# 234. *Studies in the Pyrolysis of Organic Bromides. Part XII.** *The Unimolecular Decompositions of Ethyl Bromide and 4-Bromopent-1-ene.*

By P. J. Thomas.

The thermal gas-phase decompositions of ethyl bromide and 4-bromopent-1-ene in the presence of olefinic inhibitors are homogeneous first-order reactions, the rate constants $k_1$ being $2{\cdot}8 \times 10^{13} \exp(-53{,}900/\mathbf{R}T)$ sec.$^{-1}$ for EtBr and $8{\cdot}71 \times 10^{12} \exp(-44{,}700/\mathbf{R}T)$ sec.$^{-1}$ for $C_5H_9Br$. In both cases the mechanism is the unimolecular elimination of hydrogen bromide. The results are discussed in relation to previous work on the decomposition of alkyl bromides.

The thermal decomposition of ethyl bromide has been extensively studied by Daniels and his co-workers. In a recent publication [1] in which previous work is reviewed, the normal decomposition is shown to be a chain reaction. Daniels and Goldberg conclude that the reaction chains are initiated by bromine atoms produced by the reactions $C_2H_5Br + HBr \longrightarrow CH_3{\cdot}CH_3 + Br_2$; $Br_2 \longrightarrow Br + Br$, the hydrogen bromide being formed in the first instance by the molecular decomposition of ethyl bromide: $C_2H_5Br \longrightarrow C_2H_4 + HBr$. The present investigation, completed before Daniels and Goldberg's publication, deals with the isolation of the molecular mode of decomposition, by studying the reaction in the presence of added olefinic inhibitors. Previous work on the decomposition of *n*-propyl and *n*-butyl bromides [2] suggested that two mechanisms occurred in the decomposition of ethyl bromide.

The decomposition of 4-bromopent-1-ene has been studied to determine the effect of a β-vinyl substituent on the rate of unimolecular elimination.

## Experimental

A commercial sample of ethyl bromide was dried ($CaCl_2$) and carefully fractionated. The middle fractions of constant physical properties were retained, b. p. 38·6°/760 mm. (corr.), $n_D^{25}$ 1·4222 (lit.,[3] b. p. 38·4°, $n_D^{25}$ 1·4220). The 4-bromopent-1-ene, a gift from Dr. P. A. T. Hoye, was prepared by bromination of pent-4-en-2-ol with phosphorus tribromide in the presence of pyridine and had b. p. 116·50°/756 mm., 74°/150 mm., $n_D^{25}$ 1·4580.[4] *cyclo*Hexene was purified as in Part V.[5]

The reactions were followed by measuring the rate of pressure increase in a static system, the technique and apparatus being essentially that previously described,[6,7] the bromides being admitted to the reaction vessel from a vapour reservoir. Olefinic inhibitors were stored in a

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* Part XI, *J.*, 1958, 3016.

[1] Daniels and Goldberg, *J. Amer. Chem. Soc.*, 1957, **79**, 1314.

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

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

[4] Hoye, Ph.D. Thesis, University of London, 1953.

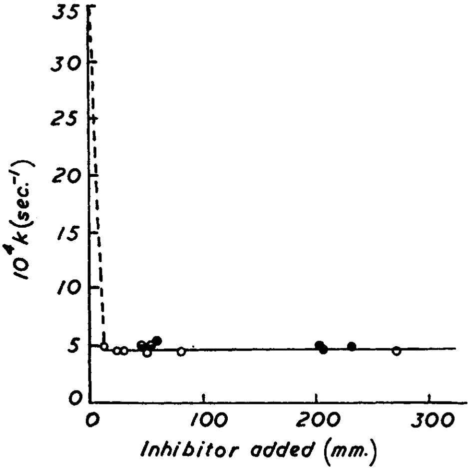
[5] Green and Maccoll, *J.*, 1955, 2449.

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

[7] Maccoll and Thomas, *J.*, 1955, 979.

separate reservoir and, when required, were admitted to the reaction vessel before the bromides. No pre-mixing device was used.

*Ethyl Bromide.*—Although the investigation was primarily concerned with the effect of olefinic inhibitors, runs were carried out to ensure that Daniels and Veltman's results [8] could be reproduced in the present apparatus. In reaction vessels recently coated with a carbonaceous film by decomposition of allyl bromide, or in which inhibitors had been used, the reaction rate was irreproducible and invariably less than the rate previously reported. In a reaction vessel coated by the slow decomposition of the reaction products, a more reproducible reaction was observed. The initial first-order rate coefficient for an initial pressure of 360 mm. at 387° was $2{\cdot}8 \times 10^{-4}$ sec.$^{-1}$, to be compared with $3{\cdot}16 \times 10^{-4}$ sec.$^{-1}$ calculated from the rate equation reported by Daniels and Veltman.[8] The present value is lower, and induction periods were observed in all the pressure–time curves, in agreement with the later observation by Daniels and Goldberg.[1] The rate of decomposition was markedly reduced by added *cyclo*hexene. With increasing concentrations of *cyclo*hexene a limiting value was reached after which the rate became independent of the *cyclo*hexene concentration (Figure). The reaction was also inhibited by propene and by 2 : 4-dimethylpent-2-ene, the same limiting rate being observed as with *cyclo*hexene. These two inhibitors are less efficient than *cyclo*hexene; a greater concentration was required to produce the same degree of inhibition. The residual reaction was thus shown to be independent of the concentration (above a certain limit) and nature of the olefinic inhibitor.



*Effect of inhibitors upon the rate of pyrolysis of ethyl bromide.*

○, *cyclo*Hexene.
●, Propene.
◑, 2 : 4-Dimethylpent-2-ene.

When the concentration of inhibitor was insufficient for complete inhibition, the observed kinetics were complex and characteristic of a partially inhibited decomposition of an alkyl bromide.[2] It was difficult to ascribe a significant value to a first-order rate constant in these circumstances and no points are included for the partially inhibited reaction in the Figure. In the region of partial inhibition, prolonged induction periods in the chain component make it possible to determine the rate-coefficient for the maximally inhibited reaction in the initial stages, although complete inhibition throughout the reaction is not attained. The value of $k_1$ in the presence of 60 mm. of propene was obtained in this manner.

The maximally inhibited decomposition was catalysed by clean glass surfaces, but the reaction was reproducible and homogeneous in reaction vessels coated with a thin film of carbonaceous material. The results of two series of experiments in a reaction vessel packed with glass tubing with a surface : volume ratio five times that of the empty vessel are included in Table 2. A definite increase in rate of the order of 15% was observed in the packed vessel but having regard to the large increase in the surface : volume ratio, it may be concluded that the heterogeneous component in the unpacked vessel is small and the reaction essentially homogeneous.

The maximally inhibited reaction is of the first order. The initial first-order rate

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[8] Daniels and Veltman, *J. Chem. Phys.*, 1939, **7**, 757.

coefficients, measured in a series of runs at 430° in an unpacked reaction vessel, are shown in Table 1, where $p_i$ is the concentration of *cyclo*hexene and $p_0$ the initial pressure of ethyl bromide.

TABLE 1. *Reaction at* 430°.

| $p_0$ (mm.) ... | 568 | 526 | 374 | 274 | 196 | 109 | 70 | 43 | 31 | 25 |
|---|---|---|---|---|---|---|---|---|---|---|
| $p_i$ (mm.) ... | 89 | 34 | 64 | 50 | 25 | 13 | 12 | 16 | 14 | 18 |
| $10^4k_1$ (sec.$^{-1}$) | 4·55 | 4·82 | 4·61 | 4·46 | 4·50 | 4·54 | 4·77 | 4·54 | 4·65 | 4·79 |

Mean value $k_1$ at 430° = 4·71 × $10^{-4}$ sec.$^{-1}$.

The rate coefficient $k_1$ shows no dependence on the initial pressure of ethyl bromide. In individual runs, the first-order character was maintained to about 50% of decomposition, after which the rate steadily diminished. This may have been due partly to the occurrence of the addition reactions $HBr + C_2H_4 \longrightarrow C_2H_5Br$ and $HBr + C_6H_{10} \longrightarrow C_6H_{11}Br$, and partly to the polymerisation of the ethylene formed. At 430° the first-order rate diminished after 40% of reaction and small quantities of non-condensable gases were formed in the later stages. The temperature range of the investigation was curtailed at 430° for this reason.

The temperature-dependence of the first-order rate constants was determined from the mean values for series of runs at different temperatures. The results are shown in Table 2. The rate constants can be expressed as $k_1 = 2{\cdot}8 \times 10^{13} \exp(-53{,}900/\boldsymbol{R}T)$ sec.$^{-1}$.

TABLE 2.

| Temp. ......... | 430° | 416°p | 414° | 404·5° | 398° | 392° | 385·5°p | 382° |
|---|---|---|---|---|---|---|---|---|
| No. of runs ... | 15 | 12 | 17 | 1 | 8 | 5 | 5 | 6 |
| $10^4k_1$ (sec.$^{-1}$) ... | 4·71 | 2·42(2·14) | 1·84 | 1·06 | 0·75 | 0·52 | 0·39(0·34) | 0·30 |

p = runs in packed vessel; figures in parentheses are interpolated values for $k_1$ in the unpacked vessel.

4-*Bromopent*-1-*ene*.—This compound decomposed at a measurable rate in the range 300—350°, accompanied by an overall pressure increase of about 80%. The reaction has been studied by measuring the rate of pressure increase, which has been interpreted on the basis of the reaction $C_5H_9Br \longrightarrow C_5H_8 + HBr$. It was verified analytically that the pressure increase ($\Delta p$) observed was a direct measure of the amount of hydrogen bromide formed. In a series of runs the contents of the reaction vessel were rapidly condensed into a trap cooled in liquid air.

TABLE 3.

| $p_0$ (mm.) ............ | 206 | 208 | 210 | 217 | 209 | 204 | 107 | 112 |
|---|---|---|---|---|---|---|---|---|
| $\Delta p$ (mm.) ......... | 65 | 74 | 127 | 104 | 112 | 85 | 52 | 52 |
| $p_{HBr}$ anal. (mm.) | 68 | 74 | 124 | 98 | 112 | 87 | 54 | 56 |

The mixture of reactant and products was then removed from the appparatus and the hydrogen bromide estimated by conventional methods. By carrying out similar determinations in which the reaction vessel was filled with known pressures of pure hydrogen bromide only, the analytical results could be related directly to the equivalent partial pressures of hydrogen bromide in the reaction vessel. The partial pressures of hydrogen bromide calculated from the analyses are compared in Table 3 with the total pressure change $\Delta p$ immediately before condensation. Good agreement between the two methods was obtained. The elimination of hydrogen bromide from 4-bromopent-1-ene can result in the formation of one of two possible pentadienes, $CH_2{:}CH{\cdot}CH_2{\cdot}CH{:}CH_2$ or $CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH_2$, but the composition was not determined.

The normal decomposition of 4-bromopent-1-ene indicated marked kinetic complexity and was not investigated in detail. The pressure–time curves for individual runs were sigmoid and the first-order rate coefficient increased rapidly as the reaction proceeded. The addition of small quantities of *cyclo*hexene did not affect the initial, but reduced the maximum rate of decomposition. Previous work [2] has shown that this behaviour is characteristic of a system in which a chain mechanism with a prolonged induction period is superimposed upon a molecular mechanism. With increasing pressures of *cyclo*hexene the maximum rate of decomposition was reduced to a limiting value identical with that of the initial induction period in the normal reaction. A *cyclo*hexene : bromide concentration ratio of 2 : 3 was required to suppress the chain reaction entirely.

Only the maximally inhibited reaction was studied in detail. As with ethyl bromide, additions of inhibitors, insufficient to produce complete inhibition throughout the reaction, nevertheless prolonged the induction period in the chain mechanism sufficiently to enable the initial first-order rate coefficients of the maximally inhibited reaction to be measured. The lack of dependence of the rate coefficients of this residual reaction on the *cyclo*hexene concentration is shown in Table 4. The decomposition was catalysed by clean glass surfaces but where the walls of the reaction vessel were coated with a thin carbonaceous film, either by the decomposition of the reaction products or by the decomposition of allyl bromide, the reaction rate was reduced and became more reproducible. The results of a series of experiments in a packed reaction vessel with a surface : volume ratio five times that of the empty vessel are shown in Table 6. No appreciable increase in rate was observed in the packed vessel and it may be concluded that the reaction is essentially homogeneous.

TABLE 4.

| | | | | | | |
|---|---|---|---|---|---|---|
| $p_0$ (mm.) | 158 | 150 | 157 | 158 | 150 | 147 |
| $p_i$ (mm.) | 49 | 70 | 161 | 161 | 184 | 300 |
| $10^4k_i$ (sec.$^{-1}$) | 7·90 | 8·45 | 7·84 | 8·42 | 8·45 | 8·22 |
| $p_i/p_0$ | 0·31 | 0·47 | 1·02 | 1·02 | 1·23 | 2·04 |

The reaction is of the first order. This was demonstrated by the linearity of the logarithmic plots for the first 50% of decomposition and by the independence of the initial, first-order rate-coefficients of the initial pressure (Table 5).

TABLE 5. *Reaction at* 336·5°.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $p_0$ (mm.) | 218 | 158 | 150 | 147 | 124 | 120 | 97 | 54 | 51·6 |
| $p_i$ (mm.) | 96 | 49 | 161 | 184 | 127 | 79 | 201 | 51 | 44 |
| $10^4k_1$ (sec.$^{-1}$) | 7·9 | 8·42 | 8·45 | 8·22 | 7·76 | 7·46 | 7·84 | 8·36 | 8·51 |

Mean $k_1$ at 336·5° = $8{\cdot}08 \times 10^{-4}$ sec.$^{-1}$.

The ratio of the final : initial pressure for the maximally inhibited reaction was *ca.* 1·8. This will be partly due to equilibria being established between hydrogen bromide and the olefinic products and also the *cyclo*hexene present.[5] The formation of small quantities of hydrogen or methane and the coloration of the products indicated that the later stages of the reaction are probably further complicated by the polymerisation of the olefinic products. The decrease in the first-order rate coefficient observed after 50% of reaction may be attributed to the same causes.

TABLE 6.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Temp. | 349·5° | 341·5° | 337·3° | 336·5° | 335·5° | 313·5° | 301·5° |
| No. of runs | 5 | 6 | 2 | 9 | 8p | 4 | 6 |
| $10^4k_1$ (sec.$^{-1}$) | 16·7 | 10·0 | 8·37 | 8·08 | 7·71 (7·59) | 1·70 | 0·85 |

p = packed reaction vessel. The figure in parentheses is the interpolated value for $k_1$ in the unpacked vessel.

The variation of the first-order rate coefficients with temperature is shown in Table 6, the rate constant being expressed by the equation $k_1 = 8{\cdot}71 \times 10^{12} \exp(-44{,}700/\boldsymbol{R}T)$ sec.$^{-1}$, which is to be compared with the Arrhenius equation for the unimolecular decomposition of *sec.*-butyl bromide,[9] $k_1 = 3{\cdot}39 \times 10^{13} \exp(-46{,}370/\boldsymbol{R}T)$ sec.$^{-1}$.

## DISCUSSION

The rates of thermal decomposition of ethyl bromide and 4-bromopent-1-ene have been shown to be reduced to a limiting value by added *cyclo*hexene. The maximally inhibited or residual reactions, which are independent of the *cyclo*hexene concentrations,

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[9] Kale, Maccoll, and Thomas, *J.*, 1958, 3016.

have been characterised as homogeneous, first-order reactions involving the elimination of hydrogen bromide:

$$C_2H_5Br \longrightarrow C_2H_4 + HBr;\ E = 53{\cdot}9 \text{ kcal./mole}$$
$$C_5H_9Br \longrightarrow C_5H_8 + HBr;\ E = 44{\cdot}7 \text{ kcal./mole}$$

The frequency factor in both cases is *ca.* $10^{13}$ sec.$^{-1}$. The observed activation energies are too low for non-chain radical mechanisms to be involved and radical-chain mechanisms will be suppressed by the inhibitor present. It is concluded that the reactions proceed by the molecular splitting of hydrogen bromide, *i.e.*, the unimolecular elimination mechanism. This mechanism is consistent with the observed characteristics of the decompositions and is to be expected from previous studies of the thermal decomposition of related alkyl bromides.

Blades and Murphy[10] have reported an investigation of the decomposition of ethyl bromide by a flow technique with toluene as the carrier gas. Under these conditions any free-radical formation leads to the formation of dibenzyl. Dibenzyl was not detected in the products and Blades and Murphy concluded that the reaction proceeded by the unimolecular elimination of hydrogen bromide. The first-order rate constant was given by the equation

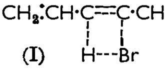
$$k_1 = 7{\cdot}3 \times 10^{12} \exp\,(-52{,}300/\boldsymbol{R}T) \text{ sec.}^{-1},$$

in good agreement with the present work. The temperature range was 527—626°, compared with 380—430° in this investigation.

The normal uninhibited decomposition of ethyl bromide has been fully discussed by Daniels and Goldberg.[1] The uninhibited decomposition of 4-bromopent-1-ene is complex and the chain mechanism of decomposition was considered unsuitable for a detailed investigation.

In 4-bromopent-1-ene, the β-methyl group in *sec.*-butyl bromide is replaced by a vinyl group. The Arrhenius equations for the unimolecular decompositions of these two compounds have been compared in the previous section. The relative rates of decomposition at 380° are $k_1(C_5H_9Br) : k_1(C_4H_9Br) = 1{\cdot}05 : 1$.

The decomposition of 4-bromopent-1-ene can occur in two ways, forming either penta-1 : 3- or penta-1 : 4-diene. The former involves elimination between the bromine atom and a hydrogen atom in the allylic position and the formation of a conjugated diene. Both factors would be expected to facilitate elimination if the rate-determining stage involved a transition state of the conventional four-centre type (I), in which the bonds are broken and formed simultaneously. The bond dissociation energy of the C–H bond at the 3-position should be considerably less than that of the corresponding bond in *sec.*-butyl bromide, and the hydrogen atom should be more easily removed. The transition state should also be stabilised by the conjugation which will develop between the forming double bond and the double bond already present. That neither of these factors leads to an increased rate of elimination from 4-bromopent-1-ene relative to *sec.*-butyl bromide indicates that the important rate-determining stage of the reaction is concerned solely with an activation of the C–Br bond. The breaking of the C–H bond and formation of the double bond occur in a later non-rate-determining stage.



$$CH_2{:}CH{\cdot}\underset{\underset{H}{|}}{C}{=\!=}\underset{\underset{Br}{|}}{C}{\cdot}CH_3$$

(I)

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William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1.

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[10] Blades and Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 6219.