Mechanism of the Pyrolysis of 3-Bromopentane

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Received 9th January, 1967

The gas-phase dehydrobromination of 3-bromopentane has been shown to be a homogeneous first-order reaction, unaffected by the presence of cyclohexene. The rate constants follow the Arrhenius equation $k_1 = 10^{13 \cdot 51} \exp(-45{,}440/RT)$. These observations are consistent with a molecular mechanism but not with the chain mechanism for bromide pryolysis proposed by Wojciechowski and Laidler.

Wojciechowski and Laidler [1] have proposed a general chain mechanism for the pyrolysis of organic bromides, which they claim explains the observed kinetic order in the uninhibited elimination reactions of the butyl bromides, though they make no attempt to explain the behaviour in the presence of cyclohexene. Their scheme is in direct contradiction to the unified molecular theory of halide pyrolysis formulated as the result of experimental studies over a period of years.[2] The object of the present work is to attempt to decide between the two possibilities; the pyrolysis of 3-bromopentane provides a possible test. The scheme proposed by Wojciechowski and Laidler involves surface initiation and termination (using their nomenclature):

$$\mathrm{M+S \rightarrow R+SBr} \quad (1)$$

$$\mathrm{SBr \rightarrow S+Br} \quad (2)$$

$$\mathrm{Br+M \rightarrow HBr+L} \quad (3)$$

$$\mathrm{L+M \rightarrow T+M} \quad (4)$$

$$\mathrm{T \rightarrow Br+M'} \quad (5)$$

$$\left.\begin{array}{l}\mathrm{L+SBr} \quad (6)\\ \mathrm{T+SBr} \quad (7)\end{array}\right\} \rightarrow \text{termination of chains,}$$

where M is parent bromide, S is surface sites, R is an alkyl radical, L and T are bromoalkyl radicals and M′ the olefin product. The L and T radicals are the same as S and P radicals postulated by Maccoll and Thomas,[3] the L radical is one that cannot directly form the olefin by eliminating the bromine atom, i.e., a radical that is formed by hydrogen abstraction from a position other than the β-carbon atom. The T radical can eliminate the bromine atom to continue the chain. Their scheme ignores the possibility of the prefential formation of a T radical in step (3). The authors claim that if chain termination occurs via (6), the overall order will be 1·5; if via (7), unity, though how they deal with S and SBr in the steady-state treatment is not clear. They further postulate that the free radical involved in termination will be that in which the odd electron is located on the terminal atom. Thus in the present case, the terminating radical will be $CH_3CH_2CHBrCH_2\dot{C}H_2$, which is an

L radical. Hence on the basis of the W-L scheme, the reaction should be of order 1·5. The present study shows it unambiguously to be of order one.

EXPERIMENTAL

No previous work on 3-bromopentane has been reported. The experimental methods used have been described.[4] The stoicheiometry of the reaction

$$C_5H_{11}Br \rightarrow C_5H_{10} + HBr \qquad (A)$$

was confirmed by allowing various initial pressures of substrate to decompose for several half-lives and then determining the ratio of final to initial pressure. This led to an average value of 1·86, consistent with scheme (A) when it is remembered that the dead space in the apparatus (not greater than 4 % of the reactor volume), any reverse reaction and olefin polymerization tend to reduce the ratio compared with the expected value of 2·00. First-order rate constants calculated from $k_1 = t^{-1} \ln [p_0/(2p_0 - P_t)]$, where P_t is the total pressure

TABLE 1.—EFFECT OF VARYING INITIAL PRESSURE

T = 316·1°C		T = 337·2°C (packed vessel)	
p_0 (mm)	$10^4\,k_1$ (sec^{-1})	p_0 (mm)	$10^3\,k_1$ (sec^{-1})
73·5	4·73	116·9	1·70
81·0	4·53	121·0	1·64
91·5	4·45	128·4	1·64
98·9	4·59	165·0	1·74
108·7	4·63	190·3	1·74
118·3	4·62		

TABLE 2.—EFFECT OF ADDED CYCLOHEXENE

	T = 301·4°C			T = 316·1°C	
p_0 (mm)	p_i^* (mm)	$10^4\,k_1$ (sec^{-1})	p_0 (mm)	p_i^* (mm)	$10^4\,k_1$ (sec^{-1})
86·0	34·5	2·05	41·5	109·1	4·68
78·0	26·8	2·24	61·2	63·0	4·52
87·8	66·0	2·10	65·3	75·2	4·76
91·8	36·8	2·27	71·9	95·6	4·65

*p_i is the pressure of cyclohexene

The temperature variation of k_1 (table 3) leads to the Arrhenius equation,

$$k_1 = 10^{13\cdot51} \exp(-45{,}440/RT)\ (\text{sec}^{-1}).$$

TABLE 3.—EFFECT OF TEMPERATURE ON RATE CONSTANTS

T (°C)	347·8	337·7	327·4	316·1	307·4	296·4	285·8
No. of runs	5	5	5	6	5	5	5
$10^5\,k_1$ (sec^{-1})	336	179	100	45·9	22·6	12·3	5·83

As will be shown, the values of the Arrhenius parameters are consistent with those reported for other secondary bromides.

at time t and p_0 the initial pressure, showed no trend with initial pressure (table 1) in either the empty or packed reaction vessel. Increasing the surface-to-volume ratio from ~1 to ~5 cm^{-1} had no effect on the rate of reaction, since the mean value of $10^3\,k_1$ (337·2°C, table 1) is 1·69 sec^{-1} (packed vessel) compared with 1·71 sec^{-1} calculated from the Arrhenius equation. The reaction is thus homogeneous and follows a first-order law. Finally the effect of an inhibitor, cyclohexene, was studied (table 2) leading to average values of $10^4\,k_1$ = 2·17 and 4·44 sec^{-1} to be compared with average values of 2·26 and 3·59 sec^{-1} obtained from experiments in the absence of cyclohexene. Since no inhibition is observed, by accepted criteria, the reaction is unimolecular.

DISCUSSION

The value of the activation energy (45·4 kcal mole^{-1}) rules out the possibility of a radical non-chain reaction.[5] Similarly, a chain reaction is ruled out by the absence of an inhibitory effect when the pyrolysis is carried out in the presence of cyclohexene. There remains, since the reaction is of the first order, only the single-stage unimolecular mechanism. Arrhenius parameters for other secondary bromides that have been

TABLE 4.—ARRHENIUS PARAMETERS FOR SECONDARY BROMIDE PYROLYSES

bromide	log A (A in sec^{-1})	E (kcal mole^{-1})	ref.
2-propyl	13·60	47·70	6
	13·62	47·80	3
	12·74	47·00	7
2-butyl	13·04	45·90	8
	12·63	43·80	9
	13·53	46·47	10
3-pentyl	13·51	45·44	this work
cyclo-pentyl	12·84	43·70	11
	11·9	41·40	12
cyclo-hexyl	13·51	46·10	13

studied are shown in table 4; values for 3-bromopentane are in line with those for other secondary bromides.

Since 3-bromopentane decomposes according to a first-order law and by a unimolecular mechanism, it would appear that the Wojciechowski and Laidler mechanism for bromide pyrolyses is not valid.

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