528. *Gas-phase Photolysis of Ethyl Bromide.*

By R. Barker and Allan Maccoll.

Photolysis of ethyl bromide to ethylene and hydrogen bromide has been studied to obtain information about the radical-chain mechanism which is also present in the pyrolysis of this compound. The reaction has been studied in the gas phase at 150—300°. Above a certain pressure (which is dependent on temperature) the rate is given by:

$$-\mathrm{d}[C_2H_5Br]/\mathrm{d}t = \text{Constant}.I_0^{\frac{1}{2}}[C_2H_5Br],$$

where I_0 is the incident-light intensity, and the quantum yield (for hydrogen bromide formation) is large ($\gg 1$). The first-order rate constant has an activation energy of 10·5 kcal./mole. At lower pressures a second-order reaction becomes increasingly important: this follows the equation:

$$-\mathrm{d}[C_2H_5Br]/\mathrm{d}t = \text{Constant}.I_0[C_2H_5Br]^2.$$

The photolysis exhibits well-defined induction periods. Hydrogen bromide slightly accelerates the reaction and propene markedly inhibits it.

Maccoll and Thomas[1] showed that, in the pyrolysis of alkyl bromides, unimolecular elimination of hydrogen bromide is common to all the compounds studied. Primary alkyl bromides, in addition, decompose by another mechanism which can be effectively suppressed by the use of an inhibitor, *e.g.*, cyclohexene.[2] The second mechanism, in the case of ethyl bromide, has been variously described as (i) a radical non-chain process,[3] (ii) a radical chain process,[4] and (iii) a radical chain process initiated by a slow heterogeneous reaction between ethyl bromide and the hydrogen bromide formed initially in the reaction.[5] Mechanism (i) is now known to be incorrect.

Friedman, Bernstein, and Gunning[6] photolysed ethyl bromide in the gas phase in the presence of a ten-fold excess of cyclopentane and of mercury, and measured the ^{13}C isotope effect: this was found to be invariant over a temperature range 30—250°. Cyclopentane removed nearly all the ethyl radicals formed: $C_2H_5\cdot + C_5H_{10} \longrightarrow C_2H_6 + C_5H_{11}\cdot$ (very little ethylene was found) and bromine atoms were removed by mercury. The quantum yield for the production of ethane was unity and did not vary over the temperature range covered. In this system this value can be equated to the quantum yield for the primary process $C_2H_5Br + h\nu \longrightarrow C_2H_5 + Br$. We have studied the photolysis further.

Experimental

Commerical ethyl bromide was dried over phosphorus pentoxide and fractionated twice through a 3-ft. column packed with glass helices. The portion boiling at 38·0°/750 mm. was collected (cf. lit.[7]) and had n_D^{25} 1·4212 (lit.,[7] 1·42196). Hydrogen bromide was prepared by dehydrating a 25% aqueous solution of hydrogen bromide with phosphorus pentoxide, passed through a trap cooled in carbon dioxide–alcohol to remove bromine, and dried by repeated distillation through phosphorus pentoxide. Before use it was thoroughly outgassed. A commercial sample of hydrogen was passed over palladised asbestos at 300°, dried (Anhydrone), and passed through a trap cooled in liquid nitrogen. The bulb in which it was stored was flushed several times with hydrogen before finally being filled. Commercial propene was dried and outgassed.

---

[1] Maccoll and Thomas, *Nature*, 1955, **176**, 392.
[2] Green, Maccoll, and Thomas, *J.*, 1960, 184, and earlier references.
[3] Daniels and Veltman, *J. Chem. Phys.*, 1939, **7**, 756.
[4] Peri and Daniels, *J. Amer. Chem. Soc.*, 1950, **72**, 424.
[5] Goldberg and Daniels, *J. Amer. Chem. Soc.*, 1957, **79**, 1314.
[6] Friedman, Bernstein, and Gunning, *J. Chem. Phys.*, 1957, **26**, 528.
[7] Timmermans, " Physico-Chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950, p. 233.

Irradiations were carried out in a cylindrical fused-silica cell, 5 cm. long and 5 cm. in diameter, of total volume 98·4 c.c., on the ends of which quartz windows were sealed. The cell was attached to a conventional high-vacuum system through a capillary, graded silica–Pyrex seal. The cell was housed in an aluminium-block thermostat in the form of a hollow cylinder, 25 cm. long with an outside diameter of 11·5 cm. and inside diameter 5·6 cm. The block was in two halves which were fitted together with prongs to make an efficient seal. This enabled one-half of the block to be removed for inspection of the cell without removal of the cell from the vacuum-line. The heating element was a single coil of 20-gauge nichrome wire wound on mica and overwound at the ends of the block where heat loss was a maximum. Thermal insulation was provided by asbestos wool and a final asbestos-sheet covering. The heating element was energised from the a.c. mains and controlled by a bimetallic strip and a relay. By this means the temperature of the thermostat could be regulated to $\pm 0{\cdot}2°$. A thermocouple-well ran approximately three-quarters of the length of the block and temperatures were measured with a copper–constantan thermocouple; this showed that the variation in temperature along the thermostat was less than 0·4°. The thermostat was supported by two legs on an optical bench.

The pressure of gases inside the reaction cell was measured by a glass spiral gauge in conjunction with a mercury manometer: this excluded mercury from contact with the cell or its contents. A trap cooled in liquid nitrogen prevented any mercury from the mercury diffusion pump from passing back into the vacuum-system. The source of ultraviolet radiation was a low-pressure mercury lamp (Thermal Syndicate Ltd.) in the form of a U-tube, 30 cm. long and 1 cm. in diameter. The lamp was run off a high-reactance transformer (1000 v), a constant-voltage transformer being interposed between it and the mains to ensure that the energy supplied to the lamp remained constant. The lamp became only warm during operation and cooling was not necessary. The light emitted by the lamp was nearly wholly that of the mercury resonance line at 2537 Å: a small amount of light of λ 1890 Å was found to be present and was removed by filtration with a solution N in both sodium acetate and acetic acid contained in a quartz cell of 1 cm. light-path. The lamp was housed in an aluminium box which had a 0·6 cm. hole equipped with a shutter on one side. The lamp and the remainder of the optical system were mounted on an optical bench. A quartz lens was used to obtain a parallel beam of light, which was passed through the reaction cell. The thermostat was thermally isolated from the optical system with asbestos-board screens, and the whole of the apparatus except the lamp was housed in an asbestos-board box.

The high-vacuum system allowed continuous measurement of the pressure of the gases in the reaction cell to be made by means of the spiral gauge and permitted reactants to be admitted into the cell and products to be condensed out of it (for subsequent titration) at the end of a run. Air was excluded from the reaction cell at all times; when necessary, dry oxygen-free nitrogen was let into the cell.

Before a run was started the thermostat was brought to the required temperature and maintained at this value by adjusting the energy regulator as required. The lamp was switched on about 0·5 hr. before the start of a run, with the shutter closed. The cell was evacuated to 10^{-4}—10^{-5} mm. by a mercury diffusion pump backed with a mechanical pump. A sample of outgassed ethyl bromide was admitted to the reaction cell from the vapour-reservoir, nitrogen being admitted to the other side of the spiral gauge at the same time, to equate (approximately) the pressure across it. Other gases were admitted to the cell, where necessary, through an adjacent cold finger. After the tap had been closed, isolating the cell from the remainder of the vacuum-system, the ethyl bromide was allowed to equilibrate with the cell for about 15 min., note being taken of whether there was any dark reaction as indicated by a pressure rise. Similarly, after irradiation, the pressure was noted for a suitable length of time. Under all the conditions used, no dark reaction was detected.

The reaction was followed continuously by measuring the pressure. This procedure was checked by titrating the hydrogen bromide formed during the run with standard borax solution, assuming an overall reaction, $C_2H_5Br \longrightarrow C_2H_4 + HBr$. These two methods gave satisfactory agreement as shown in Fig. 1, where decomposition up to 24% of the ethyl bromide was carried out. The points are experimental and the straight line is the theoretical one. When the products were condensed in liquid nitrogen, the apparent amount of non-condensable gas was always $<3\%$ of the total pressure increase. The reaction was normally carried out to 5% decomposition or less. Pressure–time plots at two temperatures are shown in Fig. 2. There is an induction period which gives rise to a sigmoid plot over the initial decomposition range. After this induction period the pressure–time plot gives a good straight line throughout the range of decomposition covered, except at the lowest temperatures used (<200°). Here there is a falling-off from linearity after about 3% decomposition. This can be explained in terms of the thermal equilibrium $C_2H_5Br \rightleftharpoons C_2H_4 + HBr$ which has been studied by Lane, Linnett, and Oswin.[8] From the equilibrium constant which these authors determined, the percentage decomposition of ethyl bromide at the equilibrium point can be calculated. The values so obtained (1 atm. pressure of ethyl bromide being assumed) were:

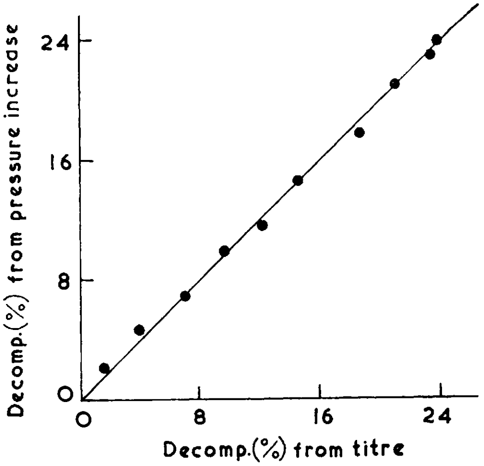


FIG. 1. Stoicheiometry of the reaction. Decomposition (%) from pressure increase plotted against decomposition (%) from titre.

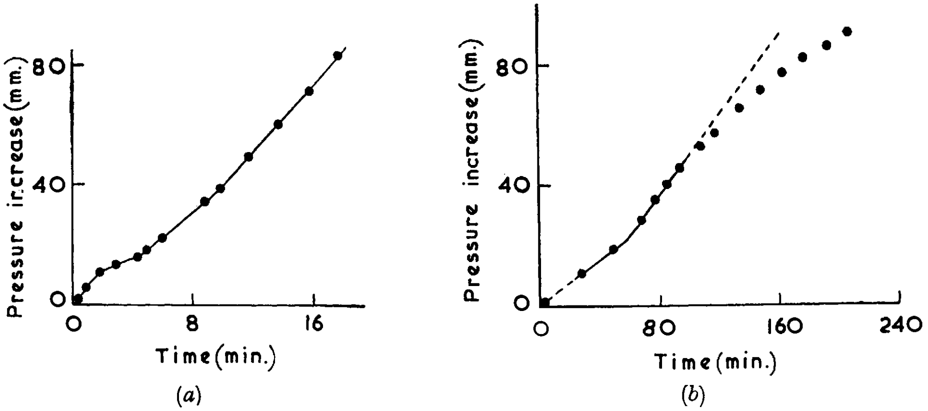


FIG. 2. Pressure–time plots. (*a*) 293·0°. (*b*) 187·2°.

	Temp.	300°	242°	200°	168°
Decomp. (%) of C_2H_5Br at equil.		46	21	16	5·7

Thus, in the temperature range 160—200° the equilibrium lies very much over to the ethyl bromide side. It is therefore not surprising that a fall-off in the rate of photolysis after only a slight decomposition takes place over this temperature range.

First-order rate constants were calculated by dividing the rate of pressure increase by the initial pressure of ethyl bromide: this method was thought to be justifiable since the reaction

---

[8] Lane, Linnett, and Oswin, *Proc. Roy. Soc.*, 1953, *A*, **216**, 361.

was carried out to only a small amount of decomposition and, after the initial induction period, the rate of pressure increase remained constant over the range of the reaction (except at the lowest temperatures studied, where the straight-line portion of the pressure–time graph was used).

Light-intensity measurements were made with a uranyl oxalate actinometer. The light intensity in front of and behind the reaction cell was measured and, with the decadic extinction coefficient of ethyl bromide at 2537 Å taken as 1·02 (ref. 9) and the quantum yield for the uranyl oxalate actinometer as 0·6, the amount of light absorbed by the ethyl bromide during a run was calculated. From this and the amount of reaction which had taken place, the quantum yield for the overall reaction was calculated. This quantum yield varied as the experimental conditions were changed in a manner similar to that of the first-order rate constant. That this should be so can be seen from a simple calculation (on assuming that the light absorption is low, as was the case here).

Results

The experiments were carried out in a clean-walled silica cell over the temperature range 160—300°. The first few runs were irreproducible, the rate (under constant conditions) slowly increasing with time. After about twenty runs had been carried out in the reaction cell, the rate became reproducible at a value about twice the original one. If air was let into the cell the rate fell to its original low value and then started to increase again as further runs were carried out, until it reached the steady reproducible value one more. Because of this, only dry oxygen-free nitrogen was let into the cell, when necessary. After experiments with added propene had been carried out, experiments with ethyl bromide alone gave lower (though quite reproducible) rates than previously. All the results quoted here were obtained with a " conditioned " reaction cell and before the experiments with added propene were carried out.

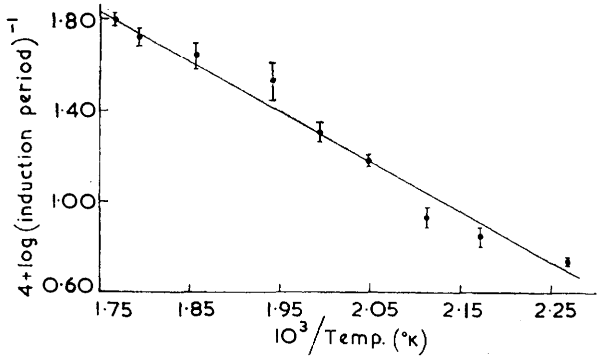


FIG. 3. Variation of induction period with temperature.

The induction period, which was obtained by extrapolating the straight-line portion of the pressure–time plot to zero pressure increase (*i.e.*, zero decomposition), showed a regular variation with temperature. A plot of log of the reciprocal of the induction period against the reciprocal of the absolute temperature is shown in Fig. 3. This gives an activation energy of 10·4 kcal./mole, which is close to the value obtained from the variation of the first-order rate constant with temperature. A surprising fact is that the induction period can apparently not be regenerated by switching off the incident light for a period of up to 10 min. (the induction period is then ~2 min.) and then switching the light on again. That this is not due to the presence of hydrogen bromide formed in the system is shown by the fact that in runs carried out with added hydrogen bromide the induction period is still present.

The first-order rate constant, k_1, was measured as a function of the initial pressure of ethyl bromide at two temperatures as shown in Fig. 4. The quantum yields associated with the horizontal parts of these two curves are 500 and 54 for 293° and 200°, respectively. These values have not been corrected for the increased absorption of light at higher temperatures.[6] Below a certain pressure, which is dependent upon the temperature, k_1 is markedly dependent

---

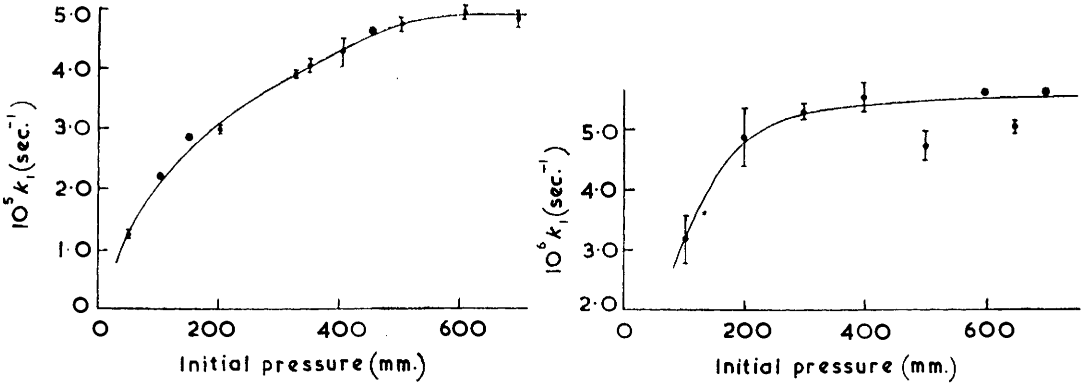
[9] Porret and Goodeve, *Proc. Roy. Soc.*, 1938, *A*, **165**, 31.

on pressure. The following Table shows values of k_1 and the second-order rate constant (k_2), which have been calculated for the lower initial-pressure region at 293°:

C_2H_5Br, initial press. (mm.)	50·1	102·9	150·6	200·1
10^5k_1 (sec.$^{-1}$)	1·25	2·18	2·93	3·00
10^7k_2 (sec.$^{-1}$ mm.$^{-1}$)	2·50	2·12	1·95	1·50

Although the second-order rate constant is not independent of pressure over the range 50—100 mm. of ethyl bromide, it tends to a constant value as the pressure decreases and probably reaches such a value below 50 mm. The apparatus used was not suitable for making kinetic measurements below 50 mm.

The variation of k_1 (in the region where it is independent of pressure) with temperature gives a good Arrhenius plot with an activation energy of 10·5 kcal./mole (this has been corrected for the variation in absorption of light by ethyl bromide over the temperature range used [6]). This is shown in Fig. 5.



(*a*) (*b*)

FIG. 4. Variation of k_1 with initial pressure (p_i). (*a*) 293·0°. (*b*) 200·2°.

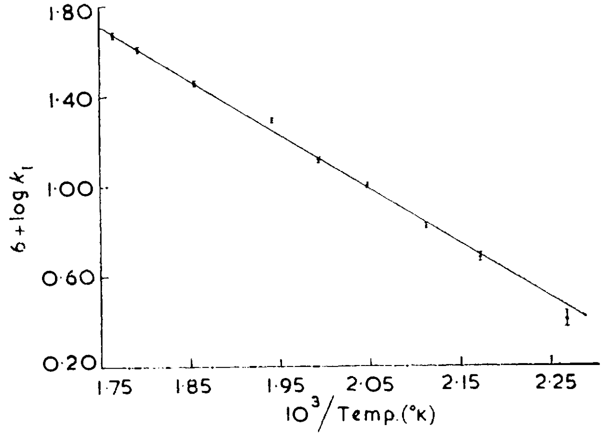


FIG. 5. Arrhenius plot.

Measurements were made of k_1 at different incident-light intensities. The light intensity was varied by placing gauzes of known transmission in the light-path: the transmission of these gauzes to 2537 Å light was measured on an ultraviolet absorption spectrophotometer.

The relationship between k_1 and the incident-light intensity was determined at a number of initial pressures of ethyl bromide. At 293° these were:

C_2H_5, initial press. (mm.)	600	300	150	50
Intensity exponent	0·52	0·56	0·64	0·9

The value of the intensity exponent is 0·5 at the higher pressures of ethyl bromide and it increases as the pressure decreases, tending to a value of unity at pressures below 50 mm.

We can calculate the amount of the thermal reaction expected over the temperature range used in this work. The values so obtained,[3] compared with values of k_1 for photolysis, are:

Temp.	k_1 for photolysis (sec.$^{-1}$)	k_1 for pyrolysis (sec.$^{-1}$)
293·0°	470×10^{-7}	$3·31 \times 10^{-7}$
265·8	2870×10^{-8}	$3·09 \times 10^{-8}$
215·2	$101{,}000 \times 10^{-10}$	$1·78 \times 10^{-10}$
167·8	$(2·58 \times 10^{7}) \times 10^{-13}$	$4·90 \times 10^{-13}$

No dark reaction was found experimentally over this temperature range.

Some experiments were carried out with added hydrogen bromide. The pressure of ethyl bromide used was 550 mm.; k_1 is independent of pressure here. Hydrogen bromide had a slight accelerating effect on the rate. The following Table shows that dp/dt divided by the total pressure (p_t) (where dp/dt is the rate of pressure increase) is independent of the amount of hydrogen bromide added to the system.

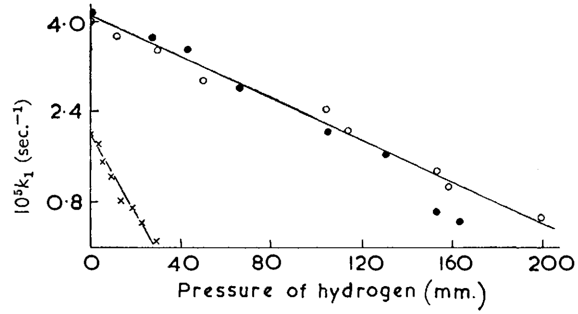


FIG. 6. Effect of added hydrogen (at 293·0°).

C_2H_5Br pressures (mm.): ● 600, ○ 300, × 100.

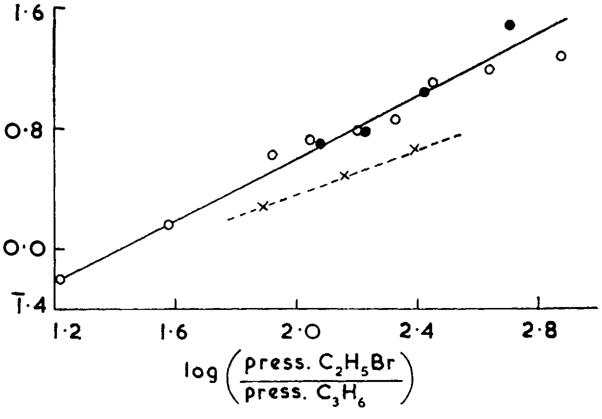


FIG. 7. Effect of added propene (at 293°).

Key as Fig. 6.

Temp. = 293·0°. Initial pressure of ethyl bromide = 550 mm.

HBr, press. (mm.)	0	21·6	50·3	101·6	149·8
dp/dt (10^{-2} mm./sec.)	2·27	2·34	2·53	2·61	2·85
$\frac{dp/dt}{p_t}$ (10^{-5} sec.$^{-1}$)	4·09	3·99	4·11	3·92	4·09

Addition of hydrogen to ethyl bromide caused a marked decrease in the rate of reaction.

A plot of k_1 against pressure of added hydrogen gives a straight line, as shown in Fig. 6. About 250 mm. of added hydrogen appeared to quench the reaction almost entirely.

The rate of photolysis decreased markedly on the addition of very small amounts (2—3 mm.) of propene. The rate of the inhibited reaction was inversely proportional to the partial pressure of propene over an ethyl bromide pressure range of 300—600 mm. (see Fig. 7). Propene also had the effect of prolonging the induction period.

DISCUSSION

The following facts have to be explained in a kinetic mechanism of the gas-phase photolysis of ethyl bromide. (1) At higher pressures ($\gg$500 mm.) the rate follows the kinetic equation $-d[C_2H_5Br]/dt = K[C_2H_5Br]I_0^{\frac{1}{2}}$, where I_0 is the incident-light intensity and K is a constant. At lower pressures ($\leqslant$500 mm.), mixed kinetics are exhibited by the system; it is likely that at initial ethyl bromide pressures of <50 mm. the kinetic equation is $-d[C_2H_5Br]/dt = K'[C_2H_5Br]^2I_0$. (2) The overall reaction can be stoicheiometrically represented by the equation $C_2H_5Br \longrightarrow C_2H_4 + HBr$. (3) The quantum yield for the reaction is high, being ~500 at 293° and ethyl bromide pressures above 500 mm. (4) The reaction exhibits well-defined induction periods which vary in a regular manner with temperature. (5) The overall activation energy is 10·5 kcal./mole. (6) Hydrogen bromide slightly accelerates the reaction. (7) Hydrogen decreases the rate of reaction, the effect being linearly related to the pressure of hydrogen. (8) Small amounts of propene markedly inhibit the reaction and prolong the induction period: the inhibited rate is inversely proportional to the partial pressure of propene.

The following mechanism is proposed:

$$C_2H_5Br + h\nu \longrightarrow C_2H_5 + Br\cdot \qquad (1)$$
$$Br\cdot + C_2H_5Br \longrightarrow HBr + C_2H_4Br \qquad (2)$$
$$C_2H_4Br\cdot \longrightarrow C_2H_4 + Br\cdot \qquad (3)$$
$$C_2H_4Br\cdot + Br\cdot \longrightarrow \text{Chain-ending} \qquad (4)$$
$$C_2H_5\cdot + Br\cdot \longrightarrow \text{Chain-ending} \qquad (5)$$
$$Br\cdot + Br\cdot + M \longrightarrow \text{Chain-ending} \qquad (6)$$
$$Br\cdot + \text{Wall} \longrightarrow \text{Chain-ending} \qquad (7)$$

The chain-propogating steps (2) and (3) have been postulated previously in a mechanism for the uninhibited pyrolysis of ethyl bromide.[5] The chain-ending steps (4), (5), and (6) (where M = ethyl bromide) are all possibilities which will give the kinetic equation which is found at the higher pressures. The rate equation found at lower pressures is given by a mechanism constituted of steps (1), (2), (3), and (7).

The above general scheme satisfactorily accounts for the experimental facts 1—4. Assuming a mechanism consisting of steps (1), (2), (3), and, say, (4) leads to a kinetic equation of the form

$$-\frac{d[C_2H_5Br]}{dt} = \left(\frac{k_1k_2k_3}{2k_4}\right)^{\frac{1}{2}}[C_2H_5Br]I_0^{\frac{1}{2}}$$

if $k_2k_3 \gg k_1I_0k_4$.

A mechanism utilising steps (1), (2), (3), and (7) gives

$$-\frac{d[C_2H_5Br]}{dt} = \left(\frac{k_1k_2}{k_7}\right)[C_2H_5Br]^2I_0$$

From the mechanism postulated for the higher pressures, the overall activation energy (E) is given by

$$E = \tfrac{1}{2}(E_1 + E_2 + E_3 - E_4) = 10{\cdot}5 \text{ kcal./mole.}$$

$E_1 = 0$, and step (4), a radical-radical reaction, is likely to have zero activation energy. We have then

$$E = \tfrac{1}{2}(E_2 + E_3) = 10{\cdot}5 \text{ kcal./mole.}$$

Anderson and Van Artsdalen[10] obtained a value of 13·6 kcal./mole for the activation energy of the reaction

$$\mathrm{Br + C_2H_6 \longrightarrow HBr + C_2H_5} \tag{8}$$

by studying the photobromination of ethane. In the photobromination of ethyl bromide, for which the equivalent rate-determining step is (2), the rate was found to be roughly equal to that of photobromination of ethane. E_2 is probably only slightly smaller than E_8, $E_2 < 13{\cdot}6$ kcal./mole, and $E_3 \geqslant 7{\cdot}4$ kcal./mole.

We can calculate values of ΔH_r [heats of reaction] for steps (2) and (3) by using known thermodynamic data. We first calculate $\Delta H_f(C_2H_4Br)$ from the relation

$$D(C_2H_4Br\text{–}H) = \Delta H_f(C_2H_4Br) + \Delta H_f(H) - \Delta H_f(C_2H_5Br),$$

where ΔH_f is the heat of formation, and D(A–B) is the A–B bond-dissociation energy. Then

$$\Delta H_{r_2} = \Delta H_f(HBr) + \Delta H_f(C_2H_4Br) - \Delta H_f(Br) - \Delta H_f(C_2H_5Br)$$

for reaction (2), and

$$\Delta H_{r_3} = D(C_2H_4\text{–}Br) = \Delta H_f(C_2H_4) + \Delta H_f(Br) - \Delta H_f(C_2H_4Br)$$

for reaction (3). The following values have been used (expressed in kcal./mole at 25°): $D(C_2H_4Br\text{–}H) = 97{\cdot}5$ [assumed to be the same as $D(C_2H_5\text{–}H)$ (ref. 11)]; $\Delta H_f(HBr) = -8{\cdot}7$ (ref. 12); $\Delta H_f(C_2H_5Br) = -15{\cdot}3$ (ref. 8); $\Delta H_f(C_2H_4) = 12{\cdot}5$ (ref. 12); $\Delta H_f(Br) = 26{\cdot}7$ (ref. 12); $\Delta H_f(H) = 52{\cdot}1$ (ref. 12). These give $\Delta H_f(C_2H_4Br) = 30{\cdot}1$ kcal./mole; $\Delta H_{r_2} = 10{\cdot}0$ kcal./mole, and $\Delta H_{r_3} = D(C_2H_4\text{–}Br) = 8{\cdot}1$ kcal./mole. As $E_2 < 13{\cdot}6$ kcal./mole, the value of ΔH_{r_2} implies that $E_{-2} < 3{\cdot}6$ kcal./mole. The fact that hydrogen bromide does not inhibit the photolysis of ethyl bromide implies an activation energy of >2 kcal./mole for the reaction $HBr + C_2H_4Br \longrightarrow Br + C_2H_5Br$ (cf. refs. 13 and 10).

Work on the photoaddition of hydrogen bromide to olefins[14] indicates that the activation energy for the reverse of reaction 3 is zero, so that the calculated value of ΔH_{r_3} can be equated to E_3. Thus the agreement between experimental and calculated values of E_2, E_3, and E_{-2} is satisfactory.

Hydrogen bromide has an extinction coefficient of 0·72 for light of 2537 Å (ref. 7), which is close to the value for ethyl bromide. It is known that the quantum yield for the process

$$\mathrm{HBr} + h\nu \longrightarrow \mathrm{H\cdot + Br\cdot} \tag{9}$$

is unity. If we assume that bromine atoms so produced contribute to the stationary-state concentration of bromine atoms, the rate of overall photolysis of the mixture will increase according to the pressure of added hydrogen bromide. By adding the above steps to the overall mechanism, a rate can be worked out containing the factor $(k_1I_0[C_2H_5Br] + k_9I_0[HBr])$. The results obtained experimentally are not comprehensive enough to permit their detailed comparison with this rate equation, but it can be seen that the increase in the rate of photolysis on addition of hydrogen bromide is of the right order.

---

[10] Anderson and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 479.

[11] Mortimer, Pritchard, and Skinner, *Trans. Faraday Soc.*, 1952, **48**, 220.

[12] "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Standards Circular 500, Washington, 1952.

[13] Kistiakowsky and Van Artsdalen, *J. Chem. Phys.*, 1944, **12**, 469.

[14] Vaughan, Rust, and Evans, *J. Org. Chem.*, 1942, **7**, 477.

It was found for the uninhibited pyrolysis of ethyl bromide that, when large pressures of hydrogen and nitrogen were added (>50 mm.), the first-order rate constant decreased linearly with the pressure of added gas.[15] This effect, however, was much less than that noted in the present work. Semenov [16] has pointed out that step (2) can take two forms:

$$Br\cdot + C_2H_5Br \longrightarrow HBr + \cdot CH_2\cdot CH_2Br \qquad (2a)$$

$$Br\cdot + C_2H_5Br \longrightarrow HBr + CH_3\cdot CHBr\cdot \qquad (2b)$$

and that (2*a*) is more endothermic than (2*b*). Only the bromoalkyl radical formed in step (2*a*) can decompose directly to ethylene and a bromine atom and so propagate the chain. The radical from (2*b*) can only recombine or react:

$$CH_3\cdot CHBr\cdot + CH_3\cdot CH_2Br \longrightarrow CH_3\cdot CH_2Br + \cdot CH_2\cdot CH_2Br \qquad (10)$$

to give a chain-propagating radical. Added hydrogen or nitrogen may act as an inert diluent, slowing down reaction (10) and increasing the probability of combination of $CH_3\cdot CHBr\cdot$ with an available radical. The kinetics of such a process are complex but might conform to the behaviour found experimentally.

The rate of photolysis of ethyl bromide in the presence of propene is inversely proportional to the partial pressure of propene. This implies that the chain-ending step of the inhibited reaction is

$$Br\cdot + C_3H_6 \longrightarrow \text{Chain-ending} \qquad (11)$$

The propene does not just prolong the induction period since the rate, after the induction period is over, is not the normal rate (when no propene is present) but is an inhibited rate dependent upon the amount of propene originally added. That is to say, all the propene is not consumed during the induction period. If this were so, then a value for the normal length of the chain in the photolysis of ethyl bromide could be calculated, by assuming that one molecule of propene reacts with one atom of bromine. If a calculation of this type is made the value of the normal chain length is about 20, which is far too small. This two-fold effect is observed in the inhibition of the pyrolysis of n-propyl bromide by propene.[17] It can be explained if the propene first inhibits the rate of formation of a steady-state concentration of radicals and also reduces the stationary concentration of radicals, so that the resultant rate is lowered. The lowest value of k_1 determined in the inhibiting experiments was 4×10^{-7} sec.$^{-1}$ for 18·6 mm. of added propene, with 300 mm. of ethyl bromide at 293°. This is just under 10^{-2} of the uninhibited rate constant. The quantum yield for the reaction at this temperature and pressure is about 350. In fact, some of this reaction must be thermal.

One of us (R. B.) acknowledges the award of a D.S.I.R. Maintenance Grant.

William Ramsay and Ralph Forster Laboratories,
University College,
Gower Street, London, W.C.1.
[Received, December 19th, 1962.]

---

[15] Fugassi and Daniels, *J. Amer. Chem. Soc.*, 1938, **60**, 771.

[16] Semenov, " Some Problems of Chemical Kinetics and Reactivity," Pergamon, London, 1958, Vol. I, p. 236.

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