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Vacuum Ultraviolet Photolysis of Ethyl Bromide at 123.6nm

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A vacuum ultraviolet photolysis of ethyl bromide was studied in the pressure range of 0.5-19.9 torr and at 123.6 nm krypton resonance line. The pressure effect on the reaction was studied by increasing the reactant pressure and by adding an inert gas, *e.g.*, He. In the observation the monatomic gas is found to be no effect in the reaction.A scavenger effect of the reaction was also performed by adding NO gas as a radical scavenger and was found to be quite efficient to scavenge a radical product C_2H_6. The observation of the major reaction product C_2H_6 was interpreted in terms of a molecular elimination. Nontheless the decreasing phenomenon of $\phi_{C_2H_4}/\phi_{C_2H_6}$ with pressure rise was attributed to the existance of the two electronically excited states. One state proceeds to the molecular elimination and the other to carbon-bromine bond fission. The excitation and the decomposition mechanisms between two excited states and the reaction products were interpreted in terms of the first excitation which proceeds the molecular elimination, and the second excitation which resulted from the first excited state by collisional cross over decomposes by carbon-bromine bond fission.

Introduction

Recent studies on the vacuum ultraviolet photolyses of ethylhalides have shown many possible primary processes[1-9] often competing the molecular elimation with the radical formation. In general, alkyl halides dissociate to alkyl radicals and halogen atoms when alkyl halides are irradiated within the first absorption band, while they proceed the molecular elimination within the second band absorption[1].

Substituted halogen atoms also play an important role on their reaction patterns. The photolysis of ethyl fluoride at 147 nm shows the molecular elimination of HF and H_2 as major products and lesser extend C–F and C–C bond fission. In the case of ethyl chloride at both 147 nm and 123.6 nm, the molecular elimination of HCl was dominant primary process. Whereas ethyl iodide at 147 nm[10] proceeds through C–I bond cleavage.

Energy dependence on the reaction pattern has also shown interesting phenomenon. Photolyses of CD_3CHCl_2[11] using a medium pressure Hg arc and ethyl bromide[12,13] at 253.7 nm are both characterized by the predominant carbon-halogen bond fission processes.

Since the substitution of halogen atom and the wavelength variation of energy sources play important roles on dissociations of alkyl halides, our investigation on the photolysis of ethyl bromide at 123.6 nm is a logical extend for our continuing effort to better understant these effects.

Experimental

Photolyses were carried out at room temperature in a conventional static system with 336 cm^3 borosilicate glass reaction vessel. The heterogeneity was prevented by using an all glass gas circulating pump. Total conversions were held at less than 1 % of the reactant sample. The light source was a liquid nitrogen cooled krypton resonance lamp equipped with a CaF_2 window (1 mm thickness)[14-17] and operated by a microwave generator, KIVA Instruments, Inc. Model MPG-4M. Intensity variations of the lamp were 6.2×10^{13} to 2.3×10^{14} photons/sec throughout the whole experiment. Chemical actinometry was based on the production of acetylene in the photolysis of ethylene[18] ($\phi=1.0$ at 123.6 nm and room temperature), and the agreement within ±5 % before and after each run was used as our criteria of good run.

Product identification was done by a home made isothermal gas chromatograph equipped with single hydrogen flame ionization detector. Column conditions were 3m×1/8" O.D. SS column packed with chromosorb Century Series 108 and flow rate of carrier gas with 50 m*l*/min. The reaction products, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, C_3H_6, C_4H_{10}, and the reactant, C_2H_5Br, were identified by comparing their retention time with those of authentic samples and their detector sensitivities were subsequently determined.

The reactant, C_2H_5Br, was obtained from the Eastmann Kodak Co., and purified to better than 99.99 % by fractional distillation and low temperature trap-to-trap distillation. Other reagents used in this study, *i.e.*, nitric oxide(NO) stated purity 99.5 %, ethylene 99.5 %, acetylene 99.6 %, ethane 99.0 %, propane 99.0 %, propylene 99.0 %, and *n*-butane 99.0 %, were obtained from Matheson Co. and were subjected to trap-to-trap distillation at 77 °K and the purity checks better than 99.9 % by GC were always confirmed prior to their use. Helium hydrogen, and compressed air used for GC were obtained from Tongbu

TABLE 1: Quantum Yields of Reaction Products Obtained in 123.6 nm Photolysis of C_2H_5Br

Runs	Pressure	C_2H_4	C_2H_6	C_2H_2	CH_4
1	0.5 Torr C_2H_5Br	0.39	0.19	0.076	0.020
2	0.5 Torr C_2H_5Br	0.41	0.18	0.072	0.022
3	0.8 Torr C_2H_5Br	0.38	0.15	0.058	0.012
4	1.0 Torr C_2H_5Br	0.44	0.22	0.058	0.020
5	1.4 Torr C_2H_5Br	0.44	0.20	0.051	0.018
6	1.7 Torr C_2H_5Br	0.47	0.25	0.061	0.023
7	2.0 Torr C_2H_5Br	0.49	0.32	0.048	0.024
8	3.0 Torr C_2H_5Br	0.58	0.38	0.060	0.026
9	3.7 Torr C_2H_5Br	0.52	0.30	0.058	0.020
10	3.9 Torr C_2H_5Br	0.54	0.38	0.039	0.012
11	4.1 Torr C_2H_5Br	0.59	0.44	0.049	0.023
12	4.9 Torr C_2H_5Br	0.58	0.27	0.120	0.021
13	6.3 Torr C_2H_5Br	0.52	0.33	0.077	0.024
14	7.2 Torr C_2H_5Br	0.67	0.33	0.140	0.041
15	9.4 Torr C_2H_5Br	0.61	0.44	0.077	0.032
16	14.6 Torr C_2H_5Br	0.53	0.40	—	—
17	19.9 Torr C_2H_5Br	0.52	0.27	0.088	0.027
18	4.1 Torr C_2H_5Br +1.8 Torr NO	0.46	0	0.10	—
19	4.1 Torr C_2H_5Br +0.8 Torr NO	0.48	0	0.11	—
20	4.0 Torr C_2H_5Br +0.9 Torr NO	0.44	0	0.11	—
21	4.0 Torr C_2H_5Br +6.4 Torr He	0.65	0.39	0.13	0.037
22	4.1 Torr C_2H_5Br +12.4 Torr He	0.52	0.41	0.050	0.017

Industries, Inc. and were found to be suitable for FID equipped in GC.

Results

The principal reaction products in this study were CH_4, C_2H_2, C_2H_4, C_2H_6 and small minor products of C_3 and C_4 compounds. Since the minor products, *i.e.*, C_3 and C_4 compounds, were found to be only trace amounts and did not effect on our data interpretation, the quantitative analysis were not attempted though the detector responses of these compounds especially on FID were usually much greater than those of the principal products.

The results of pressure effect studies on ethyl bromide photolysis by itself and with added an inert gas, *i.e.*, He, are tabulated in Table 1 (*Run Nos.* 1–17 for C_2H_5Br and *Run Nos.* 21-22 for He) and accompanied by the plot of the quantum yield (ϕ_i) *vs.* the total pressure together with NO effect (*Run Nos.* 18–20) in Figure 1. In Table 1 and Figure 1, the product quantum yields of ethylene ($\phi_{C_2H_4}$) and $\phi_{C_2H_6}$ have shown sharp increase between 0.5 and 5 torr of total pressure from *ca.* 0.38 to its limiting value 0.59 while above 5 torr opposite tendencies have been observed. On the contrary in the case of C_2H_2 and CH_4, $\phi_{C_2H_2}$, and ϕ_{CH_4} remained constant throughout pressure change. A similar trend was found in the addition of He.

The savenger effects where NO gas pressure varying between 0.8 and 1.8 torr with constant C_2H_5Br exhibited rather striking effects. In the presence of NO gas, C_2H_6 was readily scavenged by leaving only two principal products, *i.e.*, C_2H_2 and C_2H_4. The quantitative analysis of CH_4 at the presence of NO gas, however, has experienced some difficulties due to its very close retention time with that of NO gas.

Discussion

The most striking and mechanistically important aspects of the observation as a whole may be that a large portion of the major product C_2H_4 was formed from radically non-scavengeable source and only small portion from scavengeable one. In Table 1 (*Run Nos.* 18–20), $\phi_{C_2H_4}$ exhibited a small change by the addition of NO. One interpretation of this observation is that the precursor of the major portion of C_2H_4 is an electronically excited state of C_2H_5 Br and it proceeds the decomposition to give HBr and C_2H_4 by a molecular elimination reaction. And further, no observations of C_4H_{10} and $C_2H_4Br_2$ eliminate a possibility that the precursor of C_2H_4 is a short lived C_2H_5 radical. On the other hand, the small decrease of $\phi_{C_2H_4}$, *e.g.*, 0.13, with NO presence does not completely leave out the possibility of a radical process in the process of C_2H_4 production.

The study of pressure effect with an inert gas, He, and without it (*Run Nos.* 1–17 and 21–22) exhibited the large production of C_2H_6 which was also readily scavenged by NO (*Run Nos.* 18–20). These suggest that the productions of C_2H_6 are caused both cases from a radical precursor not an ionic product since the energy source used in this system is less than the ionization energy of C_2H_5Br[19].

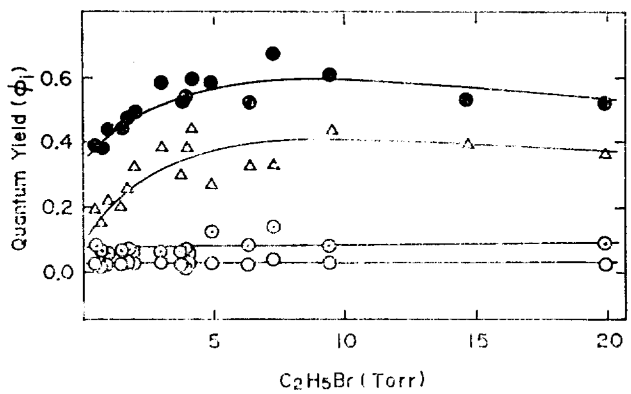

Figure 1. Quantum yields *vs.* total pressure of C_2H_5Br from 0.5 to 19.9 torr. (○) CH_4; (⊙) C_2H_2; (△) C_2H_6; (●) C_2H_4.

On the basis of foregoing discussion, two electronically excited states were assumed. One of these states is the initially electronically excited state, $C_2H_5Nr^{\dagger(1)}$, which produces C_2H_4 by the molecular HBr elimination reaction and which can also proceed collisionally induced cross over to another electronically excited state, $C_2H_5Br^{\dagger(2)}$, and the second excited state dissociates by carbon-bromine bond fission to yield a scavengeable C_2H_5 radical. The nature of the primary processes, therefore, may be summarized as

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

$$C_2H_5Br^{\dagger(1)} \longrightarrow C_2H_4 + HBr \quad (2)$$

$$C_2H_5Br^{\dagger(1)} \longrightarrow \textit{Other non-scangeable products} \quad (3)$$

$$C_2H_5Br^{\dagger(1)} + M \longrightarrow C_2H_5Br^{\dagger(2)} + M \quad (4)$$

Since the energy of the photon is 231 kcal/mol. and for the reaction, $C_2H_5Br \rightarrow C_2H_4 + HBr$, $\Delta H = 20$ kcal/mol[20], there must be thus 211 kcal of excess energy to be distributed between C_2H_4 and HBr such that the energy content of C_2H_4 should not greatly exceed 80 kcal/mol, which is the energy required for C_2H_4 to eliminate H_2[21]. If some or all of the C_2H_4 molecules possess energies significantly less than 80 kcal/mol, then some or all of the HBr molecules would have energies in excess of H–Br bond strength, 87 kcal/mol, and would dissociate into H and Br atoms. Since the plot of $\phi_{C_2H_4}/\phi_{C_2H_2}$ *vs.* pressure in Figure 2 reflects the competition reactions, these may be presented by eqs. 5 and 6.

$$C_2H_5Br^{\dagger(1)} \longrightarrow C_2H_4^* + HBr$$

$$C_2H_4^* + M \longrightarrow C_2H_4 + M \quad (5)$$

$$C_2H_4^* \longrightarrow C_2H_2 + H_2 \quad (6)$$

ϕ_{CH_4} remained unchanged with pressure change, and thus the ratio $\phi_{CH_4}/\phi_{C_2H_6}$ in Figure 3 decreased with $\phi_{C_2H_6}$ increase in the pressure range of 0.5–3.9 torr. The precursor of CH_4, therefore, is presumably the initially formed excited state and by eq. 7

$$C_2H_5Br^{\dagger(1)} \longrightarrow CH_4 + CHBr \quad (7)$$

The foregoing mechanism is summarized in general scheme:

ϕ_i at 4.1 Torr

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

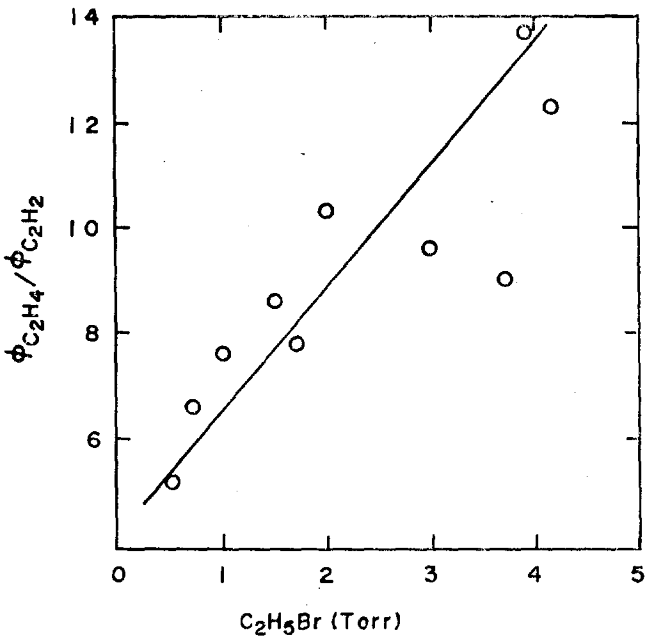

Figure 2. $\phi_{C_2H_4}/\phi_{C_2H_2}$ *vs.* Pressure of C_2H_5Br.

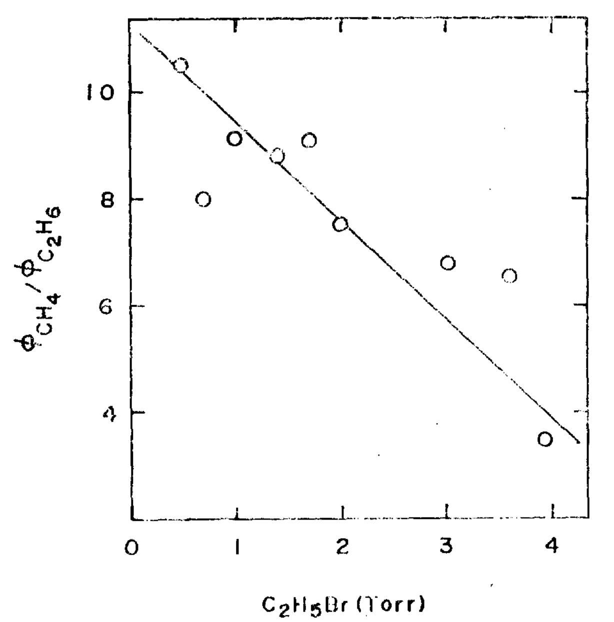

Figure 3. $\phi_{CH_4}/\phi_{C_2H_6}$ *vs.* Pressure of C_2H_5Br in the range of 0.5–3.9 torr.

$$C_2H_4^* + M \longrightarrow C_2H_4 + M \qquad 0.46$$
$$C_2H_4^* \longrightarrow C_2H_2 + H_2 \qquad 0.05$$
$$CH_4 + CHBr \qquad 0.02$$
$$C_2H_5Br^{\dagger(1)} + M \xrightarrow{k} C_2H_5Br^{\dagger(2)} + M$$
$$C_2H_5Br^{\dagger(2)} \longrightarrow C_2H_5 + Br$$
$$C_2H_5 + C_2H_5Br \longrightarrow C_2H_6 + C_2H_4Br \qquad 0.44$$
$$C_2H_5 \longrightarrow C_2H_4 + H \qquad 0.13$$

Since D band absorption of C_2H_5Br occurs around 157 nm with broad diffusion[22,23], the absorption may be ascribed to the formation of a Rydberg state ($5p \leftarrow \ddot{Br}$) at 123.6 nm. And it may be the most probable reason that the observation of the predominant molecular elimination product is due

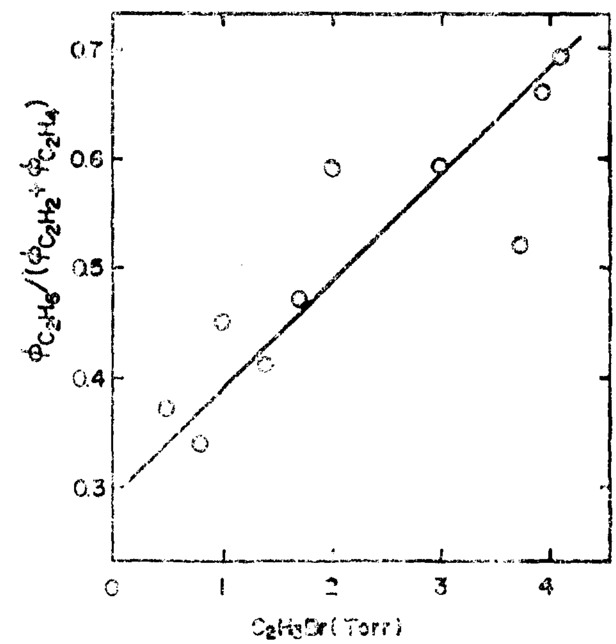

Figure 4. $\phi_{C_2H_6}/(\phi_{C_2H_2}+\phi_{C_2H_4})$ *vs.* Pressure of C_2H_5Br.

to Rydberg transition. In Figure 4 since the slope of the line represents k_2/k_1, and assuming as usual value of 10^7/torr/sec for k , one would get a relatively long life time, $\sim 5\times 10^{-9}$ sec for the initially formed excited state $C_2H_2Br^{\dagger(2)}$. considering the long life time of $C_2H_5Br^{\dagger(1)}$ compared with that of $C_2H_5Cl^3$, *e.g.*, 3.6×10^{10} sec, and the observation of the molecular elimination as the major dissociation mode in C_2H_5Cl, it was suggested that $C_2H_5Br^{\dagger(1)}$ state must enjoy longer gap time and it, therefore, must have more chances to cross over to the collisionally induced excited state than its chlorine counter part. And hence the larger yield of radical product, *i.e.*, C_2H_6, may be formed from $C_2H_5Br^{\dagger(1)}$.

Conclusion

Two markedly different dissociation modes, *i.e.*, 60 % of molecular elimination and 40 % of radical products, have been observed in the vacuum ultraviolet photolysis of ethyl bromide at 123.6 nm krypton resonance line. The studies of pressure and scavenger effects on this system suggest that the first electronically excited state which is responsible for the molecular elimination was produced by absorbing photons, and it could undergo to the second excited state by collisionally induced cross over, which is the prescuror of radical products.

Our comparison study gives on a strong evidence of the tendency that $C_2H_5F > C_2H_5Cl > C_2H_5Br > C_2H_5I$ is the order of the molecular elimination dissociation mode.

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Activation Enthalpies for Plastic Deformation

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Activation energies for plastic deformation calculated from traditional phenomenological equations have been criticized frequently since the values are different by authors, and also by experimental conditions. The reasons of different activation enthalpies are clarified in this study. Our method for calculating activation enthalpies based on the authors' theory of plastic deformation was presented and discussed. The method was applied to various cases of alloys, the calculated activation enthalpies are listed and compared with the activation energies obtained by the traditional methods in order to show the reasonableness of our method. The physical meaning of the actiaation enthalpies which we found was clarified.

1. Introduction

Many theories for plastic deformation have been proposed. The representative ones are those proposed by Nabarro,[1] Gifkins *et al.*,[2] Herring,[3] and Coble.[4] According to these authors, the strain rate is expressed as a linear function of stress and as an iverse function of grain size raised to the power of one to three. In actual cases, however, these theories are in agreement with experiments only in a limited region of stress, so the flow equation is expressed phenomenologically as the following:[5]

$$\dot{s}=\frac{ADGb}{kT}\left(\frac{b}{d}\right)^{p}\left(\frac{f}{G}\right)^{n} \quad (1)$$

where A is a dimensionless constant, D is the appropriate diffusion coefficient, G is the shear modulus, b is the Burger's vector, k is Boltzman's constant, T is absolute temperature, d is the grain size, f is stress, and n and p are the stress and grain size index, respectively. Equation (1) can be transformed into the following at constant stress and grain size:

$$\dot{s}=\frac{A'}{G^{n-1}T}\exp\left(-\frac{Q}{RT}\right) \quad (2)$$

and

$$A'=AD_0b^{p+1}f^n/kd^p \quad (3)$$

where A' represents a temperature-independent constant,