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MIXED ETHYL BROMIDE AND ETHYL CHLORIDE PYROLYSES

Mixed Ethyl Bromide and Ethyl Chloride Pyrolyses

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The order of the uninhibited pyrolysis of ethyl bromide in the gas phase has been confirmed as 1.5. Mixed pyrolyses of ethyl chloride and ethyl bromide, both in the absence and presence of cyclohexene, are consistent with the ethyl chloride and the maximally inhibited ethyl bromide decompositions being molecular. The decomposition of ethyl chloride has been re-investigated. The rate equation over the temperature range $419.4\text{--}499.1^\circ$ was $\log_{10} k_1 = 13.46 - 56,620/2.303 RT$ (sec^{-1}).

The rate of elimination of HCl from ethyl chloride in the gas phase is unaffected by olefinic inhibitors and is first order and independent of the surface-to-volume ratio in seasoned vessels.¹ It has been claimed to be a homogeneous molecular reaction, there being no experimental evidence to the contrary, though it is possible to produce both homogeneously and heterogeneously initiated and terminated radical chain schemes to explain the results other than the lack of inhibition. Wojciechowski and Laidler² even claim to have explained the latter, but their scheme does not give the correct kinetic order for this case, though an alternate one may possibly do so.

On the other hand, ethyl bromide clearly decomposes, at least in part, by a radical chain reaction resulting in sigmoid pressure-time curves.³ The rate is decreased in the presence of olefinic inhibitors and the maximally inhibited rate gives good first-order pressure-time curves, not at all sigmoid in character.⁴ The maximally inhibited reaction has been claimed to be a molecular elimination, but this view is disputed by Wojciechowski and Laidler.² The present investigation attempts to throw a little more experimental light on the situation.

EXPERIMENTAL

The experiments were performed in a standard static apparatus. Ethyl chloride and ethyl bromide were prepared from commercial samples by shaking with concentrated acid (sulphuric, hydrochloric), 50 % sodium bicarbonate solution and finally water. Each was separated, dried over calcium sulphate and fractionated through a 1 m column packed with glass helices. The fractions used had b.p. 12.3° , 38.4° at 760 mm (lit. $12.3\text{--}12.5$, 38.45). A commercial sample of cyclohexene was shaken with ferrous sulphate, dried over calcium sulphate and distilled in an atmosphere of nitrogen.

The surface of the reaction vessel was seasoned by pyrolyzing allyl bromide in the vessel. Hydrogen chloride and hydrogen bromide were determined by potentiometric titration against standard silver nitrate solution after freezing the products of reaction into a vessel containing distilled water.

RESULTS

ETHYL BROMIDE

The most thorough investigation of the uninhibited decomposition of ethyl bromide is that of Goldberg and Daniels³ from which they concluded that the

reaction is first order, though the first-order specific rate varied with initial pressure of ethyl bromide. Blades⁶ claimed that Goldberg and Daniels' results are more consistent with 1.5 order kinetics and as the overall order is frequently used as a guide to initiation and termination steps in radical chain mechanisms, this point was investigated.

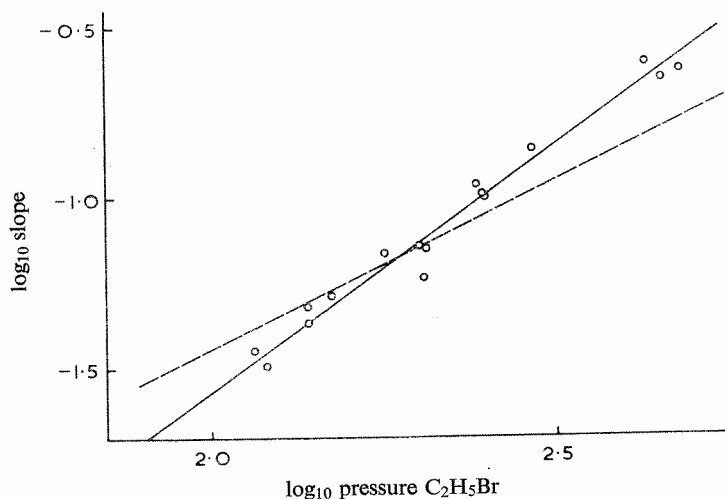


FIG. 1.—The order of the uninhibited ethyl bromide pyrolysis.
—, 1.5; ---, 1.0.

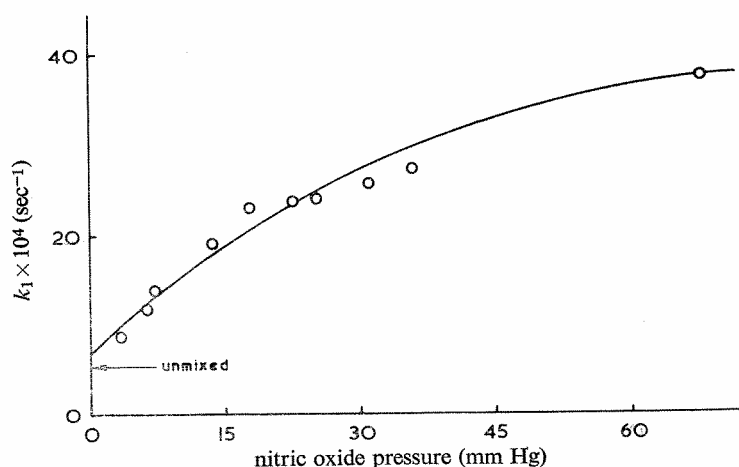


FIG. 2.—The effect of NO on ethyl bromide pyrolysis.

Fig. 1 shows a plot of log slope (of pressure-time curve) against log pressure of bromide at 399°, the slope and pressure being those at the end of the induction period. The full line is drawn at slope 1.5 and the broken line at slope 1.0. This clearly indicates that the uninhibited reaction, like that of *n*-propyl bromide,⁷ is nearer to 1.5 order. The 1.5-order specific rate obtained from fifteen runs at 398.8° is 0.167 (± 0.007) moles^{-1/2} ml^{1/2} sec⁻¹ (calc. from Goldberg and Daniels, 0.18).

Wojciechowski and Laidler,¹ for the action of nitric oxide on halide pyrolyses, states that it is possible to devise radical chain mechanisms that give the same rate in the presence and absence of NO, and also imply that NO has no effect on halide pyrolyses. The action of NO on alkyl halide pyrolyses has not been reported except for a comment by Daniels and Veltman⁸ that it did not *decrease* the rate of decomposition of ethyl bromide. Fig. 2 shows a plot of the first-order specific rate of ethyl bromide pyrolysis against NO pressure at 398.6°. (Reasonable first-order plots were obtained up to about 30 % reaction.) Clearly an increase in rate occurs.

ETHYL CHLORIDE

A preliminary investigation produced rates slightly different from Barton and Howlett's^{1a} results and as we wished to use cyclohexene as olefinic inhibitor in the mixed pyrolyses and Barton and Howlett had used propene which is a less efficient inhibitor,⁹ a study of the pyrolysis of ethyl chloride was undertaken.

The qualitative features of their work were all confirmed. The reaction goes to completion, the ratio of the final to initial pressure being 1.94 ± 0.01 (mean of 26 runs throughout the full temperature range), which is in good agreement with ratios found in other chloride pyrolyses. The only organic products that we found, apart from ethylene, were traces of methane and hydrogen attributable to subsequent decomposition of ethylene. Very small amounts of ethane may have escaped detection. The reaction is first order, the specific rates being independent of pressure in the range 100-400 mm. While the pressure sensing diaphragm used was not suitable for accurate low pressure work, runs at pressures down to 2 mm confirmed Howlett's results that the rate falls rapidly with decreasing pressures below ~ 10 mm¹⁰ (the first-order specific rate is half the high-pressure value at *ca.* 2-3 mm).

TABLE 1.—EFFECT OF CYCLOHEXENE AND TEMPERATURE VARIATION ON ETHYL CHLORIDE PYROLYSIS

| temp., °C | p_i , mm | | p_0 , mm | $10^5 k_1 \text{ sec}^{-1}$ |
|-----------|------------|--------|------------|-----------------------------|
| 499.1 | — | 5 runs | > 100 | 269 ± 2 |
| 483.7 | 52.8 | | 225.5 | 130 |
| 483.7 | — | 5 runs | > 100 | 128 ± 1 |
| 471.3 | — | 5 runs | > 100 | 68.3 ± 0.7 |
| 456.3 | 103.6 | | 192.2 | 30.7 |
| 456.3 | — | 5 runs | > 100 | 30.8 ± 0.2 |
| 443.7 | 102.6 | | 400.3 | 15.7 |
| 443.7 | — | 6 runs | > 100 | 15.7 ± 0.1 |
| 430.8 | 130.5 | | 217.6 | 7.58 |
| 430.8 | 91.0 | | 290.9 | 7.45 |
| 430.8 | — | 5 runs | > 100 | 7.47 ± 0.20 |
| 419.4 | 179.1 | | 374.7 | 3.69 |
| 419.4 | 146.6 | | 405.2 | 3.34 |
| 419.4 | — | 5 runs | > 100 | 3.88 ± 0.18 |

p_i , pressure of cyclohexene; p_0 , initial pressure of ethyl chloride.

The high-pressure rate is almost unaffected by an increase by a factor of 5 in the surface-to-volume ratio of the reaction vessel (mean of six runs at 451.9°, $10^4 k_1 = 2.56 \text{ sec}^{-1}$ compared with 2.44 and mean of 5 runs at 426.8°, $10^4 k_1 = 0.625 \text{ sec}^{-1}$ compared with 0.593). Neither propylene nor cyclohexene (table 1) had any effect on the rate of reaction.

The variation of rate with temperature (table 1) over the range 419.4-499.1° resulted in a good straight-line Arrhenius plot, the least-squares rate equation being

$$\log_{10} k_1 = 13.46(\pm 0.03) - 56,620(\pm 90)/2.303RT, k_1 \text{ in sec}^{-1},$$

which compares well with the determinations of Hartman, Bosche and Heydtmann^{1b} ($\log_{10} A = 13.51$, $E = 56.6 \text{ kcal/mole}^{-1}$) using a standard static system with a different seasoning procedure from ours over the temperature range 389-471° and Tsang^{1c} ($\log_{10} A = 13.16$, $E = 56.46 \text{ kcal/mole}^{-1}$) using a shock-tube method over the temperature range 547-727°. The earlier figures of Barton and Howlett^{1a} as recalculated by Barton and Head¹¹ are $\log_{10} A = 14.60$, $E = 60.8 \text{ kcal/mole}^{-1}$ (temp. range 398-493°).

MIXED PYROLYSIS

When ethyl chloride is introduced into a reaction vessel containing decomposing ethyl bromide, the rate of reaction, as measured by the pressure increase, rises. The results are shown in table 2, where t_c is the time of introduction of ethyl chloride, the introduction of ethyl bromide being taken as zero time; t_f is the time when the last pressure reading p_f was taken (approx. half-life for the bromide decomposition). The ethyl chloride specific rates shown are calculated assuming that the rate of reaction of ethyl bromide is unchanged. The unmixed specific rate of decomposition of ethyl chloride at this temperature was found experimentally to be $1.01 \times 10^{-5} \text{ sec}^{-1}$.

TABLE 2.—MIXED EtCl AND EtBr—UNINHIBITED—399.3°

| EtBr mm | EtCl mm | t_c sec | $10^4 k_1$ (EtCl) ^a sec ⁻¹ | p_f (theor.) ^b mm | p_f (expt.) mm |
|------------|------------|--------------|---|-----------------------------------|---------------------|
| 264.2 | 181.2 | 345 | 1.01 | 572.7 | 597.4 |
| 218.9 | 169.5 | 490 | 0.92 | 488.1 | 507.2 |
| 157.4 | 103.8 | 570 | 2.89 | 325.5 | 356.6 |
| 208.1 | 163.4 | 700 | 2.04 | 464.7 | 497.8 |
| 284.0 | 100.7 | 540 | 2.79 | 524.2 | 554.0 |
| 122.6 | 105.1 | 720 | 2.56 | 273.8 | 299.4 |
| 150.4 | 121.8 | 545 | 2.13 | 333.0 | 361.6 |

t_f for all runs, 1,800 sec; ^a assuming EtBr rate unchanged; ^b calc. using unmixed rates.

Table 3 shows the results of HBr and HCl analyses compared with calculations from the unmixed rates, t_b being the time of introduction of ethyl bromide. From these it is seen that not all the increase in rate is due to increased production of HCl though this is certainly the larger effect. Clearly the two reactions interact.

TABLE 3.—HBr/HCl ANALYSES—UNINHIBITED—399.3°

| EtBr mm | t_b sec | EtCl mm | t_c sec | t_f sec | HBr/HCl | | |
|------------|--------------|------------|--------------|--------------|-------------------|-------------------|--------------------|
| | | | | | ind. ^a | EtCl ^b | anal. ^c |
| 191.2 | 420 | 185.7 | 0 | 2,220 | 20.4 | 1.2 | 10.4 |
| 218.4 | 0 | 214.9 | 755 | 1,800 | 42.3 | 2.4 | 7.2 |
| 168.2 | 0 | 174.1 | 740 | 2,655 | 24.3 | 1.4 | 3.5 |

^a calc. using unmixed rates; ^b calc. using EtCl rate $2 \times 10^{-4} \text{ sec}^{-1}$ (mean from table 2);
^c expt.

The rate of pyrolysis of ethyl chloride, as previously indicated, is unchanged by the presence of olefinic inhibitor. The specific rate is $5.36 \times 10^{-5} \text{ sec}^{-1}$ at 425.1°.

The rate of pyrolysis of ethyl bromide is reduced by olefinic inhibitors,^{3, 4} the first-order specific rate of the maximally inhibited reaction (cyclohexene) at 425.1° being $4.09 \times 10^{-4} \text{ sec}^{-1}$ (Thomas⁴ gives $3.70 \times 10^{-4} \text{ sec}^{-1}$), whereas the uninhibited reaction has a first-order specific rate³ of approximately $18 \times 10^{-4} \text{ sec}^{-1}$.

The results of mixed pyrolyses carried out in the presence of cyclohexene are shown in table 4, where t_b and t_c are times of introduction of bromide and chloride respectively, into the reaction vessel; t_f and p_f are as in table 2. From these results there is no change in overall rate and HBr/HCl analyses (table 5) confirm that the reactions are proceeding independently at their unmixed rates.

TABLE 4.—MIXED EtBr AND EtCl—INHIBITED—425.1°

| p_i mm | EtBr mm | t_b sec | EtCl mm | t_c sec | t_f sec | p_f (theor.) ^a mm | p_f (expt.) mm |
|-------------|------------|--------------|------------|--------------|--------------|-----------------------------------|---------------------|
| 89.5 | 209.2 | 510 | 77.1 | 0 | 1,710 | 374.3 | 371.6 |
| 16.4 | 111.8 | 900 | 74.9 | 0 | 2,100 | 238.1 | 237.7 |
| 56.3 | 80.4 | 740 | 274.0 | 0 | 2,540 | 431.2 | 437.5 |
| 43.9 | 54.2 | 405 | 61.0 | 0 | 2,205 | 150.2 | 147.4 |
| 42.8 | 92.6 | 390 | 134.0 | 0 | 1,590 | 273.6 | 273.4 |
| 42.8 | 86.3 | 455 | 115.0 | 0 | 1,655 | 246.7 | 243.5 |
| 33.8 | 71.5 | 450 | 173.2 | 0 | 1,650 | 287.1 | 287.6 |
| 146.0 | 99.0 | 0 | 62.3 | 520 | 1,800 | 217.0 | 214.3 |

^a calc. using unmixed inhibited rates; p_i , pressure of inhibitor.

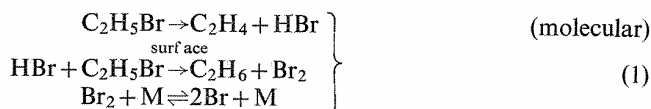
TABLE 5.—HBr/HCl ANALYSES—INHIBITED—425.1°

| p_i mm | EtBr mm | t_b sec | EtCl mm | t_f sec | HBr/HCl | |
|-------------|------------|--------------|------------|--------------|-------------------|-------|
| | | | | | ind. ^a | anal. |
| 43.9 | 54.2 | 405 | 61.0 | 2,260 | 4.12 | 3.84 |
| 42.8 | 92.6 | 390 | 134.0 | 1,590 | 3.30 | 3.95 |
| 42.8 | 86.3 | 555 | 115.1 | 1,775 | 3.26 | 3.20 |
| 33.8 | 71.5 | 450 | 173.2 | 1,650 | 1.88 | 1.76 |

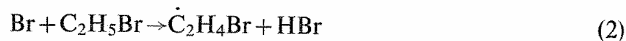
^a calc. from unmixed inhibited rates.

ETHYL CHLORIDE WITH HBr AND Br₂

Goldberg and Daniels³ proposed that the radical chain reaction in ethyl bromide was initiated by



followed by the usual propagation steps



In view of this, runs with hydrogen bromide and bromine added to ethyl chloride were performed. These are shown in tables 6 and 7 from which it is clear that considerable acceleration is caused, and with hydrogen bromide this acceleration is

surface dependent. Addition of cyclohexene in sufficient quantity prevented the acceleration.

TABLE 6.—ETHYL CHLORIDE WITH HBr

| unpacked vessel (452.1°) | | | | | | | |
|---------------------------------|-------|-------|-------|-------|-------|--------|--------|
| p_{HBr} (mm) | 71.4 | 133.9 | 217.0 | 306.6 | 455.1 | 508.8 | 0 |
| p_0 (mm) | 239.5 | 342.1 | 169.5 | 220.4 | 115.5 | 115.9 | >100 |
| $10^4 k_1$ (sec ⁻¹) | 3.82 | 4.38 | 5.83 | 6.40 | 7.21 | 7.81 | 2.46 * |
| packed vessel (450.8°) | | | | | | | |
| p_{HBr} (mm) | 35.8 | 112.7 | 177.6 | 313.7 | 414.0 | 0 | |
| p_0 (mm) | 336.8 | 270.3 | 292.4 | 271.1 | 236.6 | >100 | |
| $10^4 k_1$ (sec ⁻¹) | 5.68 | 7.18 | 10.6 | 7.68 | 18.4 | 2.34 * | |

* calculated.

TABLE 7.—ETHYL CHLORIDE WITH Br₂ (403.0°)

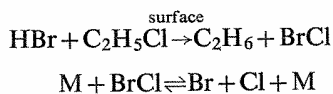
| | | | | | | |
|---------------------------------|-------|-------|-------|-------|-------|--------|
| p_{Br_2} (mm) | 6.4 | 20.0 | 38.6 | 58.3 | 65.2 | 0 |
| p_0 (mm) | 258.7 | 171.0 | 193.3 | 267.3 | 425.5 | >100 |
| $10^4 k_1$ (sec ⁻¹) | 1.58 | 6.45 | 11.2 | 11.8 | 11.2 | 0.14 * |

* calculated.

DISCUSSION

Apart from confirming the order of the ethyl bromide pyrolysis, demonstrating the effect of nitric oxide on decomposing ethyl bromide and re-determining the Arrhenius parameters for ethyl chloride, the importance of this paper lies in the results of the mixed pyrolyses. In the absence of inhibitor there is an interaction between the ethyl chloride and ethyl bromide decompositions and the increase in rate is caused mainly by an increase in ethyl chloride decomposition (i.e., HCl formation). In the presence of cyclohexene, no such increase occurs and there is no evidence of interaction.

The effects of hydrogen bromide and bromine on ethyl chloride, in the light of the ethyl bromide mechanism suggests that a surface-catalyzed reaction between hydrogen bromide and ethyl chloride



competes with the initiation reactions (1) above. It is already known that decomposing ethyl bromide sensitizes the decomposition of acetaldehyde¹² whereas decomposing ethyl chloride has no appreciable effect.¹³

All the known results are fully consistent with the previously proposed mechanisms,¹⁴ i.e., that ethyl chloride decomposes by a molecular elimination, while ethyl bromide decomposes by a mixed radical chain and molecular mechanism, the maximally inhibited rate in the presence of olefinic inhibitors being a molecular elimination.

We thank the Department of Scientific and Industrial Research for a studentship (N. C.) and Prof. A. Maccoll for advice and encouragement.

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- ¹⁴ e.g., Maccoll in *Theoretical Organic Chemistry*, (Butterworths, London, 1960).