235. *Studies in the Pyrolysis of Organic Bromides. Part XIII.*[1] *The Limiting Rate of Decomposition of* iso*Butyl Bromide in the Presence of Inhibitors.*

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Whereas *iso*butyl bromide normally decomposes by a mechanism involving radical-chains, the introduction of olefinic inhibitors reduces the rate to a limiting value, independent of the nature of the inhibitor. The first-order rate over the range 360—420° is given by $k_1 = 1{\cdot}12 \times 10^{13}$ exp $(-50{,}400/\boldsymbol{R}T)$ sec.$^{-1}$. The reaction occurring at maximal inhibition is the homogeneous, unimolecular elimination of HBr to form *iso*butene.

BY analogy with other bromides containing a primary C–Br bond (Parts XII,[1] II,[2] and X [3]) it might be expected that *iso*butyl bromide would pyrolyse to yield *iso*butene and hydrogen bromide by a radical-chain mechanism. In the case of ethyl [1] and *n*-propyl and *n*-butyl [3] bromides, elimination of the chain component of the reaction isolated the unimolecular dehydrobromination. We now study the latter mechanism for *iso*butyl bromide.

EXPERIMENTAL AND RESULTS

*iso*Butyl bromide, prepared from *iso*butanol by the red phosphorus–bromine method, was washed with water, concentrated hydrochloric acid, water, 10% potassium carbonate solution, and water, dried ($CaCl_2$), and fractionally distilled, b. p. 91·35°/762·4 mm., n_D^{25} 1·4338 (Timmermans [4] gives b. p. 91·40°/760 mm., n_D^{25} 1·4340). A good commercial sample of *iso*butyl bromide, purified in the same way, gave results consistent with those obtained with the prepared material.

Preliminary runs in a seasoned vessel at 353° gave pressure–time curves of definitely sigmoid character, which suggested that a radical-chain mechanism was involved. Addition of *cyclo*hexene reduced the rate by a factor of about ten, indicating that at this temperature the radical-chain mechanism predominates. The radical-chain mechanism has not yet been exhaustively studied, and will not be considered here.

The apparatus and technique employed were essentially those described in Part I,[5] the rate of elimination being measured by the rate of pressure increase at constant volume. The stoicheiometry $C_4H_9Br \longrightarrow C_4H_8 + HBr$ was not checked by comparison of the HBr produced with the pressure increase. As mentioned in Part VI,[6] hydrogen bromide adds rapidly to *iso*butene in the absence of oxygen to form *tert.*-butyl bromide. Hence the HBr found analytically is much less than that estimated from manometric measurements, and the end point moves slowly in the direction of increasing HBr, owing to the hydrolysis of *tert.*-butyl bromide. However, the final pressure increase measured in a number of instances was found to be only slightly less than the initial pressure of the bromide. An analysis by Allen [7] for the dead-space correction shows that for an apparatus of the type used, if the theoretical value of p_f/p_0 is 2, then the measured value will be about 1·9. Values of p_f/p_0 (Table 1) show that the pressure approximately doubles during the course of a run, which is consistent with the overall reaction's being that suggested.

To determine the order of the reaction, a series of runs was done at 421·2° and rate coefficients corresponding to kinetics of order 0·5, 1, and 1·5 were derived. In no case were good straight lines obtained, but the constancy of the first-order coefficients over a wide range of initial pressures strongly suggests the first-order character of the reaction, at least in the early

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[1] Part XII, preceding paper. A preliminary report of the Arrhenius parameters recorded here was given in *J. Chem. Phys.*, 1953, **21**, 178.

[2] Agius and Maccoll, *J.*, 1955, 973.

[3] Maccoll and Thomas, *J.*, 1957, 5033.

[4] Timmermans, " Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

[5] Maccoll, *J.*, 1955, 965.

[6] Harden and Maccoll, *J.*, 1955, 2454.

[7] Allen, *J. Amer. Chem. Soc.*, 1934, **56**, 2053.

stages. The first-order rate constants are shown in Table 2, p_i being the pressure of *cyclo*hexene. They increased as the reaction proceeded; this can reasonably be identified as incomplete inhibition, also noted in the inhibition of the decomposition of *n*-propyl bromide by propene,[3] where it was shown that although the rate tended to increase during a run, the rate curve at least had a common tangent to the maximally inhibited curve. Thus rate constants derived in the initial stages of a run are significant. The increasing rate effect was more serious at lower temperatures than at the higher.

TABLE 1.

Temp.	p_i (mm.)	p_o (mm.)	p_t (mm.)	p_t/p_o	Temp.	p_i (mm.)	p_o (mm.)	p_t (mm.)	p_t/p_o
416·0°	129	124	227	1·81	395·4°	110	122	219·5	1·80
416·0	136	172	310	1·80	394·6	82	149	267·5	1·80
416·0	132	160	289·5	1·83	393·4	120	144	266	1·85
409·9	127	140	253·5	1·81					

TABLE 2. *Reactions at* 421·2°.

p_i (mm.)	211	203	215	225	200·5	193	209	80	79
p_o (mm.)	262	238	181·5	180	159	140	138	102	65·5
10^4k_1 (sec.$^{-1}$)	16·81	16·35	16·35	17·35	15·20	15·36	15·59	17·12	15·28

To identify the limiting rate with that of unimolecular elimination, a criterion proposed by Smith and Hinshelwood[8] was employed. These authors suggested that if two or more inhibitors reduce the rate of a reaction to the same value, then this is evidence that the maximally inhibited rate is that of an internal rearrangement rather than of a modified chain reaction. Since propene is a less efficient inhibitor than *cyclo*hexene[3] it was not tested, but *cyclo*hexene together with *cyclo*pentadiene and 2 : 4-dimethylpent-2-ene were used. Reproducible results could not be obtained with *cyclo*pentadiene, and this was presumed to be due to dimerisation of the inhibitor in the dead space. Values of the limiting rate obtained with 2 : 4-dimethylpent-2-ene are shown in Table 3, together with values of $k_{calc.}$ obtained from *cyclo*hexene-inhibited runs interpolated by use of the Arrhenius equation reported below. The results of Tables 2 and 3 confirm that the maximally inhibited reaction is unimolecular.

TABLE 3.

Temp. 386·6°	$k_{calc.} = 2·24 \times 10^{-4}$ sec.$^{-1}$		Temp. 388·4°	$k_{calc.} = 2·40 \times 10^{-4}$ sec.$^{-1}$	
p_i	p_o	10^4k_1 (sec.$^{-1}$)	p_i	p_o	10^4k_1 (sec.$^{-1}$)
201·5	168	2·93	224	170	2·57
144·5	128	2·54	235·5	147·4	2·53
142	114	2·31	249·5	140	2·30

No appreciable increase in rate was observed for a number of inhibited runs in a packed vessel of surface : volume ratio four times that of the unpacked vessel. The reaction is therefore homogeneous, which supports the conclusion of the last paragraph as to its nature.

TABLE 4.

No. of runs	Temp.	10^4k_1 (sec.$^{-1}$)	$10^4k_{calc.}$ (sec.$^{-1}$)	No. of runs	Temp.	10^4k_1 (sec.$^{-1}$)	$10^4k_{calc.}$ (sec.$^{-1}$)
7	411·9°	8·59	9·04	5	384·3°	2·08	1·93
6	402·2	5·12	5·45	5	371·0	0·854	0·855

TABLE 5.

No. of runs	12	3	9	8	8	2	6
Temp.	421·4°	420·9°	417·5°	411·7°	401·8°	401·6°	394·3°
10^4k_1 (sec.$^{-1}$)	16·02	16·32	12·11	9·60	5·00	5·75	3·46

No. of runs	5	5	6	5	6	6
Temp.	391·4°	387·3°	386·6°	376·6°	366·0°	363·1°
10^4k_1 (sec.$^{-1}$)	2·96	2·28	2·45	1·34	0·628	0·493

Rates in the unpacked vessel are in Table 5. In view of the lack of dependence of the rate upon either the initial pressure of *iso*butyl bromide or of *cyclo*hexene, these have been grouped

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[8] Smith and Hinshelwood, *Proc. Roy. Soc.*, 1942, *A*, **180**, 237.

together according to temperature. The rate can be expressed as $k_1 = 10^{13\cdot05} \exp(-50{,}400/\boldsymbol{R}T)$ sec.$^{-1}$. In the Arrhenius plot, the scatter of the points about the best straight line was wider than usual, no doubt owing to the difficulty of producing complete inhibition.

DISCUSSION

By the use of two different inhibitors a homogeneous, first-order decomposition of *iso*butyl bromide into *iso*butene and HBr, identified as an intramolecular elimination, has been isolated. The parameters of the rate equation are compared with those of previously studied bromides containing primary C–Br bonds in Table 6. The close similarity of the Arrhenius parameters for *n*-propyl, *n*-butyl, and *iso*butyl bromide decompositions confirms the proposed interpretations of the results.

TABLE 6.

Bromide	$10^{-13}A$ (sec.$^{-1}$)	E (kcal./mole)	Part
Ethyl	2·8	53·9	XII
n-Propyl	0·8	50·7	X
n-Butyl	1·5	50·9	X
*iso*Butyl	1·1	50·4	This work

An examination of the relative rates of elimination in the series ethyl, *n*-propyl, and *iso*butyl bromides, in which the β-hydrogen atom concerned in the elimination is attached to a primary, secondary, and tertiary carbon atom respectively, reveals the relatively small influence of the carbon–hydrogen bond upon the rate. Thus the rate for ethyl bromide at 380° being taken as unity, the relative rates for *n*-propyl and *iso*butyl bromides are 3·5 and 6·5 respectively. Barton *et al.*[9] showed that (—)-menthyl chloride, which contains β-hydrogen atoms attached to both secondary and tertiary carbon atoms, undergoes homogeneous unimolecular elimination in the region of 430° and yields approximately a 3 : 1 ratio of *p*-menth-3-ene to *p*-menth-2-ene. Thus within a single molecule, elimination with a β-hydrogen atom attached to a tertiary carbon atom occurs about three times as fast as elimination with a β-hydrogen atom attached to a secondary carbon atom. This ratio is in fair agreement with the ratio of the rates of decomposition of *n*-propyl and *iso*butyl bromide.

The difficulty of producing complete inhibition throughout the whole reaction suggests long chains in the uninhibited decomposition. Indeed there is evidence that along the series $CH_3{\cdot}CH_2Br$, $CH_3{\cdot}CH_2{\cdot}CH_2Br$, and $(CH_3)_2CH{\cdot}CH_2Br$ the chain length increases. If this is considered together with the observation [6,10] that there is no appreciable chain component in the pyrolysis of a bromide where the bromine atom is attached to a secondary or tertiary carbon atom, two generalisations regarding the occurrence or non-occurrence of a chain mode of decomposition in bromide pyrolysis can be made. First, for a chain decomposition to occur, the bromine atom to be eliminated must be attached to a primary carbon atom. Secondly, the chain length will increase as the β-hydrogen atom concerned in the elimination changes from CH_3– to CH_2– to CH–. Preliminary evidence [11] suggests that phenethyl bromide decomposes, in the absence of inhibitors, by a chain mechanism, which is further confirmation of the chain mechanism's being favoured by a weak β-carbon–hydrogen bond.

After this work had been completed the uninhibited decomposition of *iso*butyl bromide was reported by Sergeev [12] who found the decomposition to follow kinetics of order 1·5, but the results were not very reproducible. Also, bromine was found to accelerate the

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[9] Barton, Head, and Williams, *J.*, 1952, 453.

[10] Maccoll and Thomas, *J.*, 1955, 979, 2445; Green and Maccoll, *J.*, 1955, 2449; Harden, *J.*, 1957, 5024; Harden and Maccoll, *J.*, 1957, 5028.

[11] Stephenson, unpublished work.

[12] Sergeev, *Doklady Akad. Nauk S.S.S.R.*, 1956, **106**, 299.

rate markedly, and propene to retard it slightly. The rate constants could be represented by the Arrhenius equation

$$k = 1{\cdot}8 \times 10^{6} \exp\,(-30{,}000/\boldsymbol{R}T)\ \text{mm.}^{-\frac{1}{2}}\ \text{sec.}^{-1}$$

and Sergeev concludes that chains are generated on the wall of the reaction vessel. These observations are in essential accord with some made during the progress of the present investigation. Summarising the Russian work on *n*- and *iso*-propyl bromides [13] and the four butyl bromides,[12] Sergeev comes to essentially the conclusions reached here, namely that primary alkyl bromides decompose predominantly by a chain mechanism, whereas secondary and tertiary bromides decompose mainly by unimolecular elimination. In the next Part it will be shown that as the length of the alkyl chain increases in the straight-chain primary bromides, the chain component of the decomposition decreases relative to the unimolecular component.

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[13] Semenov, Sergeev, and Kapralova, *Doklady Akad. Nauk S.S.S.R.*, 1955, **105**, 301.