

EXPERIMENTAL

α -Bromophenylacetic acid (Aldrich) of 98% purity (titration with 0.05N NaOH solution) was used. The products benzaldehyde (Aldrich) and benzyl bromide (Aldrich) were quantitatively analyzed by GLC (10% SP 1200–1% H_3PO_4 , Chromosorb W AW DMCS 80–100 mesh). The identities of the substrate and products were further verified by NMR and mass spectrometry.

Kinetic experiments were carried out in a static reaction system, and in the presence of at least a large excess of toluene inhibitor. The rate coefficients, according to reaction (2) were determined by titrimetric determination of HBr with a solution of 0.05N NaOH for benzaldehyde formation, and by GLC for benzyl bromide formation. The temperature was maintained within $\pm 0.2^\circ\text{C}$ with a calibrated platinum-platinum-13% rhodium thermocouple, and no temperature gradient was found along the reaction vessel. The sub-

Table I Homogeneity of the Reaction at 290.6°C^a

S/V (cm^{-1}) ^b	$10^4 k_1$ (s^{-1}) ^c	$10^4 k_1$ (s^{-1}) ^d
1	10.73	8.95
6	10.66	9.12

^a In the presence of toluene inhibitor.

^b S = Surface area; V = Volume.

^c Clean Pyrex vessel.

^d Vessel seasoned with allyl bromide.

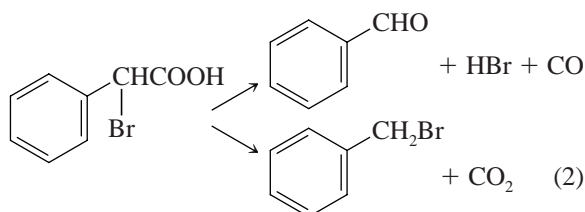
Table II Effect of the Inhibitor Toluene on Rates at 290.6°C^a

P_s (Torr)	P_i (Torr)	P_i/P_s	$10^4 k_1$ (s^{-1})
25	—	—	13.09
61	66.5	1.1	11.02
39.5	81	2.1	9.25
36.5	159	4.4	8.97
32.5	171	5.3	8.93
25	201	8.0	8.95

^a Vessel seasoned with allyl bromide, P_s = pressure of the substrate; P_i = pressure of the toluene suppressor.

strate was dissolved in chlorobenzene and injected directly into the reaction vessel through a silicon rubber septum.

RESULTS AND DISCUSSION



The homogeneity of the reaction was examined, under the free radical inhibitor toluene, by using a packed reaction vessel 6.0 times greater surface-to-volume ratio than the unpacked reaction vessel (Table I). The rate coefficients were unaffected in packed and unpacked vessel seasoned with allyl bromide. Very little effect was found in the clean packed and unpacked Pyrex reaction vessel. The effect of the free radical inhibitor toluene is shown in Table II. The kinetic determinations had to be carried out in the presence of at least four times the concentration of toluene to suppress any possible free radical chain processes of the substrate and/or product. No induction period was observed, and the rates are reproducible with a standard deviation not greater than $\pm 5\%$ at a given temperature.

Table III Invariability of Rates Coefficients with Initial Pressure at 297.7°C^a

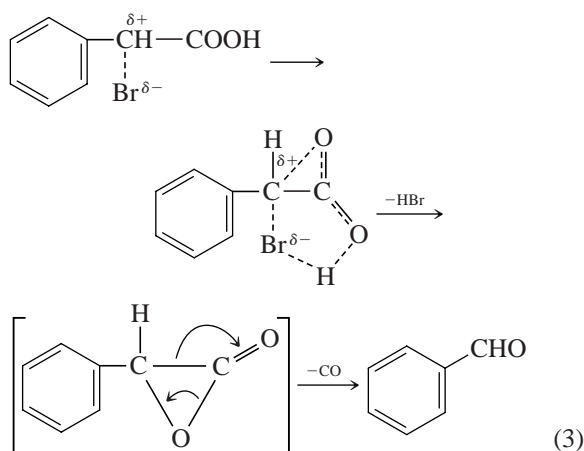
P_0 (Torr)	20	32	48	52.5	70
$10^4 k_1$ (s^{-1})	13.78	13.86	13.72	14.10	13.68

^a Vessel seasoned with allyl bromide and in the presence of at least fourfold of toluene inhibitor.

The first-order rate coefficient for the pyrolysis of this bromoacid was found to be independent of the initial pressure (Table III), and the variation of the rate coefficients with temperature is shown in Table IV. The given Arrhenius expression in Table IV was obtained by the least-square procedure and 90% confidence limits.

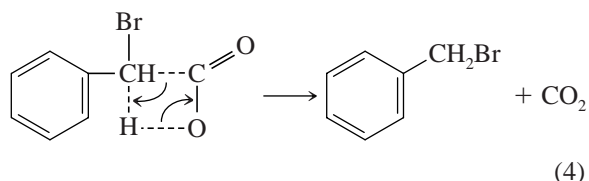
Since the C—Br bond polarization, in the sense of $C^{\delta+}-Br^{\delta-}$, may be rate determining, the results shown in Table V suggest the decomposition of the α -bromophenylacetic acid to be polar in nature.

This is derived from the fact that the greater stabilization of the benzylic carbocation of α -bromophenylacetic acid in the transition state, through the assistance of the acidic H and by the participation of the oxygen carbonyl, leads to a faster HBr elimination compared to α -bromopropionic acid. Therefore, the mechanism of this decomposition, as in α -halocarboxylic acids [1–3], appears to proceed through a semi-polar five-membered cyclic transition state as shown in reaction (3).

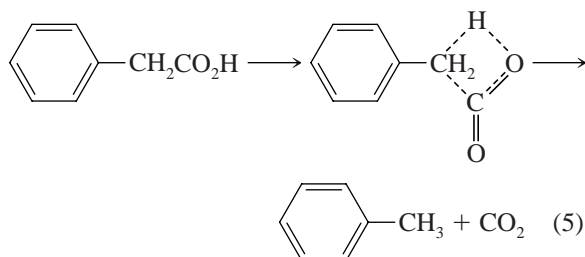


The small amount of benzyl bromide obtained beyond the range of 30% decomposition at the three highest pyrolysis temperatures suggests a different mecha-

nism. In this sense, and in association with the mechanism of benzoylformic acid pyrolysis [5] and benzyl alcohol formation from mandelic acid decomposition [6], together with the value of $\log A$ of 13.82 ($\Delta S^\ddagger = 5.7 \text{ J mol}^{-1} \text{ K}^{-1}$; $\Delta H^\ddagger = 197.6 \text{ kJ mol}^{-1}$) at 310°C (Table IV), suggests of a four-membered transition state structure. Consequently, the mechanism may be depicted as in reaction (4):



This mechanistic consideration may well find support from the kinetic study of the very low-pressure thermolysis of phenylacetic acid yielding toluene and CO_2 [7]. The said reaction was assumed to probably undergo via a four-membered cyclic transition state as described in reaction (5). The results of the work of Colussi et al. [7] differs from a previous investigation on the thermal decomposition of phenylacetic acid [8], where a radical process was described.



It is not unreasonable to believe that the mechanism for benzylbromide formation may be associated with the pyrolysis of β,γ -unsaturated acids [9] (reaction 6). However, the π -system of an aromatic ring is less polar than an olefinic double bond [10] and a decrease in reactivity may be expected. This means that the double bond of the benzene ring is less nucleophilic

Table IV Variation of Rate Coefficients with Temperature^a

Formation of Benzaldehyde							
Temperature °C	260.1	270.2	280.1	290.6	297.7	309.4	315.0
$10^4 k_1, \text{ s}^{-1}$	1.15	2.30	4.54	8.95	13.83	27.53	36.07
$\log k_1 (\text{ s}^{-1}) = (12.23 \pm 0.26) - (164.9 \pm 2.7) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}; r = 0.99982$							
Formation of Benzyl bromide							
Temperature °C	297.7	309.4	315.0				
$10^4 k_1, \text{ s}^{-1}$	1.49	3.40	4.91				
$\log k_1 (\text{ s}^{-1}) = (13.82 \pm 0.50) - (192.8 \pm 5.5) \text{ kJ mol}^{-1} (2.303 \text{ RT})^{-1}; r = 0.99995$							

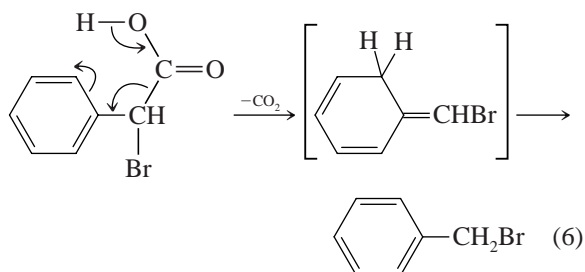
^a Vessel seasoned with allyl bromide and in the presence of at least fourfold of toluene inhibitor.

Table V Comparative Rate Coefficients at 310.0°C

Substrate	$10^4 k_1$ (s ⁻¹)	Relative		log A (s ⁻¹)	ΔS^\ddagger (J mol ⁻¹ K ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)
		Rate	E_a (kJ mol ⁻¹)			
CH ₃ CHBrCOOH ^a	1.82	1.0	180.3 ± 3.4	12.41 ± 0.29	-21.2	185.2
C ₆ H ₅ CHBrCOOH	28.58	15.7	164.9 ± 2.7	12.23 ± 0.26	-24.7	169.7

^a Reference [3].

than the aliphatic double bond. Consequently, reaction (6) may not be energetically favorable.



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