The Elimination Kinetics of 2-Bromo-3-Methylbutyric Acid in the Gas Phase

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Abstract

The kinetics of 2-bromo-3-methylbutyric acid in the gas phase was studied over the temperature range of 309.3–357.0°C and pressure range of 15.5–100.0 torr. This process, in seasoned static reaction vessels and in the presence of the free radical inhibitor cyclohexene, is homogeneous, unimolecular, and follows first-order rate law. The observed rate coefficients are represented by the following Arrhenius equations: $\log k_1(\mathrm{s}^{-1}) = (12.72 \pm 0.25) - (181.8 \pm 2.9)\ \mathrm{kJ\ mol}^{-1}(2.303RT)^{-1}$. The primary products are isobutyraldehyde, CO, and HBr. The polar five-membered cyclic transition state type of mechanism appears to be preferred in the dehydrohalogenation process of α-haloacids in the gas phase.

Introduction

The pyrolytic elimination of 2-bromopropionic acid in the gas phase gave exclusively acetaldehyde, CO, and hydrogen bromide [1]. According to this result, the H atom of the carboxylic COOH assisted the leaving Br atom rather than the adjacent H atom of the CH_3 group. In this respect, the present work wanted to examine the elimination kinetics of 2-bromo-3–methylbutyric acid in the gas phase to find: (a) whether the $(CH_3)_2CH$ in place of CH_3 in 2-bromobutyric acid stabilize C—Br bond polarization in the transition state for a faster rate, and (b) if the Cβ—H bond adjacent to the C—Br bond through hyperconjugation may compete in the HBr elimination and produce the corresponding unsaturated carboxylic acid.

Experimental

The substrate 2-bromo-3-methylbutyric acid of 99.9% purity (10% SP 1200 –1% H_3PO_4. Chromosorb W AW 80-100 mesh) was acquired from Aldrich. The pyrolysis products isobutyraldehyde (Aldrich), isobutene (Matheson), and propane (Matheson) were analyzed in a column of 5 ft. of Porapak Q 60–80 mesh, while CO and CO_2 in a 4 ft. column of Carbosive B 60–80 mesh. The HBr gas analysis was estimated by titration with a solution of 0.05N NaOH.

The identities of the substrate and products were confirmed with a mass spectrometer and by infrared and nuclear magnetic resonance spectroscopy.

The pyrolysis experiments of the bromoacid dissolved in chlorobenzene were carried out in a static system, seasoned with allyl bromide and in the presence of a free radical inhibitor cyclohexene. The rate coefficients were determined manometrically and/or by HBr titration. The temperature was found to be within ±0.2°C when measured

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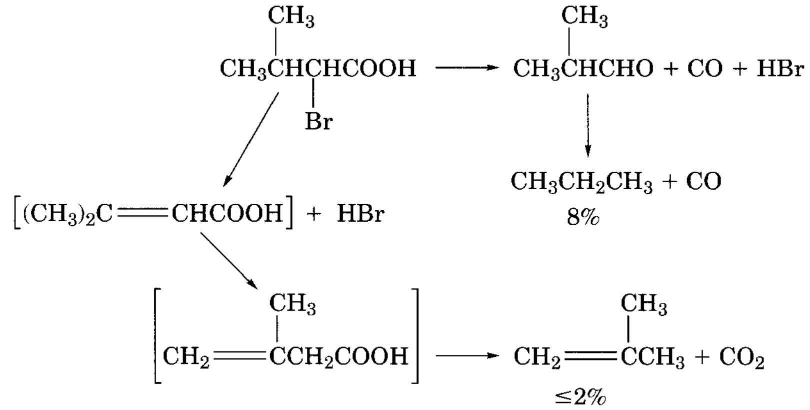
with a calibrated platinum-platinum-13% rhodium thermocouple and no temperature gradient was found in the reaction vessel. The substrate in chlorobenzene was injected directly into the reaction vessel with a syringe through a silicone rubber septum.

Results and Discussion

The experimental stoichiometry for reaction (1), in a static system seasoned with allyl bromide and maximally inhibited with cyclohexene, was examined by comparing the amount of decomposition of the bromo acid substrate calculated from pressure measurements with that obtained by titration of HBr with 0.05N sodium hydroxide solution (Table I).



Additional verification of the stoichiometry of eq. (1), was made by carrying out the pyrolysis process until no further pressure increase was observed. The average ratio of the final pressure, P_f, to the initial pressure, P_0, which should be equal to 3, was found at five different temperatures and ten half-lives to be a little greater than 3 (Table II). The small departure from the theoretical $P_f = 3P_0$ results from the small decomposition of the product isobutyraldehyde [eq. (1)].

2-Bromo-3-methylbutyric acid yielded, up to 45% reaction, mostly isobutyraldehyde, carbon monoxide, and HBr gas. However, small amounts of isobutene and propane were obtained [eq. (1)]. Isobutene may well be the result of a molecular decomposition process from the β-unsaturated carboxylic acid intermediate [2,3]. The α-unsaturated acid in the presence of HBr isomerize to the β-unsaturated acid. Pure isobutyraldehyde in HBr gas was found to give small amounts of propane and CO.

The homogeneity of this elimination was examined under the chain suppressor cyclohexene in a vessel with a surface-to-volume ratio of 6.0 cm^{-1} times greater than that of a normal vessel which is equal to one. The packed and unpacked clean Pyrex vessels showed a significant effect on the rates. However, when the packed and

TABLE I. Pressure change versus HBr titration at 329.4°C.

Time, min.	3	4	6	8	10
Reaction, % press.	16.0	20.7	28.7	34.7	41.9
HBr Titration, %	15.5	21.3	31.4	35.3	42.8

TABLE II. Ratio of final to initial pressure.[a]

Temp.,°C	P_0, torr	P_f, torr	P_f/P_0
320.7	54	174	3.22
329.4	46.5	166.5	3.24
339.0	53	171.5	3.27
350.3	62	203	3.27
357.0	60	203	3.38

[a] In the presence of cyclohexene inhibitor; the ratio of inhibitor to substrate is at least two.

unpacked vessels are seasoned with allyl bromide, no effect on the rate coefficients was obtained.

The effect of the free radical chain inhibitor cyclohexene is shown in Table III. Accordingly, the pyrolysis of the bromo acid in seasoned vessels had to be carried out in the presence of at least twice the amount of the inhibitor. No induction period was observed.

The rate coefficients determined in seasoned vessels and in the presence of the inhibitor are independent of the initial pressure of the substrate, and the first-order plots are satisfactorily linear to at least 45% decomposition (Table IV). The rate coefficients are reproducible with a standard deviation not greater than ±5% at a given temperature.

The variation of the first-order rate coefficient with temperature shown in Table V leads to the following Arrhenius equation, where 95% confidence coefficient are used: $\log k_1(\mathrm{s}^{-1}) = (12.72) \pm 0.25) - (181.8 \pm 2.9)\ \mathrm{kJ\ mol}^{-1}(2.303RT)^{-1}$.

Even though the isopropyl group in RCHBrCOOH (Table VI), increases the stabilization of the C—Br bond polarization, which is rate determining in the transition state, the acidity of the Cβ—H bond does not assist the HBr elimination. Consequently, a small formation of the unsaturated carboxylic acid and a high yield of isobutyraldehyde is obtained. The $(CH_3)_2CH$ in RCHBrCOOH increases the rate more than CH_3 as expected (Table VI). This work ratifies the dehydrobromination mechanism of 2-bromopropionic acid [1], which means that the polar five-membered cyclic transition state appears to be preferred in the dehydrohalogenation process of α-haloacids in the gas phase [1,4]. Thus,

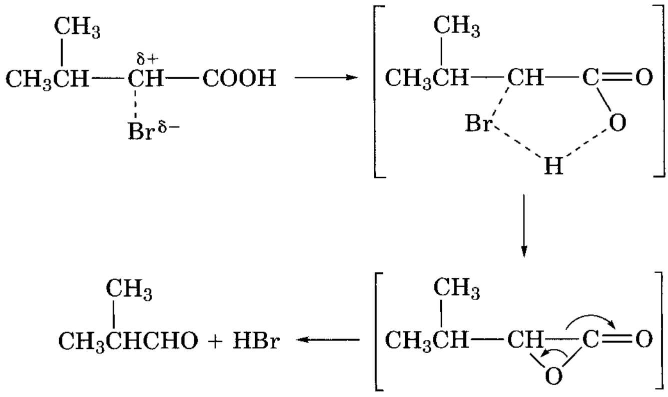


TABLE III. Effect of cyclohexene inhibitor on rates at 329.4°C.

P_s, torr	P_i, torr	P_i/P_s	$10^4k_1, s^{-1}$
59	–	–	12.51
83	53	0.6	9.08
114	73.5	1.1	9.08
75	191	2.6	8.88
49	161.5	3.3	8.98

P_s = Pressure of the substrate. P_i = pressure of the inhibitor.

TABLE IV. Invariability of rate coefficient with initial pressure at 339.0°C.

P_0, torr	15.5	37.5	69.0	100.0
$10^4k_1, s^{-1}$	15.92	16.10	16.02	15.90

TABLE V. Variation of the rate coefficient with temperature.

Temp.,°C	309.3	320.7	329.4	339.0	350.3	357.0
$10^4k_1, s^{-1}$	2.57	5.46	9.01	15.92	30.43	44.86

TABLE VI. Kinetic parameters for the pyrolysis of RCHBrCOOH at 350°C.

R	$10^4k_1, s^{-1}$	E_a, kJ/mol	log A, s^{-1}	Ref.
CH_3	19.64	180.3 ± 3.4	12.41 ± 0.29	[1]
$(CH_3)_2CH$	30.02	181.8 ± 2.9	12.72 ± 0.25	this work

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