

612. *Studies in the Pyrolysis of Organic Bromides. Part XI.* The Maximally Inhibited Rate of Decomposition of sec.-Butyl Bromide.*

By M. N. KALE, ALLAN MACCOLL, and P. J. THOMAS.

The pyrolysis of *sec.*-butyl bromide in the presence of *cyclohexene*, which has previously been shown to be a highly efficient chain inhibitor in bromide pyrolyses, has been found to be a first-order reaction. It shows slight inhibition. The relation of this work to that of Sergeev is discussed.

IN Part IV¹ of this series, an investigation of the dehydrobromination of *sec.*-butyl bromide in the gaseous phase was reported. It was noted that "there is a slight tendency for the rate to be less in the presence of added propene, but experimental scatter precludes quantitative conclusions." Sergeev² has recently reported a similar investigation, the rate constants being represented by

$$\log k_1 = 13.04 - 45,500/2.303RT$$

These Arrhenius parameters are to be compared with 12,63 and 43,800, reported in Part IV.

The temperature range investigated by Sergeev was 326—398°, to be compared with 300—350° (Part IV). In view of the possible incursion of a chain mechanism in the pyrolysis of *sec.*-butyl bromide, it was deemed desirable to repeat the investigation, using *cyclohexene* which is much more efficient than propene³ as an inhibitor.

EXPERIMENTAL

The apparatus, experimental technique, and calculation of rate constants were as previously described.⁴ The reaction vessel, however, was of somewhat greater diameter (3"). In order to ensure that the temperature scale was identical with that used previously, and that there were no other apparatus factors, a series of some six runs with *isopropyl* bromide at each of three temperatures was carried out. The results are shown in Table I, the calculated values being taken from the Arrhenius equation of Part III.⁵ In view of the good agreement for the three temperatures, it was concluded that results obtained in the present apparatus were strictly comparable with those recorded in the earlier paper.

* Part X, *J.*, 1957, 5033.

¹ Maccoll and Thomas, *J.*, 1955, 2445.

² Sergeev, *Doklady Akad. Nauk S.S.S.R.*, 1956, **106**, 299.

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

⁴ Maccoll, *J.*, 1955, 965.

⁵ Maccoll and Thomas, *J.*, 1955, 979.

TABLE 1. Values of $10^4 k_1$ (sec.⁻¹).

Temp.	This work	Obs. (Pt. III)	Calc. (Pt. III)
312°	0.594	0.592	0.589
329	1.85	1.80	1.86
347	5.88	5.83	5.89

Re-investigation of the uninhibited reaction confirmed the observation ¹ that the pressure increase accurately represented the degree of decomposition. A study of the temperature variation of the rate constant led to the Arrhenius equation

$$\log k_1 = 13.179 - 45,400/2.303RT$$

At the higher temperatures there is little difference between the rate constants observed in the present work and those of Part IV. However, at the lowest temperature of the range studied, the present rates are some 10% lower than those previously reported.

A number of runs were carried out in the presence of varying amounts of *cyclohexene*. The results are shown in Table 2, p_i being the *cyclohexene* partial pressure and p_o the initial partial pressure of the bromide.

TABLE 2. *Pyrolysis at 318°.*

p_i/p_o	0	0.05	0.2	0.4	0.8	1.2	1.9	2.2	3.0
$10^4 k_1$ (sec. ⁻¹)	2.52	2.53	2.29	2.37	2.18	2.21	2.38	2.37	2.28

These results show a definite, though small, decrease compared with those for the uninhibited reaction, the mean rate constant in the presence of inhibitor ($p_i/p_o > 0.2$) being 2.30×10^{-4} sec.⁻¹, which is to be compared with the value 2.52×10^{-4} sec.⁻¹ obtained in the absence of inhibitor.

Investigation of the stoichiometry of the reaction in the presence of added *cyclohexene* showed that the rate of pressure increase was still a true measure of the rate of elimination of hydrogen bromide. Percentage decompositions obtained from pressure measurements are compared with those obtained by direct titration of the hydrogen bromide produced in Table 3.

TABLE 3.

Decomp. (%) (press.)	73.8	62.6	51.5	39.2	27.6	16.1
Decomp. (%) (anal.)	74.4	62.0	52.0	38.8	28.0	15.8

The first-order character was confirmed by the lack of variation of the rate constants with initial bromide pressure.

The temperature variation of the rate constants was thus investigated by measuring the rate of pressure increase in the presence of *cyclohexene* ($p_i/p_o > 0.2$) at a series of temperatures. The results are shown in Table 4, which includes the results of the investigation of the uninhibited reaction.

TABLE 4.

Temp.	Uninhibited reaction		Inhibited reaction		Temp.	Uninhibited reaction		Inhibited reaction	
	No. of runs	$10^4 k_1$ (sec. ⁻¹)	No. of runs	$10^4 k_1$ (sec. ⁻¹)		No. of runs	$10^4 k_1$ (sec. ⁻¹)	No. of runs	$10^4 k_1$ (sec. ⁻¹)
353.8°	4	22.3	6	20.9	318.8°	—	—	7	2.30
341.5	5	10.45	6	9.49	318.2	4	2.47	—	—
332.6	4	6.16	6	5.62	311.5	4	1.56	6	1.38
325.0	4	3.86	6	3.43	298.5	4	0.652	6	0.567

The results for the inhibited reaction fitted very well the Arrhenius equation

$$\log k_1 = 13.530 - 46,470/2.303RT.$$

DISCUSSION

The pyrolysis of *sec.*-butyl bromide in the gas phase has been shown to be a first-order homogeneous reaction leading to hydrogen bromide and butene. In the absence of inhibitors, the decomposition has been shown to contain a small chain component, which

however, can be eliminated by addition of *cyclohexene*. This bears out our earlier contention⁶ that the main factor, in the case of the bromides, determining whether the reactant can support chains is the presence of a weak C-H bond, the abstraction of hydrogen from which leads to a P radical.⁵ Thus attack by a bromine atom on *sec.*-butyl bromide can lead to a P radical $\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot\text{CHBr}\cdot\text{CH}_3$ or an S radical $\text{CH}_3\cdot\text{CH}_2\cdot\dot{\text{C}}\text{Br}\cdot\text{CH}_3$, and the fact that the chains do not make a very great contribution to the overall rate (about 15% at the lowest temperature studied) is no doubt connected with the fact that attack on a hydrogen atom connected to a secondary carbon atom can lead to either an S or a P radical.

The absolute rates reported in this paper are about 10% faster than those observed by Sergeev. The same discrepancy occurs in the cases of *tert.*-butyl bromide² and of *iso*-propyl bromide.⁷ The most likely explanation of the difference appears to lie in the temperature scales, a difference of one degree sufficing to account for the differences in rates in the present case.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

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⁶ Harden and Maccoll, *J.*, 1957, 5028.

⁷ Semenov, Sergeev, and Kaprilova, *Doklady Akad. Nauk S.S.S.R.*, 1955, **105**, 300.
