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Vacuum Ultraviolet Photolysis of Ethyl Bromide at 104.8-106.7 nm

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Vacuum ultraviolet photolysis of ethyl bromide was studied at 104.8–106.7 nm (11.4–11.6 eV) in the pressure range of 0.2–18.6 torr at 25 °C using an argon resonance lamp with and without additives, *i. e.*, NO and He. Since the ionization potential of CH_3CH_2Br is lower than the photon energy, the competitive processes between the photoionization and the photodecomposition were also investigated. The observations indicated that 50% of absorbed light leads to the former process and the rest to the latter one. In the absence of NO the principal reaction products for the latter process were found to be CH_4, C_2H_2, C_2H_4, C_2H_6, and C_3H_8. The product quantum yields of these reaction products showed two strikingly different phenomena with an increase in reactant pressure. The major products, C_2H_4, and C_2H_6, showed positive effects with pressure whereas the effects on minor products were negative in both cases, *i.e.*, He and reactant pressures. Addition of NO completely suppresses the formation of all products except C_2H_4 and reduces the C_2H_4 quantum yield. These observations are interpreted in view of existence of two different electronically excited states. The initial formation of short-lived Rydberg transition state undergoes HBr molecular elimination and this state can cross over by collisional induction to a second excited state which decomposes exclusively by carbon-bromine bond fission. The estimated lifetime of the initial excited state was $\sim 4\times 10^{-10}$ sec. The extinction coefficient for CH_3CH_2Br at 104.8–106.7 nm and 25 °C was determined to be $\varepsilon=(1/PL)\ln(I_0/I_t)=2061\pm 160\ \mathrm{atm^{-1}cm^{-1}}$ with 95% confidence level.

Introduction

In this study 104.8–106.7 nm photolysis of ethyl bromide was carried out in the pressure range 0.2–20 torr. Previous studies have shown that the modes of primary photochemical decomposition are wavelength dependent.[1]

In the ultraviolet region electronic transitions of haloalkanes are termed $n\rightarrow\sigma^*$ and their broad maximum appears at about 250 nm [2] and the short wavelength side of this absorption frequently extends into the vacuum ultraviolet region where it may overlap the far more intense absorption associated with Rydberg type transitions. Therefore, it is quite probable that in certain cases the primary products of photodecomposition differ in two regions of the spectrum. For example, Fujimoto and Wijnen[3] have investigated the photolysis of $CD_3\,CHCl_2$ where at greater than 220 nm the carbon-halogen bond fission is a predominant primary photodecomposition process, while Cremieux and Herman[4] reported that the major primary process of photodecomposition of CH_3CH_2Cl at 123.6 nm was molecular elimination of HCl.

Tschuikow-Roux and co-workers have investigated the photolyses of CH_3CH_2F,[5] CH_3CH_2Cl,[6] and other fluoroethyl chlorides[7–10] at 147 nm and 123.6 nm. They reported the major primary process as molecular elimination and in the shorter wavelength photolysis the portion of molecular elimination increased. So they suggested that carbon-halogen bone fission should be associated with the first ($n\rightarrow\sigma^*$) absorption band of the species in question, while molecular elimination processes are more clearly associated with the higher "Rydberg type" transitions, for example, $n\rightarrow 4s$. The excited precursor formed at 147 nm may be sufficiently long-lived to undergo collisional modification, as the primary process is pressure dependent while that of 123.6 nm photolysis is not.

Cremieux and Herman[4] reported the photolysis of CH_3CH_2Cl at 104.8–106.7 nm using an argon resonance lamp. They reported 40 % ionization because the photon energy is above the ionization potential of CH_3CH_2Cl, and fragmentation and molecular elimination as primary processes.

Serveral workers[11–13] have investigated the photolysis of CH_3CH_2Br at greater than 200 nm where the carbon-bromine bond fission is the major primary process, We are interested in the wavelength dependence of the primary photodecomposition process and extent of molecular elimination processes occurring in vacuum ultraviolet. In this laboratory a series of vacuum ultraviolet photolyses of CH_3CH_2Br was performed using 104.8–106.7 nm radiation which is just above the ionization potential of CH_3CH_2Br.

Experimental

Photolyses were carried out at room temperature in a conventional mercury free vacuum line with ACE greaseless stopcocks. The reaction vessel of 336 ml was fitted with a gas circulating pump made of glass only. The argon resonance lamp[14] was powered by a microwave generator, KIVA Instruments Inc., Model MPG-4M, with average power of 30 W. The window material was 0.2mm thick LiF with thin film of In metal coating[15] to prolong the lifetime of the lamp whose intensity decreased with operating time due to F-center formation of LiF. Lamp intensities were varied from 1.1×10^{14} to 1.0×10^{13} photons/sec and the reaction time was controlled for periods such that conversions were less than 2%.

Actinometry was based upon the production of acetylene from the photolysis of ethylene[16] which was assumed to give a quantum yield of unity.

Products analysis was carried out by home made gas chromatograph (GC) with a hydrogen flame ionization detector(FID) with typical sensitivity 1×10^{-11} A by comparison of retention times of the products with those of authentic samples. The detector response regarding sample variations and GC conditions were calibrated prior to the experiment. Reaction products and the reactant were separated and identified using a $1/8'' \times 3$ m Chromosorb 108 stainless column with carrier gas, *i.e.*, He 50 m*l*/min, H_2 25 m*l*/min, and compressed air flow rate 250 m*l*/min. Sampling was done *via* a six port Valco gas sampling valve. H_2 and HBr, while certainly major products, could not be determined in this experiment since the FID does not respond to them.

Ethyl bromide, obtained from Eastman Company, was purified several times by fractional distillation and low boiling-trap distillation. Argon, Takachiho, Japan, stated purity of 99.999% was used with no further purification. Other gases, all from Matheson Company, stated purities above 99.5%, were subjected to trap-to-trap distillation at 77° K and used without further purification.

Results

The principlal reaction products were C_2H_4, C_2H_6, C_2H_2, CH_4, and C_3H_8. No attempt was made to include other minor products because of their small quantities though

TABLE 1: Quantum Yields of Products in the Photolysis of C_2H_5Br at 104.8–106.7 nm

Run	$P_{C_2H_5Br}$ (torr)	Additives (torr)	Product quantum yield (ϕ_i)				
			CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_8
1	0.2		0.038	0.37	0.31	^{a}	^{a}
2	0.2		^{a}	0.38	0.29	^{a}	^{a}
3	0.2		0.041	0.36	0.31	0.12	0.033
4	0.2		0.033	0.38	0.28	0.10	^{a}
5	0.5		0.019	0.39	0.38	0.057	0.020
6	0.8		0.014	0.42	0.45	^{a}	^{a}
7	0.8		0.013	0.43	0.46	0.056	^{a}
8	0.8		^{a}	0.42	0.44	0.056	0.026
9	1.3		0.023	0.44	0.47	0.050	0.046
10	1.8		0.019	0.43	0.44	^{a}	^{a}
11	1.8		0.018	0.42	0.45	^{a}	^{a}
12	1.8		0.018	0.42	0.44	0.038	^{a}
13	2.6		0.014	0.44	0.53	^{a}	^{a}
14	2.6		^{a}	0.43	0.51	0.040	^{a}
15	2.6		0.015	0.44	0.51	0.027	^{a}
16	3.5		^{a}	0.44	0.49	^{a}	^{a}
17	4.8		0.012	0.42	0.52	^{a}	^{a}
18	4.8		^{a}	0.44	0.56	^{a}	^{a}
19	7.8		^{a}	0.44	0.57	^{a}	^{a}
20	9.8		^{a}	0.44	0.55	^{a}	^{a}
21	13.2		^{a}	0.46	0.57	^{a}	^{a}
22	18.6		^{a}	0.44	0.57	^{a}	^{a}
23	0.8	He 5.3	0.023	0.43	0.43	0.050	0.023
24	0.8	He 8.3	^{a}	0.42	0.43	^{a}	^{a}
25	0.8	He 13.0	^{a}	0.43	0.45	^{a}	^{a}
26	0.5	NO 0.5	—	0.38	0.0	0.053	0.0
27	0.8	NO 0.7	—	0.37	0.0	0.038	0.0
28	0.8	NO 1.5	—	0.38	0.0	^{a}	0.0

^{a} Trace amounts, ϕ could not be determined

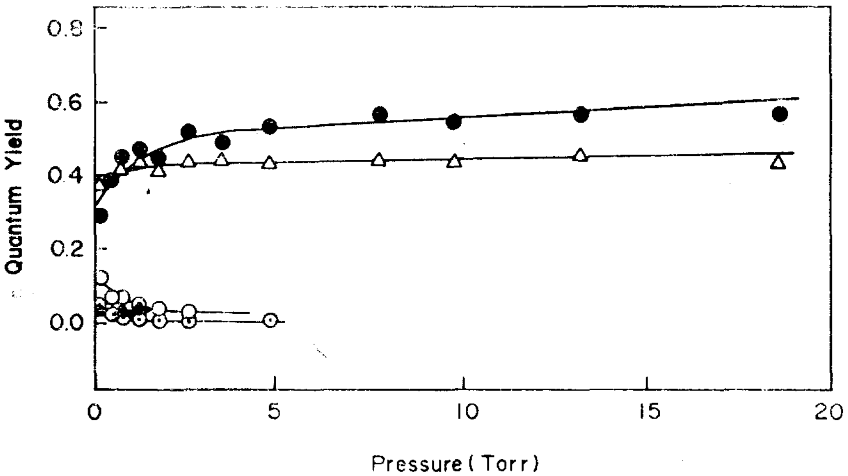

Figure 1. Variation of quantum yields of products with pressures of C_2H_5Br (0.2 –20 torr). ● C_2H_6, △ C_2H_4, ○ C_2H_2, ▲ C_3H_8, and ⊙ CH_4.

their detector responses were far greater than most of major products.

The investigation was carried out at pressures from 0.2 to 18.6 torr of ethyl bromide. The results are given in Table 1 together with the plots of the product quantum yields (ϕ_i) versus pressures in Figure 1. As shown in Figure 1, below 1 torr of reactant pressures, quantum yields of two major products, *i.e.*, C_2H_4 and C_2H_6, were markedly increases. Then, $\phi_{C_2H_4}$ reached a plateau at 1 torr and remained constant with pressure increase. In the case of C_2H_6, the plateau was not so obvious. As minor products, C_2H_2, CH_4, and C_3H_8 were also observed and their quantum yields were decreased with a pressure increase. The measured extinction coefficient of C_2H_5Br was 2061 ± 160 atm^{-1} cm^{-1}. Therefore, the possible absorption at our lowest reaction concentration, *i.e.*, 0.2 torr, became at least 65% and 93% at 0.5 torr. Whereas ϕ_i calculation in Table 1, the used actinometer C_2H_4, showed 92% absorption at 0.2 torr and 100 % at 0.5 torr, respectively. These anomalous behaviors are presented in Figure 1 where the uncalibrated ϕ_i's are plotted against pressure.

A series of scavenger effects was observed after adding 0.5–1.5 torr of NO gas to 0.5–0.8 torr of C_2H_5Br. In these observations, $\phi_{C_2H_4}$ was decreased while the precursors of C_2H_6 and C_3H_8 were readily scavenged by NO. The observation of CH_4 under NO gas addition was impractical because of its close retention time to that of NO.

In order to observe possible collisional activation during the photolysis, an inert gas, He, was added at 5.3–13.0 torr to a constant concentration, 0.8 torr of C_2H_5Br. ϕ_i's of major products were unchanged and the thermal effect therefore was concluded to be negligible in the reaction.

Discussion

Among several primary processes in competition, one can assume that carbon–bromine bond fission is a primary process, and C_2H_5 radical formed by this process must yield C_2H_4 upon decomposition and radical disproportionation. Also a large proportion of C_2H_4 should be formed by a precursor which is not scavenged by NO, a radical scavenger. A possible interpretation for this is that since C_2H_5 radicals formed by carbon-bromine bond fission whose energies ar higher than the threshould energy for decomposition, they cannot be scavenged by NO because of their short lifetimes and therefore can readily decompose to yield C_2H_4 This simple assumption may not be correct since there are insufficient radical products such as C_2H_6 or C_3H_8 in the C_2H_5Br –NO system. It is suggested that the non-scavengeable portion of C_2H_4 originates from molecular elimination from an initially formed excited state. However, our observation with considerable amounts of C_2H_4 trapped by NO eliminates the possibilities of molecular elimination as a sole source of C_2H_4.

Since the chemical reaction occurs only from electronically excited states, one can assume two electronically excited states in this system, and thus a state via molecular elimination and the other through carbon-bromine bond fission. Our observations of decreasing tendency of $\phi_{C_2H_4}$ and $\phi_{C_2H_2}$ with total pressure rise and therefore the radical precursor content increase may be interpreted as collisional quenching to an electronically ground state by collisionally induced conversion, highly vibrationally excited species must be formed and then they will decompose to C_2H_4 and further to C_2H_2. But this was not supported by our observations.

Therefore, it was assumed that the first excited state which decomposes by molecular elimination, would proceed collisionally induced crossing over to a second excited state and this second excited state then decomposes by carbon–bromine bond fission. On the basis of this hypothesis, one can assume that the initially formed excited state, $C_2H_5Br^{\dagger(1)}$ decomposes to a vibrationally excited $C_2H_4{}^*$ and HBr by molecular elimination and then the vibrationally excited $C_2H_4{}^*$ will further decompose to C_2H_2. And some portion of $C_2H_5Br^{\dagger(1)}$ is also collisionally induced to cross over to the electronically excited state $C_2H_5Br^{\dagger(2)}$ which decomposes via carbon–bromine bond fission. Accordingly the general reaction scheme of the primary processes may be given by

$$C_2H_5Br + h\nu \longrightarrow C_2H_5Br^{\dagger(1)}$$

$$C_2H_5Br^{\dagger(1)} \xrightarrow{k_1} C_2H_4{}^* + HBr(C_2H_4{}^* \rightarrow C_2H_2 + H_2) \quad (1)$$

$$C_2H_5Br^{\dagger(1)} + M \xrightarrow{k_2} C_2H_5Br^{\dagger(2)} + M \quad (2)$$

$$C_2H_5Br^{\dagger(1)} \xrightarrow{k_3} \text{other products} \quad (3)$$

Reaction (3) is a general statement for other primary processes as well. If the crossover of $C_2H_5Br^{\dagger(1)}$ to the second excited state is a simple collisional process, the plot of $1/(\phi_{C_2H_4} + \phi_{C_2H_2})$ versus total pressure should be linear and this is clearly demonstrated in Figure 2. The slope of the line in Figure 2 should be equal to k_2/k_1 and assuming k_2 to be its usual value of 10^7 $torr^{-1}sec^{-1}$, k_1 is found to be 2.5×10^9 sec^{-1}. This large value of the rate constant reflects that the lifetime of the initially formed excited state should

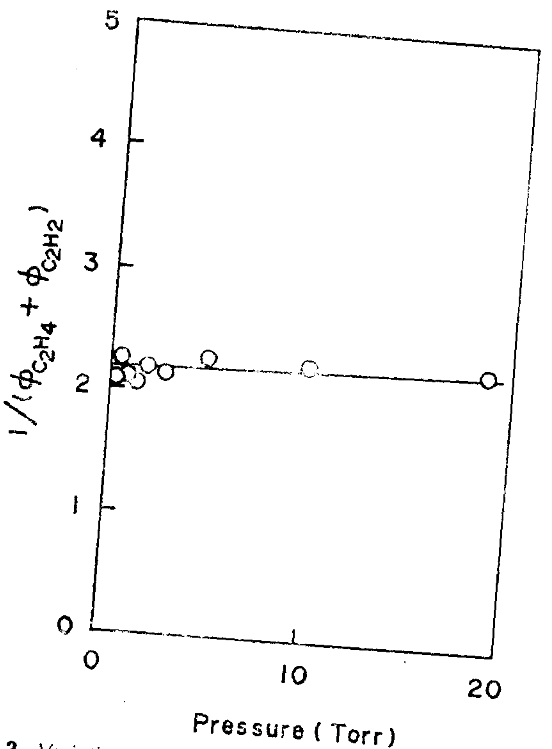

Figure 2. Variation of the reciprocal of quantum yields of $(\phi_{C_2H_4}+\phi_{C_2H_2})$ at pressure range of 0.2–20 torr.

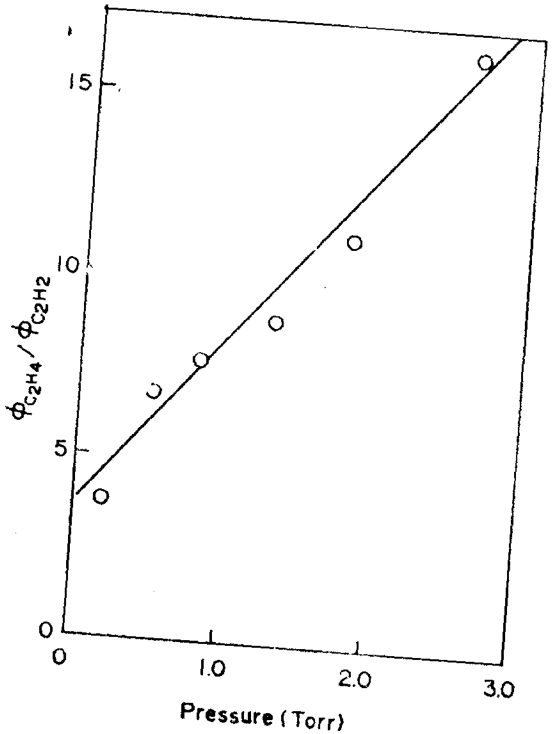

Figure 3. Quantum yields ratio of $\phi_{C_2H_4}/\phi_{C_2H_2}$ with pressure variation.

be fairly short, 4.0×10^{-10} sec. Since the photon energy is 267–272 kcal and enthalpy being 18.6 kcal/mole[17] for the reaction, $C_2H_5Br \rightarrow C_2H_4+HBr$, there are still 250 kcal of remaining energy to be distributed between C_2H_4 and HBr. Moreover considering the elimination energy of H_2 from C_2H_4 is only 80 kcal/mole,[18] vibrationally excited C_2H_4 must decompose to C_2H_2 or be collisionally stabilized. In the light of these arguments one may write.

$$C_2H_4^* \xrightarrow{k_4} C_2H_2+H_2 \tag{4}$$

$$C_2H_4^*+M \xrightarrow{k_5} C_2H_4+M \tag{5}$$

Hence, the plot of $\phi_{C_2H_4}/\phi_{C_2H_2}$ versus total pressure should also be linear which reflects the ratio of stabilization to decomposition. As given in Figure 3 this is clearly demonstrated in our observations. In Figure 3 the fitted straight line does not pass through the origin. The interpretation of this finding may be that the energy distribution of the $C_2H_4^*$ is wide spread below and above 80 kcal/mole. And again assuming k_5 to be its usual value of 10^7 $torr^{-1}sec^{-1}$, one obtains 2.2×10^6 sec^{-1} for k_4, which is not an unreasonable value[8]. This low value of rate constant reflects that the energy is distributed around or below 80 kcal/mole required for H_2 elimination. Thus, HBr and H_2 formed in the process have great excess energies and dissociate readily into H and Br atoms. However, it was not possible to confirm such a process in this study mainly due to detection difficulties with minor radical products such as $C_2H_4Br_2$, $C_4H_8Br_2$, C_4H_{10}, and possible higher molecular weight products.

The formation of CH_4 and C_3H_8 also suggests the reaction between C_1 and C_2 radicals and the primary process as carbon-carbon bond cleavage. A large decrease of ϕ_{CH_4} with presure increase indicates that the precursor of CH_4 is also $C_2H_5Br^{\dagger(1)}$ and collisionally quenched.

In this study the precursor of C_2H_6 was completely scavenged by NO and large amounts of C_2H_6 were observed at fairly low pressures. It is doubted that this may be interpreted as a simple carbon-bromine bond rupture process from and electronically excited state. Since the first ionization potential of C_2H_5Br is 10.3eV[19] and the photoionization yield being about 0.5 at photon energy of 11.5 eV as reported by Person and Nicole,[20] we have chosen to make an assumption with respect to the observation that the origin of C_2H_6 could be attributed to a photoionization and a fragmentation of C_2H_5Br under 11.4–11.6 eV photon energy by argon resonance lamp. In this process a major ionic primary process is an electron detachment from C_2H_5Br and this electron having energy above 0.5 eV[21] attaches readily to C_2H_5Br and fragmentation followed. The precursor of C_2H_6 is thus a C_2H_5 radical and completely scavengeable. And the C_2H_5 radicals formed by this process have lower energies than the threshold for decompostion and are long-lived. Then for the ionic processes the following general scheme can be writren:

$$C_2H_5Br + h\nu \longrightarrow C_2H_5Br^+ + e \tag{6}$$

$$C_2H_5Br + e \longrightarrow C_2H_5 + Br^- \tag{7}$$

$$C_2H_5 \longrightarrow \text{radical disproportionation and H abstraction from } C_2H_5Br \tag{8}$$

On the basis of forgoing discussion, reaction (9) to (13) summarize in detail the primary decomposition processes where the indicated quantum yields refer to 0.8 and 18.6 torr of C_2H_5Br, and the quantum yield for reaction (12) and (13) is obtained by difference in view of the total quantum yield of primary

		at 0.8 torr	at 18.6 torr	
$C_2H_5Br^{\dagger(1)} \rightarrow C_2H_4 + HBr^*(HBr^* \rightarrow H + Br)$	ϕ_8	0.42	0.44	(9)
$\rightarrow C_2H_4^* + HBr(C_2H_4^* \rightarrow C_2H_2 + H_2)$	ϕ_9	0.06		(10)
$\rightarrow CH_3 + CH_2Br$	ϕ_{10}	0.01	0.0	(11)
$C_2H_5Br^{\dagger(1)} + M \rightarrow C_2H_5Br^{\dagger(2)} + M$	ϕ_{11}			(12)
$\rightarrow C_2H_5 + Br$		0.50	0.56	
$C_2H_5Br + h\nu \rightarrow C_2H_5Br^+ + e$	ϕ_{12}			(13)
	ϕ_T	1.0	1.0	

Conclusion

In this investigation it was found that absorption of 104.8–106.7 nm radiation by ethyl bromide results in the 50 % formation of excited molecules and 50 % photoionization. These excited molecules have short lifetimes and the pressure dependence for the decomposition process seldom appears.

It is thus concluded that this excited state is a shortlived Rydberg type excited state as to the higher photon energy and molecules of this excited state decompose *via* molecular elimination. From this excited state a very small portion of molecules crosses over by collisional induction to another state which decomposes *via* radical processes.

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