206 J. Phys. Chem. 1989, 93, 206-208

Pyrolysis Kinetics of 2-Bromobutane and 2-Bromopentane in the Gas Phase

Gabriel Chuchani,* Rosa M. Domínguez, Alexandra Rotinov, and Ignacio Martín

Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado No. 21827, Caracas 1020-A, Venezuela *(Received: March 28, 1988; In Final Form: June 3, 1988)*

The kinetics of the gas-phase pyrolysis of 2-bromobutane and 2-bromopentane were determined in a static system over the temperature range of 310–360 °C and the pressure range of 40–180 Torr. The reactions in seasoned vessels, and in the presence of a free-radical inhibitor, are homogeneous, are unimolecular, and follow a first-order rate law. The temperature dependence of the rate coefficients is given by the following Arrhenius equations: for 2-bromobutane, log k_1 (s^{-1}) = (13.04 ± 0.05) − (188.3 ± 0.6) kJ mol^{-1} (2.303RT)$^{-1}$; for 2-bromopentane, log k_1 (s^{-1}) = (13.08 ± 0.23) − (187.0 ± 2.7) kJ mol^{-1} (2.303RT)$^{-1}$. The olefin products appear to rapidly isomerize in the presence of HBr gas until an equilibrium is reached. The elimination kinetics of these compounds suggest that the effect of the alkyl groups R in $RCHBrCH_3$ is polar (+I electron release).

Introduction

Few different secondary bromoalkane molecules have been pyrolyzed in the gas phase. In this respect, only unsubstituted isopropyl bromide[1–5] and 2-bromobutane[6–9] have been reported. The fact that alkyl bromides have not been extensively investigated in gas-phase elimination may be due to the experimental difficulty arising from a concurrent process of unimolecular and free-radical types of mechanisms. However, if the pyrolysis of organic bromides is carried out under maximum inhibition in a well-seasoned reaction vessel, the rates are that of molecular elimination.[10]

Since the analysis of isomeric butene products from the pyrolysis of 2-bromobutane was not made previously, this work aimed at examining the elimination kinetics of this compound, together with a consideration of which factor intervenes in the direction of elimination of butene formation. To obtain additional data concerning the direction of elimination of secondary bromoalkanes, the pyrolysis kinetics of 2-bromopentane were also examined.

Experimental Section

2-Bromobutane and 2-bromopentane were bought from Aldrich. These halide substrates were distilled several times, and the fraction with over 99.1% purity (gas–liquid chromatography) was used (dinonyl phthalate 20%–gas Chromosorb Q AW DMCS 60–80 mesh and diisodecyl phthalate 5%–Chromosorb G AW DMCS 60–80 mesh). 1-Butene and *cis*- and *trans*-2-butene were acquired from Matheson, whereas 1-pentene was obtained from Phillips and *cis*- and *trans*-2-pentene from K & K Labs. A column of picric acid 19%–Carbopack C 80–100 mesh was used for the quantitative analyses of the butenes, while a 24-ft column of bis(2-methoxyethyl) adipate 20%–Chromosorb P was used for the pentenes. The identities of the substrates and olefins were additionally checked by nuclear magnetic resonance spectroscopy.

The bromides were pyrolyzed in a static system and in the presence of the free-radical suppressor cyclohexene. The reaction vessel was cylindrical and had a volume of 397 cm^3. This vessel was seasoned with allyl bromide, and the rate coefficients were determined manometrically. The temperature was maintained within ±0.2° C with a calibrated iron constantan thermocouple. No temperature gradient was found in the reaction vessel.

TABLE I: Stoichiometry of the Reaction

	2-Bromobutane at 350.0 °C				
time, min	2	3	4	5	7
reaction, % (press)	18.5	28.0	35.3	40.9	51.5
reaction, % (chrom)	17.6	29.0	36.1	39.5	50.6
	2-Bromopentane at 340.3 °C				
time, min	4	7	10	13	16
reaction, % (press)	28.9	43.5	56.7	66.1	74.7
reaction, % (chrom)	28.8	43.1	57.0	67.1	76.5

TABLE II: Homogeneity of the Reaction

S/V, cm^{-1}	10^4k_1, s^{-1} [a]	10^4k_1, s^{-1} [b]
	2-Bromobutane at 330.0 °C	
1	6.38	5.30
6	7.66	5.34
	2-Bromopentane at 342.0 °C	
1	92.0[c]	15.81
6	190.0[c]	15.90

[a] Clean Pyrex vessel. [b] Vessel seasoned with allyl bromide. [c] Average k value.

TABLE III: Distribution (%) of Olefin[a]

2-Bromobutane

temp, °C	1-butene	*cis*-2-butene	*trans*-2-butene
319.9	32.5	26.3	41.2
339.9	36.9	24.4	38.8
360.0	37.0	24.2	38.2
	35.5[c]	25.0[c]	39.4[c]

2-Bromopentane

temp, °C	1-pentene	2-pentene[b]
310.1	19.7	80.3
330.0	22.5	77.6
340.3	19.6	80.3
	20.6[c]	79.4[c]

[a] Vessel S/V = 1, seasoned with allyl bromide and in the presence of the inhibitor cyclohexene. [b] The cis and trans isomers could not be separated well in the chromatographic analyses. [c] Average value.

Results and Discussion

The pyrolyses of secondary alkyl bromides performed in vessels seasoned by the decomposition of allyl bromide would be expected to follow the reaction

$$C_nH_{2n+1}Br \rightarrow \underset{\text{isomers}}{C_nH_{2n}} + HBr \qquad (1)$$

The stoichiometry of eq 1 was checked by measurements of the ratio of final, P_f, to initial pressure, P_0. The average experimentals results at four different temperatures and ten half-lives were 1.95 for 2-bromobutane and 1.92 for 2-bromopentane. The observed slight departure from the required stoichiometry of $P_f = 2P_0$ may

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TABLE IV: Yield (%) of Olefin Formation from Percentage Reaction of the Alkyl Bromide at One Temperature

2-Bromobutane at 339.9 °C

reaction, %	1-butene	*cis*-2-butene	*trans*-2-butene
17.2	40.5	22.3	37.2
26.9	39.1	23.4	37.6
34.5	37.8	24.4	37.8
45.8	36.9	24.4	38.8
	38.6[b]	23.6[b]	37.9[b]

2-Bromopentane at 340.3 °C

reaction, %	1-pentene	2-pentene[a]
28.0	18.5	81.5
45.0	20.0	80.1
66.1	19.8	80.2
75.0	19.6	80.5
	19.5[b]	80.6[b]

[a] Mixture of cis and trans isomer. [b] Average value.

TABLE V: Isomerization (%) of the Olefin Products in a Seasoned Vessel of $S/V = 1$ in the Presence of HBr Gas

olefin	temp, °C	1-butene	*cis*-2-butene	*trans*-2-butene
1-butene	319.9	29.5	25.9	44.7
	339.9	31.7	26.1	41.8
	360.0	38.6	24.2	37.2
		33.3[b]	25.4[b]	41.2[b]
cis-2-butene	319.9	23.0	32.2	44.8
	339.9	26.4	31.4	42.3
	360.0	22.3	30.6	47.1
		23.9[b]	31.4[b]	44.7[b]
trans-2-butene	319.9	19.8	27.0	53.2
	339.9	23.3	29.8	46.9
	360.0	19.1	30.5	50.4
		20.7[b]	29.1[b]	50.2[b]

olefin	temp, °C	1-pentene	2-pentene[a]
1-pentene	310.1	95.5	4.5
	330.0	96.6	3.4
	360.0	99.8	0.2
		97.3[b]	2.7[b]
2-pentene[a]	310.1	4.0	96.0
	330.0	2.1	98.0
	360.0	0.3	99.7
		2.1[b]	97.9[b]

[a] Mixture of cis and trans isomers. [b] Average value.

well be due to a small polymerization of the olefin products. To confirm the above stoichiometry, the percentage decomposition of the secondary alkyl bromide obtained from pressure measurements was found to be in good agreement with the chromatographic analyses of the reacted amount of the halide substrate (Table I). 2-Bromobutane, up to 50% reaction, yielded 1-butene and *cis*- and *trans*-2-butene, whereas 2-bromopentane, up to 75% decomposition, gave mostly *cis*- and *trans*-2-pentene and a small amount of 1-pentene.

The homogeneity of these eliminations was examined by using vessels with a surface-to-volume ratio factor of 6.0, greater than that of the unpacked vessel, which is equal to 1 (Table II). The rate was unaffected in seasoned vessels, yet a significant effect was found in clean packed and unpacked Pyrex vessels.

The analysis of the pyrolysis products of the bromides in an unpacked seasoned vessel and in the presence of the inhibitor cyclohexene are given in Table III.

Apparently, the percentage of olefin distribution, within the limits of experimental error, do not change at the pyrolysis temperature. Further examination of whether or not the formation of these olefins is invariable as the reaction progresses at a working temperature was performed. The data of Table IV seem to confirm the results of Table III.

Tables III and IV appear to indicate that the formation of the olefins from the gas-phase pyrolysis of these secondary alkyl bromides may either proceed by kinetic control, or result from a very fast isomerization until an equilibrium is reached during decomposition. To gain a better understanding of this process, each available pure olefin product was introduced under experimental conditions into the reaction vessel in the presence of HBr gas and the inhibitor cyclohexene at different temperatures (Table V). Each of the butenes undergoes isomerization, while 1- and 2-pentenes do so to a very insignificant amount. The absence or presence of an equilibrium process among these alkyl bromides had to be estimated by an approximate calculation using the thermodynamic additivity table[11] at 613.15 K (340 °C) (Table VI).

TABLE VI: Equilibrium Mixture from Thermodynamic Group Additivity at 603.15 K (330 °C)[a]

1-butene	*cis*-2-butene	*trans*-2-butene
16.7	31.5	51.8
1-pentene	*cis*-2-pentene	*trans*-2-pentene
10.9	41.3	47.8

[a] Reference 11.

TABLE VII: Effect of the Cyclohexene Inhibitor on Rates[a]

P_s, Torr	P_i, Torr	P_i/P_s	10^4k_1, s^{-1}
2-Bromobutane at 339.9 °C			
96.5			9.72
107.0	185.0	1.7	9.86
112.0	301.5	2.7	9.93
2-Bromopentane at 349.8 °C			
75.5			24.88
72.0	73.5	1.0	24.84
58.0	159.5	2.8	24.67
43.0	183.0	4.3	24.97

[a] P_s is pressure of the substrate. P_i is pressure of the inhibitor.

TABLE VIII: Invariability of the Rate Coefficients with Initial Pressure

2-Bromobutane at 360.0 °C

P_0, Torr	61.0	84.5	112.0	131.0
10^4k_1, s^{-1}	32.11	31.88	32.16	31.46

2-Bromopentane at 340.3 °C

P_0, Torr	40.0	52.0	92.0	121.0	180.0
10^4k_1, s^{-1}	13.94	14.05	14.11	14.13	13.96

TABLE IX: Variation of Rate Coefficients with Temperature

2-Bromobutane

temp, °C	319.9	330.0	339.9	349.8	360.0
10^4k_1, s^{-1}	2.86	5.40	9.98	17.81	32.16

2-Bromopentane

temp, °C	310.1	320.0	330.0	340.3	349.8	360.0
10^4k_1, s^{-1}	2.21	4.06	7.51	14.05	25.02	46.13

TABLE X: Arrhenius Parameters of the Bromides

substrate	log A, s^{-1}	E_a, kJ/mol
$CH_3CH_2CHBrCH_3$	13.04 ± 0.05	188.3 ± 0.6
$CH_3CH_2CH_2CHBrCH_3$	13.08 ± 0.23	187.0 ± 2.7

In regard to the results described in Tables III–VI, the olefin products from the pyrolysis of 2-bromobutane and 2-bromopentane appear to be rapidly isomerized by the HBr acting as a catalyst until the equilibrium of the process is reached.

The lack of a free-radical process in these reactions was investigated by carrying out several runs in the presence of different proportions of the inhibitor cyclohexene (Table VII).

The rates of pyrolysis elimination are independent of the initial pressures of the bromides, and the first-order plots are satisfactorily linear up to 50–75% decomposition (Table VIII). The temperature dependence of the reaction is shown in Table IX. The rate coefficients are reproducible with a standard deviation not greater than ±5% at a given temperature. Table X shows the

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TABLE XI: Kinetic Parameters of $RCHBrCH_3$ at 340.0 °C (613.15 K)

R	10^4k_1, s^{-1}	E_a, kJ/mol	log A, s^{-1}	ref
CH_3	3.86	199.9	13.62	3
CH_3CH_2	10.46[a]	183.2	12.63	6
		195.8[b]		6
	6.09[a]	190.3	13.00	7
		198.6[b]		7
	9.23[a]	194.4	13.53	8
		196.3[b]		8
	8.87[a]	196.6	13.70	9
	9.88	188.3 ± 0.6	13.04 ± 0.05	*c*
		196.1[b]		*c*
$CH_3CH_2CH_2$	13.99	187.0 ± 2.7	13.08 ± 0.23	*c*
		194.2[b]		*c*

[a] Analysis of isomeric butene products was not made. [b] This E_a value results from adjusting the A factor to 13.7. [c] This work.

Arrhenius parameters obtained by using the least-squares procedure. The errors were estimated to 80% confidence limits.

Adjusting the A factor of this work to 13.70[9] as well as those from ref 6–8 (Table XI) would raise the energy of activation E_a to about 196 kJ/mol, which is in good agreement with the work reported in ref 9.

The literature cites a work of Maccoll and Ross on the kinetics of the hydrogen bromide catalyzed isomerization of 1-butene to 2-butene in the gas phase.[12] As a difference from that work, the present study aimed to investigate which factor affects the dehydrobromination process during elimination of some secondary alkyl bromides. Since the olefin formation from the pyrolyses of 2-bromobutane and 2-bromopentane does not proceed by kinetic control (Tables III–V), an adequate assessment of the factor by which either the R or CH_3 group in $RCHBrCH_3$ (Table XI) affects the direction of elimination is not feasible. However, an increase of R from CH_3 to $CH_3CH_2CH_2$ in $RCHBrCH_3$ leads to a small augmentation in the overall rate (Table XI). Such a result suggests that the effect of the alkyl groups is polar (+I electron release), thus stabilizing the C–Br bond polarization, in the direction of $C^{\delta+}\ldots Br^{\delta-}$, in the transition state. This argument is associated with the results of the alkyl substituent effect in the pyrolysis of primary alkyl bromides in the gas phase, where a good correlation of log k/k_0 against σ^* values was obtained.[13]

Acknowledgment. We are grateful to the Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT) for support of Project No. 51.78.31, S1-1072.

Registry No. HBr, 10035-10-6; 2-Bromobutane, 78-76-2; 2-bromopentane, 107-81-3; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 1-pentene, 109-67-1; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8.

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Geminate Recombination Kinetics of Triplet Radical Pairs in Glycerol: Magnetic Field Effect

Peter P. Levin, Igor V. Khudyakov,* and Vladimir A. Kuzmin

Institute of Chemical Physics, Academy of Sciences of the USSR, 117334 Moscow, U.S.S.R.

(Received: November 11, 1987; In Final Form: April 8, 1988)

Laser flash technique has been used to record the geminate recombination kinetics of triplet radical pairs (RP) generated from benzophenone photoreduced with *p*-cresol in the viscous glycerol/*p*-cresol binary solvent. The RP decay kinetics fits fairly into the first-order law. At the same time the kinetics curve features a manifest slow descending "tail" that follows the $\varphi_\infty - \varphi(t) \sim t^{-1/2}$ relationship, where φ_∞ is the (total) cage effect and $\varphi(t)$ is the time-dependent cage effect. The geminate recombination kinetics is closely described in the entire time range ($0 \leq t \lesssim 10$ μs) by the function originating from Noyes' treatment of molecular dynamics, $\varphi(t) = \varphi_\infty \operatorname{erfc} (k_N t^{-1/2})$, where k_N is a constant. An increase of solvent viscosity (decrease of temperature) causes an increase of φ_∞ and deceleration of RP dissociation. The geminate recombination kinetics is described by mutual diffusion coefficients smaller than the sum of the diffusion coefficients of individual radicals. The probable reason of such behavior is that there is a strong correlation between the molecular motions of radicals positioned within several molecular diameters from each other. Application of an external magnetic field ($H \leqslant 0.34$ T) results in inhibited geminate recombination and decrease in φ_∞ by 10–50%. The extent of the magnetic effect heavily depends on H when $H \lesssim 0.1$ T and is practically independent of H when $0.1 \lesssim H \leqslant 0.34$ T. The mechanisms of the singlet–triplet evolution of the investigated RP and the magnetic effect are discussed. The S–T evolution of RP proceeds via the four mechanisms: in a separated pair the hyperfine coupling (hfc), Δg, and the relaxation mechanisms are active; in contact RP the spin–orbit coupling mechanism dominates. The latter mechanism is more or less effective in the entire range of field strengths. For $H \lesssim 0.1$ *T*, the magnetic field acts by the hfc mechanism and by slowing the paramagnetic relaxation due to the hfc anisotropy and dipole–dipole coupling between unpaired electrons.

Introduction

The dynamics of the cage effect in liquids has been attracting invariable attention of both theoreticians and experimenters (cf., e.g., ref. 1–6). Quite a few theories have been proposed to account for the cage effect,[1-5] but the situation is aggravated by scarcity of the relevant data that is also often too inaccurate. The pioneering work[7] on geminate recombination of iodine atoms invoked considerable interest. Later it was found however that the observed

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