

## TWO-CHANNEL COMPETITIVE PHOTODECOMPOSITION REACTION OF ETHYL BROMIDE AT 174.3 - 174.5 nm

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### Summary

The vacuum UV photolysis of ethyl bromide at 174.3 - 174.5 nm was studied over the pressure range 0.2 - 31.0 Torr at room temperature using a nitrogen atom resonance lamp. The pressure effect with and without helium as an additive was investigated. A scavenger effect of the reaction was also observed by adding NO as a radical scavenger. The principal reaction products were  $C_2H_4$ ,  $C_2H_6$  and  $CH_3CHBr_2$ . The product quantum yields  $\phi$  of  $C_2H_4$  and  $CH_3CHBr_2$  were constant with increasing pressure of  $C_2H_5Br$ , while that of  $C_2H_6$  was found to have a weak positive pressure dependence at low pressure but became constant on increasing the pressure. When the helium pressure was varied at a constant  $C_2H_5Br$  pressure, however, the quantum yields of all products were found to be pressure independent. The formation of  $C_2H_6$  and  $CH_3CHBr_2$  was completely suppressed by adding NO and that of  $C_2H_4$  was reduced. These results were interpreted in terms of two-channel competition between molecular elimination processes and radical formation. The decomposition modes were 20% molecular elimination and 80% radical reactions. The above results suggest that two electronically excited states exist, and that a reactant molecule which absorbs a photon proceeds to one of two different electronically excited states via one of two pathways. One of the electronically excited states plays a role as the main source of the molecular elimination products and the other state is related to the radical decomposition mode.

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### 1. Introduction

Recent studies [1 - 4] have shown that the modes of the primary photochemical processes in alkyl halides are wavelength dependent. Alkyl halides dissociate to alkyl and halogen radicals on irradiation within the first absorption band, whereas they undergo molecular elimination within the second absorption band [5].

Tschuikow-Roux and coworkers [2, 6, 7] observed that the major primary process in the photolysis of ethyl halides was molecular elimination, and that its contribution increased at shorter wavelengths. Their explanation of these results was that carbon-halogen bond fission was associated with the first ( $n \rightarrow \sigma^*$ ) absorption band of the species, while the molecular elimination processes were more clearly associated with the higher Rydberg-type transition. Since the absorption band varies from one halogen-atom-substituted ethane to another, substituted halogen atoms also play an important role in determining the mode of the reaction. Photolyses of  $C_2H_5F$  [6],  $C_2H_5Cl$  [2],  $C_2H_5Br$  [8] and  $C_2H_5I$  [9] have been investigated at 147 nm; the principal primary processes involved molecular elimination. These studies showed that the quantum yield of the molecular elimination reaction decreases as the reactant varies from  $C_2H_5F$  to  $C_2H_5I$ .

Photochemical data for  $C_2H_5Br$  in the UV region have been accumulated at a number of wavelengths [10 - 13]. Although there are some conflicting interpretations of these data, all the workers agree that the photochemistry of  $C_2H_5Br$  in the 210 - 313 nm region, where only a valence shell transition is possible, proceeds by radical reaction via C-Br bond fission. The vacuum UV photolysis of this compound has only recently attracted our attention. Our continuing photochemical studies of  $C_2H_5Br$  at 104.8 - 106.7 nm [14] 123.6 nm [15] and 147 nm [8] have shown that the primary processes are strongly energy dependent. In this paper we report the 174.3 - 174.5 nm vacuum UV photolysis of  $C_2H_5Br$ . This wavelength, which is near the lower limit of the Rydberg transition, induces both A and B band excitation of  $C_2H_5Br$  [16].

## 2. Experimental details

The photolyses were carried out at room temperature in a conventional static system using a borosilicate glass reaction vessel of volume 336 cm<sup>3</sup>. Secondary photolysis of the products was prevented by using an all-glass gas circulating pump. Total conversions were held at less than 1% of the reactant.

The light source was a nitrogen atom resonance lamp [17] equipped with a Suprasil quartz window [18] 1 mm thick which was operated using a microwave generator (KIVA Instrument Inc., model MPG-4M). The purity of the emission spectrum of the lamp was checked using a 0.3 m GCA-McPherson 218 vacuum UV monochromator with a 20  $\mu$ m slit and a scanning speed of 5 nm min<sup>-1</sup>. The main lines of the spectrum were at 174.3 and 174.5 nm with several minor contributions between 165 and 198 nm. It was estimated that the contributions to the total emission were as follows: about 10% above 172.6 nm, about 70% between 172.6 and 177.6 nm and about 20% below 177.6 nm. The intensity of the lamp varied between  $1.4 \times 10^{13}$  and  $6.7 \times 10^{13}$  photons s<sup>-1</sup> during the experiment. The possibility of deviation due to the intensity fluctuations was eliminated by repeating the actinometry readings twice before and after each run and taking only those

runs which agreed to within a 5% deviation of the readings. The chemical actinometry was based on the production of  $C_2H_2$  in the photolysis of  $C_2H_4$ , and a quantum yield of 0.75 [19] was assumed throughout the calculations.

Product analysis was performed using a Hewlett-Packard 5840A gas chromatograph which was equipped with twin-flame ionization detectors. Two columns were used in the analysis of the products, a stainless steel Chromosorb 108 column 3 m long with an outside diameter of 3.13 mm (1/8 in) for the major products  $C_2H_4$  and  $C_2H_6$  at 80 °C and a helium flow rate of 40  $cm^3\ min^{-1}$  and an Ni-20%Si DC 550 on Chromosorb P column of the same dimensions for  $C_2H_4Br_2$  at 60 - 120 °C. Sampling was performed via a six-port Valco gas sampling valve. The reaction products  $C_2H_4$ ,  $C_2H_6$  and  $C_2H_4Br_2$  were identified by comparing their retention times with those of standard samples and their sensitivities to the detectors were subsequently determined.

The  $C_2H_5Br$  reactant (Eastman Kodak) was purified to better than 99.99% by fractional and low temperature trap-to-trap distillation until the residual impurities could not be detected by gas chromatography.

### 3. Results

The principal photolysis products were  $C_2H_4$  and  $C_2H_6$ . The results are given in Table 1, and plots of the product quantum yield *versus* pressure are shown in Fig. 1. In Table 1 runs 1 - 16 show the pressure effect of  $C_2H_5Br$ : the quantum yields of  $C_2H_6$  increase slightly at low pressure but otherwise remain constant with an average value of 0.95 while the quantum yield of  $C_2H_4$  remains substantially unchanged with an average value of 0.22. Runs 17 - 20 show the total pressure effect on addition of helium: the quantum

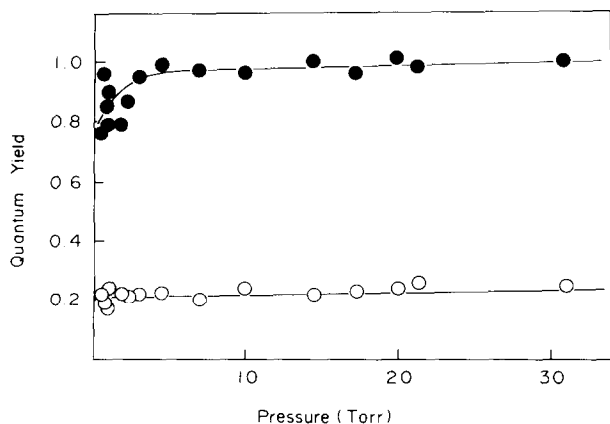


Fig. 1. Variation in the quantum yield with the  $C_2H_5Br$  pressure between 0.45 and 31.00 Torr:  $\circ$ ,  $C_2H_4$ ;  $\bullet$ ,  $C_2H_6$ .

TABLE 1

Product quantum yields of the photolysis of  $C_2H_5Br$  at 174.3 - 174.5 nm

Run	$P_{C_2H_5Br}$ (Torr)	Additive (Torr)	Quantum yield for the following species		$I_t/N \times 10^3$ (photons molecule <sup>-1</sup> )
			$C_2H_4$	$C_2H_6$	
1	0.45		0.22	0.76	24.10
2	0.85		0.19	0.96	8.55
3	0.95		0.17	0.85	7.66
4	1.00		0.24	0.79	5.70
5	1.00		0.24	0.95	5.82
6	1.85		0.22	0.79	7.83
7	2.35		0.21	0.87	4.67
8	3.00		0.22	0.95	3.08
9	4.50		0.25	0.99	2.05
10	7.00		0.20	0.97	1.32
11	10.00		0.24	0.96	1.10
12	14.50		0.22	1.00	0.76
13	17.30		0.23	0.96	0.42
14	20.00		0.24	1.01	0.55
15	21.40		0.26	0.98	0.80
16	31.00		0.25	1.00	0.72
17	1.00	He 4.90	0.24	0.86	10.80
18	1.00	He 10.00	0.21	0.86	7.20
19	1.00	He 20.40	0.23	0.86	8.20
20	1.00	He 30.00	0.22	0.87	7.50
21	1.00	NO 0.75	0.21		10.80
22	1.00	NO 4.80	0.19		7.20
23	1.10	NO 1.30	0.20		7.50
24	1.00	NO 3.80	0.20		10.80
25	19.40	NO 3.00	0.19		0.56
26	31.80	NO 3.80	0.20		0.26
27	0.80	NO 0.80	0.22		4.80
28	1.40	NO 1.80	0.20		2.80
29	0.70	NO 4.30	0.19		4.50
30	3.10	NO 3.50	0.23		1.60
31	1.25	NO 7.15	0.24		5.40
32	7.40	NO 2.20	0.20		0.52
33	1.05	NO 9.00	0.20		3.00
34	0.75	NO 10.65	0.21		6.00

yields of  $C_2H_6$  and  $C_2H_4$  are 0.86 and 0.22 respectively indicating that the monatomic gas was not very efficient at reducing the quantum yields of the major products. Runs 21 - 34 show the effects of using NO gas as a radical scavenger: the quantum yield of  $C_2H_4$  is 0.21 and  $C_2H_6$  is absent.

The secondary product  $CH_3CHBr_2$  was observed at low pressure as shown in Table 2. In runs 1 - 13 the quantum yields of  $CH_3CHBr_2$  have an average value of 0.056, while runs 14 and 15 show the results of scavenging with no  $CH_3CHBr_2$  being produced on addition of NO to the reactant. No

TABLE 2

Quantum yield of the secondary product

Run	$P_{C_2H_5Br}$ (Torr)	Additive (Torr)	$\phi_{CH_3CHBr_2}$
1	0.20		0.055
2	0.20		0.054
3	0.25		0.061
4	0.40		0.055
5	0.40		0.052
6	0.40		0.052
7	0.45		0.051
8	0.45		0.057
9	0.55		0.055
10	0.65		0.059
11	0.65		0.053
12	0.85		0.056
13	1.40		0.067
14	0.65	NO 27.3	0.000
15	0.70	NO 2.2	0.000

attempt was made to investigate the quantum yields of other minor secondary products because of their small quantities, although their detector responses were far greater than most of those of the major products.

The conversion  $It/N$  (Table 1) varied from  $1.5 \times 10^{-4}$  to  $2.4 \times 10^{-2}$  photons molecule<sup>-1</sup>, where  $I$  is the number of photons absorbed per unit time in the reaction cell,  $t$  is the irradiation time and  $N = PVN_0/RT$  is the total number of reactant molecules.

#### 4. Discussion

A large part of the  $C_2H_4$  was formed from a non-scavengeable precursor. This result may be due to the precursor of the major portion of  $C_2H_4$  being in an electronically excited state of  $C_2H_5Br$  which proceeds via the decomposition process to give  $C_2H_4$  and  $HBr$  by molecular elimination. Another possible interpretation of this result is that, since  $C_2H_5$  radicals are formed by the fission of  $C-Br$  bonds whose energies are higher than the threshold energy for decomposition, they cannot be scavenged by  $NO$  because of their short lifetimes and therefore readily decompose to yield  $C_2H_4$ . This simple assumption may not be correct since the presence of  $NO$  has little effect on the quantum yield of  $C_2H_4$ . However, the small decrease in  $\phi_{C_2H_4}$ , *i.e.* about 0.03, in the presence of  $NO$  (Table 1, runs 21 - 34) does not completely rule out the possibility of a radical process which produces  $C_2H_4$ . Like the scavengeable portion of  $C_2H_4$ , the other scavengeable products appear to originate from  $C_2H_5$  radicals which are formed by fission of the  $C-Br$  bonds of electronically excited  $C_2H_5Br$ . This result suggests that  $C_2H_5Br$  is excited by two-channel competition.

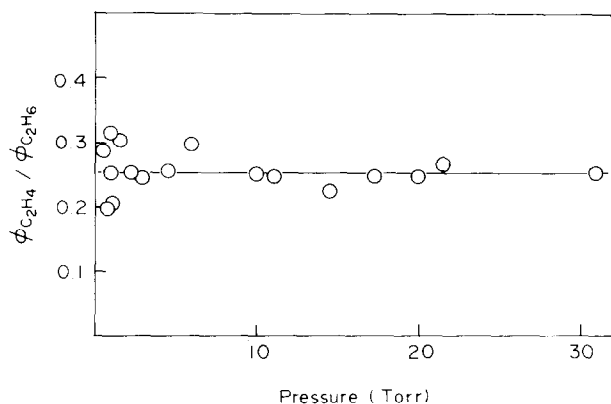
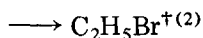
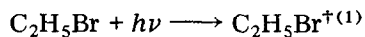


Fig. 2. Variation in  $\phi_{C_2H_4}/\phi_{C_2H_6}$  with pressure between 0.45 and 31.00 Torr.

As shown in Fig. 2 the ratio  $\phi_{C_2H_4}/\phi_{C_2H_6}$  is independent of pressure, so it can be deduced that one electronically excited state does not convert to another excited state through a collisionally induced process. This result suggests that a  $C_2H_5Br$  molecule which absorbs a photon proceeds to one of two different excited states via one of two pathways. On the basis of the foregoing proposition, in one of the initially formed excited states  $C_2H_5Br^{+(1)}$  decomposes to  $C_2H_4$  and  $HBr$  by molecular elimination, while in the other excited state  $C_2H_5Br^{+(2)}$  decomposes by  $C-Br$  bond rupture to yield a scavengeable  $C_2H_5$  radical. The nature of the photon-absorbing  $C_2H_5Br$  molecule investigated in this study can therefore be summarized as follows:



where the numbered daggers denote electronically excited states.

Since the photon energies in the region 174.3 - 174.5 nm are 163.9 - 163.7 kcal mol<sup>-1</sup> and  $\Delta H$  for reaction (1) is 20 kcal mol<sup>-1</sup> [20], there must be 144 kcal mol<sup>-1</sup> of excess energy to be distributed between  $C_2H_4$  and  $HBr$ . This energy is larger than the activation barrier for  $H_2$  elimination from  $C_2H_4$ .  $C_2H_2$  was not detected in our product analysis which suggests that  $HBr$  must carry a large fraction of the excess energy. If the  $H-Br$  bond energy is taken as 89 kcal mol<sup>-1</sup>, many of the hot  $HBr$  molecules should decompose further into hydrogen and bromine atoms and/or may also be collisionally stabilized by other molecules:



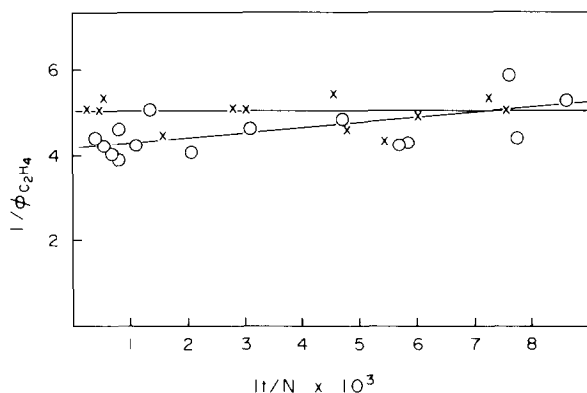
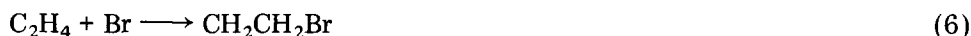


Fig. 3.  $1/\phi_{C_2H_4}$  vs.  $It/N$ : O, experiment without NO; X, experiment with NO.

In addition Fig. 3 shows that  $1/\phi_{C_2H_4}$  increases with increasing total conversion  $It/N$ . Since a decrease in  $C_2H_4$  is also shown by the reverse reaction, the mechanism may be



However, since  $1/\phi_{C_2H_4}$  does not vary with increasing  $It/N$  in the experiments using NO as an additive (Fig. 3), it can be concluded that reaction (5) does not occur.

The complete disappearance of  $C_2H_6$  and  $CH_3CHBr_2$  in the presence of NO confirms that these products are formed from radical precursors. The  $C_2H_5$  radical formed by the fission of the C—Br bond in  $C_2H_5Br^{\dagger(2)}$  may abstract the hydrogen atom from the reactant molecule:



The fact that the total quantum yield exceeds unity leads to the following mechanism:



where H is formed from reaction (3). In addition, the heat of reaction (9), *i.e.*  $-17 \text{ kcal mol}^{-1}$  [20], obtained from thermochemical data for the chemical species shows that this reaction is thermodynamically favourable.

The following mechanism is proposed for the formation of the scavengable portion of the  $C_2H_4$ :





where reaction (12) is the reverse of reaction (6). However, the heat of reaction (10) is  $38.9 \text{ kcal mol}^{-1}$  which is much higher than that of reaction (7a), *i.e.*  $-8.8 \text{ kcal mol}^{-1}$ , or reaction (7b), *i.e.*  $-5.8 \text{ kcal mol}^{-1}$ . The ratio of disproportionation to combination in reaction (11) is about 0.1 - 0.5 [21]. The combination product, *i.e.* *n*-butane, was not detected in our product analysis. Therefore it may be reasonable to eliminate reactions (10) and (11) from the mechanism. In contrast, since the value of the heat of reaction (12) is reasonable [22], *i.e.*  $8.8 \text{ kcal mol}^{-1}$ , it should be retained.

We propose the following termination steps:



The product quantum yield of  $\text{CH}_3\text{CHBr}_2$  [23] shown in Table 2 is less than the expected value since the bromine radical combination and the bromoethyl radical combination (reactions (14) and (15) respectively) compete with reaction (13). Severe contamination of the lamp window and the reaction vessel wall by the bromine molecule and  $\text{C}_4\text{H}_8\text{Br}_2$  were experienced on each run. Consequently, although the presence of the  $\text{C}_4\text{H}_8\text{Br}_2$  molecule was confirmed by gas chromatography analysis, the quantitative analysis of  $\text{C}_4\text{H}_8\text{Br}_2$  was not attempted.

As discussed earlier, two markedly different decomposition modes, *i.e.* 20% molecular elimination and 80% radical formation, were observed in the

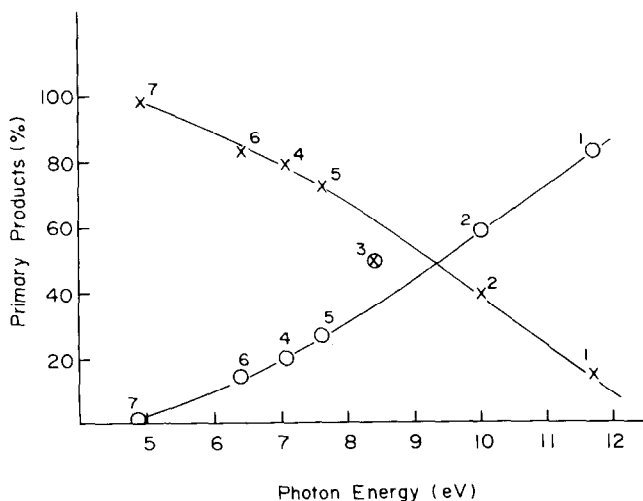


Fig. 4. Energy dependence of the photodissociation reaction of  $\text{C}_2\text{H}_5\text{Br}$  (o, molecular elimination; x, radical formation): points 1, ref. 14; points 2, ref. 15; points 3, ref. 8; points 4, this work; points 5, ref. 24; points 6, refs. 25 and 26; points 7, ref. 13.



vacuum UV photolysis of ethyl bromide by nitrogen atom resonance lines (174.3 - 174.5 nm). Finally, we briefly compare this result with that of previous work. As shown in Fig. 4, the primary processes of the photochemical reaction of  $C_2H_5Br$  are strongly dependent on the irradiation wavelength. For  $C_2H_5Br$  photolysis we found that the contribution of the molecular elimination increases as the wavelength of the light source shifts to a shorter wavelength.

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