

MAXIMALLY INHIBITED ELIMINATION OF KINETICS OF (2-BROMOETHYL)BENZENE AND 1-BROMO-3-PHENYLPROPANE IN THE GAS PHASE. ANCHIMERIC ASSISTANCE OF THE PHENYL GROUP

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The gas-phase elimination kinetics of (2-bromoethyl)benzene and 1-bromo-3-phenylpropane were studied in a static system and seasoned vessels over the temperature range 390–450 °C and the pressure range 32–104 Torr. The reactions, under maximum inhibition of 4-fold pressure of the free-radical suppressor cyclohexene and/or propene, are homogeneous, unimolecular and obey a first-order rate law. The rate coefficients are given by the following Arrhenius equations: for (2-bromoethyl)benzene, $\log k_1 \text{ (s}^{-1}\text{)} = (13.04 \pm 0.10) - (210.8 \pm 1.3) \text{ kJ mol}^{-1} (2.303RT)^{-1}$, and for 1-bromo-3-phenylpropane, $\log k_1 \text{ (s}^{-1}\text{)} = (14.09 \pm 0.27) - (227.7 \pm 3.6) \text{ kJ mol}^{-1} (2.303RT)^{-1}$. The phenyl group of (2-bromoethyl)benzene appears to provide anchimeric assistance in the HBr elimination of this compound. However, neighbouring C₆H₅ participation at the 3-position in 1-bromo-3-phenylpropane for a C-4 conformation is apparently absent. The mechanisms of these reactions are discussed.

INTRODUCTION

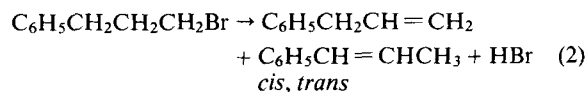
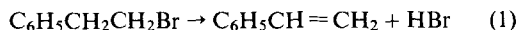
The first-order specific rate of the unimolecular gas-phase elimination of (2-bromoethyl)benzene has been determined at only one temperature, and was found to be $0.85(\pm 0.07) \times 10^{-4} \text{ s}^{-1}$ at 385.5 °C.¹ In a later study,² the pyrolysis of this compound in a flow reactor gave a frequency factor and activation energy of $13-189\,000/2.3RT^2$. In comparing the rate coefficient calculated from this equation with that at a single temperature, the reaction rate was found to be faster by a factor of about 120. Such a large difference in rate was believed to arise not only from the unimolecular elimination but probably also from some heterogeneous effect of the surface of the reactor.

The presence of a phenyl group at the 2-position of ethyl chloride, i.e. (2-chloroethyl)benzene, has been found to provide anchimeric assistance in the dehydrochlorination process.³ The rate coefficient was higher by a factor of 8.8 with respect to the *k* value of ethyl chloride. However, when the single *k* value of (2-bromoethyl)benzene of $0.85 \times 10^{-4} \text{ s}^{-1}$ at 385.5 °C is compared with the estimated rate for the corresponding unsubstituted ethyl bromide,⁴ the increase by a factor of 3.8 may also suggest participation of the neighbouring phenyl group. An interesting observation is that the rate ratio of (2-bromoethyl)benzene to ethyl bromide was found to be lower than that of

(2-chloroethyl)benzene to ethyl chloride.³ This difference was not rationalized, because the pyrolysis of (2-bromoethyl)benzene was determined at only one temperature. In view of the above facts, in this work we sought to establish if it was possible to examine the complete pyrolysis kinetics of (2-bromoethyl)benzene and the effect of a phenyl group remote to the reaction centre by interposition of a methylene group, that is, in 1-bromo-3-phenylpropane.

RESULTS AND DISCUSSION

The stoichiometries described by the reactions



in seasoned vessels and under maximum inhibition of cyclohexene, require that the final pressure, *P_f*, should be twice the initial pressure, *P₀*. The average experimental *P_f*/*P₀* values at four different temperatures and ten half-lives were 1.98 for (2-bromoethyl)benzene and 1.81 for 1-bromo-3-phenylpropane (Table 1). The departure of *P_f* = 2*P₀* from equation (2) is due to a small extent of polymerization of the olefinic products. To verify the stoichiometry of equation (1) up to

Table 1. Ratio of final (P_f) to initial pressure (P_0)^a

Compound	Temperature (°C)	P_0	P_f	P_f/P_0
(2-Bromoethyl)benzene	410	45	88	1.96
	420	50	99.5	1.99
	430	59.5	118.5	1.99
	440	42	83	1.98
1-Bromo-3-phenylpropane	400	65.8	109	1.66
	410	65.5	115.5	1.76
	430	75.5	142	1.88
	440	72.5	137.5	1.90

^a In the presence of cyclohexene and/or propene.

70% reaction and that of equation (2) up to 55% reaction, the percentage decomposition of the bromide substrate obtained from pressure measurements was examined and was found to be in good agreement with that calculated from hydrogen bromide titration with a solution of 0.05 M NaOH (Table 2).

At any working temperature, (2-bromoethyl)benzene, up to 70% decomposition, yielded styrene and HBr gas [equation (1)] whereas 1-bromo-3-phenylpropane, up to 55% reaction, gave 33% 3-phenyl-1-propene, 9.5% *cis*-1-phenyl-1-propene and 57.2% *trans*-1-phenyl-1-propene [equation (2)]. The primary product 3-phenyl-1-propene [equation (2)], when heated at a given temperature in the presence of HBr and under maximum inhibition of cyclohexene, isomerized to

about the same olefinic distribution obtained in reaction (2), i.e. 30.4% 3-phenyl-1-propene, 10.1% *cis*-1-phenyl-1-propene and 59.4% *trans*-1-phenyl-1-propene. The latter result suggests that the primary olefin product 3-phenyl-1-propene from the pyrolysis of 3-bromo-1-phenylpropane [equation (2)] appears to isomerize in the presence of HBr gas until an equilibrium is reached.

The homogeneity of these eliminations was examined with the inhibitor cyclohexene and in a vessel with a surface-to-volume ratio of six times greater than that of the normal vessel, which is equal to 1 (Table 3). The packed and unpacked clean Pyrex vessels had a marked effect on the rates. However, when the packed and unpacked vessels were seasoned with allyl bromide, no significant effect on the rate was obtained. The kinetic determination of these bromides, in seasoned vessels, had to be carried out in the presence of at least a 4-fold pressure of cyclohexene to inhibit any possible free-radical chain processes of the reactant and/or products (Table 4). The rate coefficients are reproducible with a standard deviation not greater than 5% at a given temperature.

The rate coefficients were invariant with changes in the initial pressure of the substrate (Table 5) and the first-order plots are satisfactorily linear to 55–70% decomposition. The variation of the rate coefficient with temperature is shown in Table 6.

Table 7 gives the Arrhenius parameters for the bromides calculated by a linear least-squares procedure. Errors are 95% confidence limits.

Table 2. Pressure measurements versus titration^a

Compound	Temperature (°C)	Parameter	Values						
(2-Bromoethyl)benzene	420	Time (min)	2.5	5	10	15			
		Reaction (%) (pressure)	23.0	37.3	56.0	75.6			
		HBr (%) (titration)	24.0	37.2	56.1	71.9			
1-Bromo-3-phenylpropane	410	Time (min)	2.5	5	10	15	20	25	30
		Reaction (%) (pressure)	8.8	14.2	27.4	37.2	46.5	48.0	57.8
		HBr (%) (titration)	8.9	14.8	27.3	37.2	45.4	48.0	54.7

^a In the presence of at least a 4-fold pressure of cyclohexene.

Table 3. Homogeneity of the reaction^a

Compound	Temperature (°C)	S/V (cm ⁻¹)	$10^4 k_1$ (s ⁻¹) ^b	$10^4 k_1$ (s ⁻¹) ^c
(2-Bromoethyl)benzene	420	1	14.18	101.43 ^d
		6	14.20	181.30 ^d
1-Bromo-3-phenylpropane	410	1	5.15	104.73 ^d
		6	5.54	127.51 ^d

^a In the presence of a 4-fold pressure of cyclohexene inhibitor.

^b Allyl bromide seasoned.

^c Clean Pyrex.

^d Average k value.

Table 4. Effect of cyclohexene inhibitor on rates at 410 °C

Compound	P_0^a	P_i^a	P_i/P_0	$10^4 k_1$ (s ⁻¹)
(2-Bromoethyl)benzene	101.5	—	—	202.9 ^b
	120.5	208	1.7	10.99
	103	269	2.6	10.03
	89.5	333	3.7	9.93
	74	356.5	4.8	8.44
	79	431.5	5.5	8.34
1-Bromo-3-phenylpropane	78.5	—	—	16.20 ^b
	193.5	168	0.9	6.75
	103.6	250	2.4	4.92
	69	280	4.1	4.90
	62.7	292	4.7	4.46
	63.5	383	6.0	4.40

^a P_0 = pressure of the aromatic halide; P_i = pressure of the cyclohexene inhibitor.

^b Average k value.

Table 5. Invariability of the rate coefficient with initial pressure^a

Compound	Temperature (°C)	Parameter	Values					
(2-Bromoethyl)benzene	420	P_0 (Torr)	50.5	58.5	64.0	73.5	81.5	101.5
		$10^4 k_1$ (s ⁻¹)	14.68	14.55	14.45	14.22	14.84	14.72
1-Bromo-3-phenylpropane	410	P_0 (Torr)	32.0	62.7	69.0	82.5	103.6	
		$10^4 k_1$ (s ⁻¹)	4.40	4.56	4.90	4.89	4.92	

^a In the presence of at least a 4-fold pressure of cyclohexene inhibitor.

Table 6. Temperature dependence of rate coefficient

Compound	Parameter	Values						
(2-Bromoethyl)benzene	Temperature (°C)	400	410	420	430	440		
	$10^4 k_1$ (s ⁻¹)	4.72	8.34	14.18	23.87	39.98		
3-Bromo-1-phenylpropane	Temperature (°C)	390	400	410.2	420.1	430.1	440	450
	$10^4 k_1$ (s ⁻¹)	1.41	2.66	4.64	8.69	15.55	26.26	42.36

Table 7. Arrhenius parameters of phenylalkyl bromides

Compound	Log A (s ⁻¹)	E_a (kJ mol ⁻¹)
C ₆ H ₅ CH ₂ CH ₂ Br	13.04 ± 0.18	210.8 ± 2.4
C ₆ H ₅ CH ₂ CH ₂ CH ₂ Br	14.09 ± 0.46	222.7 ± 6.1

The rate of dehydrobromination of (2-bromoethyl)benzene is significantly higher than that of the corresponding unsubstituted ethyl bromide (Table 8). This result appears to confirm that the neighbouring phenyl group is providing anchimeric assistance to the elimination in a similar way to that found in the pyrolyses of

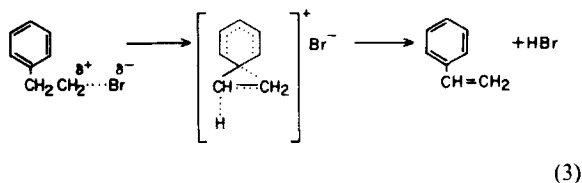
(2-chloroethyl)benzene³ and ω -phenylalkyl chlorides.³ A possible objection to this interpretation in the sense that the conjugative stabilization by the phenyl group causes a faster rate may be refuted as before.³ The present finding obviates the uncertainties arising from the argument derived in the pyrolysis of (2-bromoethyl)benzene.^{1,3} In addition to this consideration, when the position of the phenyl substituent ($\sigma^* = 0.60$)⁷ is projected on the recently reported Taft correlation of the log $k_{rel.}$ of polar 2-substituted ethyl bromides, i.e. ZCH₂CH₂Br against σ^* values,⁸ the plot of C₆H₅ position is far above the slope of the line. Therefore, participation of the C₆H₅ group at the 2-position of ethyl bromide for a C-3 conformation is favoured. However, the plot of C₆H₅CH₂ as Z

Table 8. Comparative parameters at 420°C

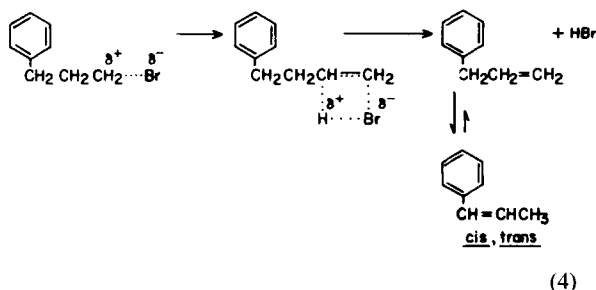
Compound	$10^4 k_1$ (s^{-1})	Relative rate per H	E_a ($kJ\ mol^{-1}$)	Log A (s^{-1})	Ref.
CH ₃ CH ₂ Br	1.82	1.0	224.6	13.19	5
C ₆ H ₅ CH ₂ CH ₂ Br	14.16	11.6	210.8 ± 2.4	13.04 ± 0.18	This work
CH ₃ CH ₂ CH ₂ Br	8.18	6.7	212.1	12.90	6
C ₆ H ₅ CH ₂ CH ₂ CH ₂ Br	8.46	6.9	227.7 ± 6.1	14.09 ± 0.46	This work

($\sigma^* = 0.215$) in ZCH₂CH₂Br, i.e. 3-bromo-1-phenylpropane, falls very close to the slope of the line for polar substituted ethyl bromide pyrolyses.⁸ This means that participation of the C₆H₅ at the 3-position of n-propyl bromide for a C-4 conformation in neighbouring group participation is apparently absent.

The mechanism for phenyl participation may be explained, as already advanced,^{3,9,10} in terms of an intimate ion pair by intramolecular solvation of the leaving bromide ion:



With regard to the mechanism of the gas-phase elimination of 3-bromo-1-phenylpropane, the reaction appears to proceed through the normal four-membered cyclic transition state:



EXPERIMENTAL

(2-Bromoethyl)benzene. The fraction of 99.5% purity of this substrate (Aldrich)(GLC: diisodecyl phthalate

5%—Chromosorb G AW DMCS, 60–80 mesh, or 10% Down Corning 200/100—Chromosorb W AW DMCS, 80–100 mesh) was used. Styrene was analysed in the Down Corning column.

1-Bromo-3-phenylpropane. This compound (Aldrich) was used when 98.6% pure after distillation (GLC: 10% OV-101 Gas—Chromosorb QII, 80–100 mesh). 3-Phenyl-1-propene and *cis*- and *trans*-1-phenyl-1-propene were analysed in the same OV-101 column.

The pyrolysis experiments were carried out in a static system, with a vessel seasoned with allyl bromide and in the presence of at least a 4-fold pressure of the inhibitor cyclohexene. The kinetics were followed manometrically and the temperature kept within $\pm 0.2^\circ\text{C}$ by means of a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was found along the reaction vessel.

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