

PRIMARY PROCESSES IN THE 121.6 nm PHOTOLYSIS OF GAS PHASE ETHYL BROMIDE

KYUNG-HOON JUNG and DAE KON OH

Department of Chemistry, Korea Advanced Institute of Science and Technology, P.O. Box 150 Chongyangni, Seoul 131 (Korea)

KOSUKE SHOBATAKE

Institute for Molecular Science, Okazaki 444 (Japan)

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Summary

The vacuum UV photolysis of ethyl bromide at 121.6 nm (235.2 kcal mol⁻¹) has been studied over the pressure range 0.5 - 100 Torr at room temperature using a hydrogen atom resonance lamp. The scavenger effect of the reaction was observed by adding NO gas as a radical scavenger. The pressure effect was also investigated with CF₄ as an additive. The major products of the reaction were CH₄, C₂H₄, C₂H₆, C₂H₂ and CH₃CHBr₂ via a two-channel competition between molecular elimination and the formation of radicals. The decomposition modes in the primary process were 58.7% molecular elimination and 41.3% radical reaction. It was estimated that the portion of hot C₂H₄ molecules produced through the molecular elimination process with more than the threshold energy ($E_0 = 80$ kcal mol⁻¹) for decomposition to C₂H₂ was 25% of the total energy distribution.

1. Introduction

The energy dependences of the reaction mode on the wavelength in the vacuum UV region have been studied in some depth in this laboratory [1 - 6]. Alkyl halides are dissociated to both alkyl and halogen radicals by irradiation within the first absorption band, whereas in the second absorption band their dissociation pattern follows molecular elimination.

Photolysis data for alkyl halides in the UV region have been accumulated at a number of wavelengths [7 - 10]. The electronic transitions of alkyl halides in these regions are termed $n \rightarrow \sigma^*$ and their broad maximum appears at about 250 nm [11].

The shorter wavelength side of this absorption frequency is extended to the vacuum UV region where it overlaps with a far more intense absorption band associated with the Rydberg transition. Thus in the vacuum UV

region both transitions occur simultaneously and show competitive behaviour between molecular elimination and radical formation.

Several possible mechanisms for the primary processes on the photolysis of ethyl bromide have been suggested at various wavelengths. The present study of photolysis at 121.6 nm is a logical extension of these studies to a shorter wavelength limit of the Rydberg transition to complement the branching mechanism of the primary process as a function of the wavelength of the incident light.

2. Experimental details

The photolyses were carried out at room temperature in a conventional high vacuum system using a borosilicate glass reaction vessel of volume 336 cm³. The light source used in this work was a sealed hydrogen atom resonance lamp fitted with an MgF₂ window 1 mm thick. The lamp was operated by a microwave generator (KIVA model MPG-4M). The monochromatic purity of the lamp was routinely checked using a 0.3 m GCA-McPherson 218 vacuum UV grating monochromator.

The photolysis time was controlled such that the total conversion was always less than 1% of the reactant. The reactant was circulated during the photolysis with an all-glass gas-circulating pump to prevent secondary photolysis of the products. The quantum yields of the main products and the photon intensity of the lamp were determined by chemical actinometry based on the production of C₂H₂ from a C₂H₄ actinometer. The intensity of the lamp was determined to be about 2×10^{14} photons s⁻¹ on the assumption of unit quantum efficiency of C₂H₂ at 121.6 nm [12]. The possibility of deviation due to the intensity fluctuations was eliminated by repeating the actinometry readings twice before and after each run and by taking only those runs which agreed to within a 5% deviation of the readings.

The design criteria of the light path length (19.5 cm) was based on a separate measurement of the absorption cross-section of ethyl bromide in the wavelength range 100 - 210 nm at room temperature using a synchrotron radiation facility (UVSOR Beamline BL2A) equipped with a Seya-Namioka vacuum UV monochromator, Hitachi SNM-2, in IMS, Okazaki. The absorption cross-section of ethyl bromide at 121.6 nm was 66.5×10^{-18} cm² molecule⁻¹ (see also Section 3) and confirmed that the total absorption of the incident light of the present system was over 99%.

Product analysis was carried out using an HP5840A gas chromatograph (GC) equipped with twin hydrogen flame ionization detectors and 30% OV101-Chromosorb P and Chromosorb 108 on nickel alloy columns (1/8 in outside diameter; 4 m length). The reaction products, *i.e.* CH₄, C₂H₂, C₂H₄, C₂H₆ and CH₃CHBr₂, were analysed at 80 °C by comparing their retention times with those of authentic samples. No attempt was made to analyse HBr, an undoubtedly important major reaction product, since the GC technique does not determine it in a quantitative manner. However, a

qualitative identification of HBr as one of the reaction products was performed by comparing the $m/e = 80$ and $m/e = 82$ peaks of the reactant batch with those of the products utilizing an HP5985B GC-MS mass spectrometer.

The reactant C_2H_5Br , obtained from Eastman Kodak Co., was purified to better than 99.99% by GC (Sigma 4B, Perkin-Elmer Co.) using 20% SE-30/Chromosorb P on a stainless steel column (1/4 in outside diameter; 2 m length) at 55 °C. CF_4 (Matheson Co.) was used after it had been passed through a 1 m platinum-coated Cu_2O column which was activated by hydrogen at 200 °C for 5 h. NO (99.0%) (Matheson Co.) was purified by low temperature trap-to-trap distillation at liquid nitrogen temperature.

3. Results

The principal products detected by GC in the 121.6 nm photolysis of ethyl bromide were CH_4 , C_2H_4 , C_2H_6 , C_2H_2 and CH_3CHBr_2 . Their product quantum yields at various photolysis times are listed in Table 1. Since all the product quantum yields are found to be independent of the relatively long photolysis times in the range 3 - 40 min, subsequent studies such as the pressure and the scavenger effect were performed at a fixed photolysis time of 20 min. The product quantum yields of CH_4 , C_2H_4 , C_2H_6 , C_2H_2 and CH_3CHBr_2 at a photolysis time of 20 min are 0.05, 0.65, 0.40, 0.11 and 0.07 respectively.

In the pressure effect studies of C_2H_5Br (Table 2 and Fig. 1) the quantum yields of the two major products show slight tendencies to increase from 0.61 to 0.65 for C_2H_4 and from 0.35 to 0.38 for C_2H_6 up to about 10 Torr and then a decreasing trend is observed for both these products, whereas the trends were less apparent for the other two products, *i.e.* C_2H_2 and CH_4 . The steady decrease in quantum yields of both C_2H_4 and C_2H_6 above 10 Torr is mainly considered to be a quenching effect of the electronically excited ethyl bromide by parent molecules, evaluated as 1.43×10^{-3}

TABLE 1

Product quantum yields at various irradiation times in the 121.6 nm photolysis of ethyl bromide

| Run | Irradiation time (min) | Quantum yields for the following products | | | | |
|-----|------------------------|---|----------|----------|--------------|--------|
| | | C_2H_4 | C_2H_6 | C_2H_2 | CH_3CHBr_2 | CH_4 |
| 1 | 3 | 0.729 | 0.414 | 0.113 | 0.077 | 0.058 |
| 2 | 10 | 0.610 | 0.361 | 0.102 | 0.060 | 0.041 |
| 3 | 20 | 0.653 | 0.407 | 0.111 | 0.071 | 0.056 |
| 4 | 30 | 0.604 | 0.389 | 0.106 | 0.066 | 0.036 |
| 5 | 40 | 0.619 | 0.412 | 0.102 | 0.060 | 0.038 |
| 6 | 55 | 0.512 | 0.361 | 0.086 | 0.049 | 0.039 |

TABLE 2

Pressure effect of collision partner and scavenger effect of NO in the photolysis

| Run | $P_{\text{C}_2\text{H}_5\text{Br}}$ (Torr) | P_{CF_4} or P_{NO} (Torr) | Quantum yields for the following products | | | | |
|-----|---|--|---|------------------------|------------------------|----------------------------|---------------|
| | | | C_2H_4 | C_2H_6 | C_2H_2 | CH_3CHBr_2 | CH_4 |
| 1 | 0.5 | | 0.611 | 0.350 | 0.107 | — | 0.065 |
| 2 | 3.7 | | 0.633 | 0.375 | 0.115 | — | 0.066 |
| 3 | 4.4 | | 0.633 | 0.380 | 0.105 | — | 0.079 |
| 4 | 6.2 | | 0.653 | 0.382 | 0.102 | — | 0.071 |
| 5 | 9.5 | | 0.654 | 0.380 | 0.121 | — | 0.070 |
| 6 | 14.6 | | 0.642 | 0.375 | 0.114 | — | 0.079 |
| 7 | 25.0 | | 0.641 | 0.318 | 0.121 | — | 0.067 |
| 8 | 35.0 | | 0.621 | 0.350 | 0.122 | — | 0.084 |
| 9 | 50.0 | | 0.621 | 0.339 | 0.122 | — | 0.089 |
| 10 | 65.0 | | 0.624 | 0.303 | 0.112 | — | 0.081 |
| 11 | 80.0 | | 0.568 | 0.257 | 0.112 | — | 0.057 |
| 12 | 100.0 | | 0.574 | 0.249 | 0.089 | — | 0.041 |
| 13 | 5.00 | 10.0 (CF ₄) | 0.601 | 0.387 | 0.105 | 0.066 | 0.045 |
| 14 | 5.00 | 20.0 (CF ₄) | 0.576 | 0.356 | 0.096 | 0.056 | 0.049 |
| 15 | 5.00 | 38.7 (CF ₄) | 0.616 | 0.369 | 0.113 | 0.043 | 0.043 |
| 16 | 5.00 | 60.0 (CF ₄) | 0.629 | 0.340 | 0.100 | 0.049 | 0.034 |
| 17 | 5.00 | 80.0 (CF ₄) | 0.630 | 0.321 | 0.102 | 0.033 | 0.036 |
| 18 | 5.00 | 100.0 (CF ₄) | 0.636 | 0.320 | 0.090 | 0.033 | 0.035 |
| 19 | 5.00 | 212.0 (CF ₄) | 0.603 | 0.255 | 0.102 | 0.033 | — |
| 20 | 5.00 | 325.0 (CF ₄) | 0.620 | 0.182 | 0.096 | 0.048 | — |
| 21 | 0.75 | 0.4 (NO) | 0.569 | 0.0 | 0.157 | 0.0 | 0.0 |
| 22 | 0.90 | 1.0 (NO) | 0.588 | 0.0 | 0.150 | 0.0 | 0.0 |
| 23 | 2.85 | 0.7 (NO) | 0.595 | 0.0 | 0.129 | 0.0 | 0.0 |
| 24 | 4.50 | 3.9 (NO) | 0.585 | 0.0 | 0.122 | 0.0 | 0.0 |
| 25 | 4.60 | 1.0 (NO) | 0.638 | 0.0 | 0.122 | 0.0 | 0.0 |
| 26 | 7.50 | 0.8 (NO) | 0.617 | 0.0 | 0.121 | 0.0 | 0.0 |
| 27 | 10.00 | 0.1 (NO) | 0.601 | 0.0 | 0.111 | 0.0 | 0.0 |
| 28 | 12.90 | 1.2 (NO) | 0.588 | 0.0 | 0.103 | 0.0 | 0.0 |
| 29 | 15.00 | 1.2 (NO) | 0.567 | 0.0 | 0.096 | 0.0 | 0.0 |
| 30 | 16.20 | 0.9 (NO) | 0.585 | 0.0 | 0.098 | 0.0 | 0.0 |
| 31 | 18.60 | 1.2 (NO) | 0.577 | 0.0 | 0.095 | 0.0 | 0.0 |
| 32 | 27.50 | 1.6 (NO) | 0.565 | 0.0 | 0.092 | 0.0 | 0.0 |
| 33 | 36.60 | 2.0 (NO) | 0.580 | 0.0 | 0.093 | 0.0 | 0.0 |
| 34 | 45.60 | 2.0 (NO) | 0.564 | 0.0 | 0.080 | 0.0 | 0.0 |

Torr⁻¹ (see also Section 4). The yield of CH_3CHBr_2 was not measured quantitatively on account of the very small amount of it and of its broad peak shape as indicated in Table 2, runs 1 - 12. The pressure effect of CF_4 as an additive in the region 10 - 325 Torr is also presented in Table 2, runs 13 - 20. The tendency of the C_2H_4 quantum yield to decrease on addition of CF_4 was smaller than that for the addition of reactant, indicating that the CF_4 molecule was less efficient at reducing the quantum yield of C_2H_4 than was the ethyl bromide molecule. However, for C_2H_6 , the quantum yield decreases continuously to a value of 0.182 at 325 Torr. The radical scavenger effect due to NO gas is shown in Table 2, runs 21 - 34, where

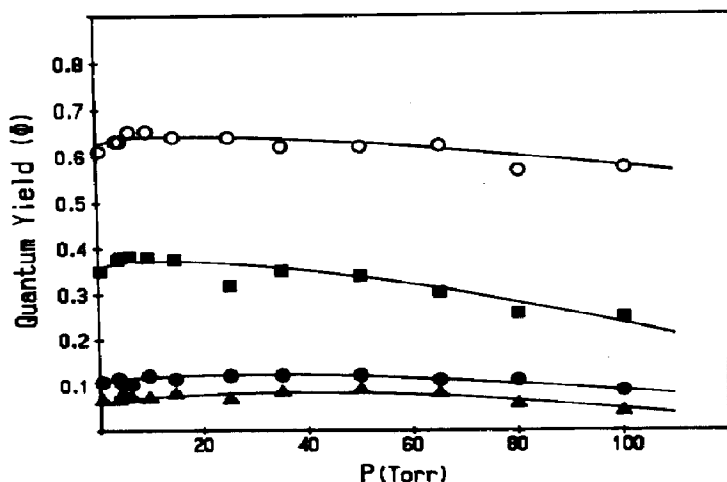


Fig. 1. Variation in the reaction product quantum yields vs. reactant pressure: \circ , C_2H_4 ; \blacksquare , C_2H_6 ; \bullet , C_2H_2 ; \blacktriangle , CH_4 .

the quantum yields of the non-scavengable products, *i.e.* C_2H_4 and C_2H_2 , are 0.61 and 0.12 respectively, at an ethyl bromide pressure of 7.5 Torr and an NO pressure of 0.8 Torr. On comparison of the quantum yield of the above with that obtained in the absence of NO gas, the quantum yield of scavengable C_2H_4 was determined to be a constant value of 0.05 at various pressures. C_2H_2 shows a strong pressure effect, unlike C_2H_4 , because the effects of collisional quenching between these molecules are significantly different.

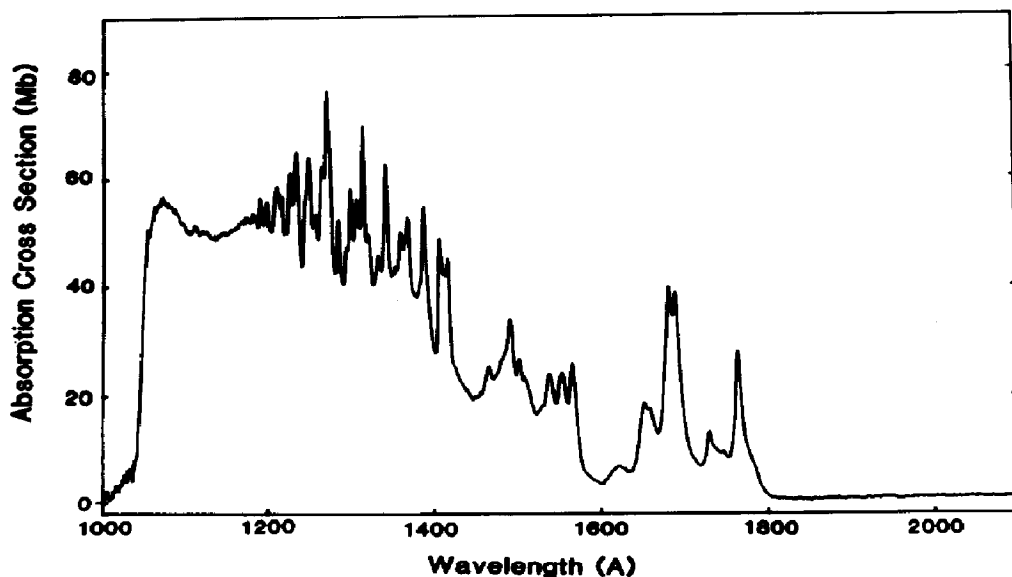


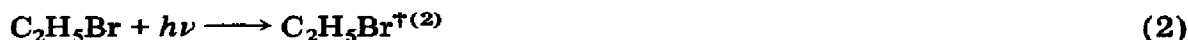
Fig. 2. Absorption cross-section of ethyl bromide vs. wavelength between 100 and 210 nm.

An extinction coefficient κ for ethyl bromide at 121.6 nm was obtained using the absorption cross-section data shown in Fig. 2. The κ value at 25 °C was determined to be $1637.9 \text{ atm}^{-1} \text{ cm}^{-1}$ from $\sigma = 66.5 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.

4. Discussion

The complete disappearance of C_2H_6 in the presence of NO confirms that this product results from a radical precursor. Also diagnostically significant is the effect of NO addition on the production of C_2H_4 . As may be seen in Table 1, a small decrease in the quantum yield of C_2H_4 , *i.e.* around 0.05, does not completely rule out the possibility of a radical process in the production of C_2H_4 . A large portion of C_2H_4 , however, is probably formed from a non-scavengeable precursor via an HBr molecular elimination process from ethyl bromide. The precursor, one of the electronically excited states ($\text{C}_2\text{H}_5\text{Br}^{\dagger(1)}$), would represent the Rydberg transition [11, 13], *i.e.* the first allowed transition of a non-bonding electron on the bromine ($4\text{P} \rightarrow 5\text{P}$). While most of the scavengeable products appear to originate from C_2H_5 radicals by C—Br bond fission of another electronically excited state ($\text{C}_2\text{H}_5\text{Br}^{\dagger(2)}$), representing an $n \rightarrow \sigma^*$ transition, *i.e.* transition of a non-bonding p electron on the bromine atom to the antibonding orbital, the other scavengeable product, CH_4 , is probably formed from CH_3 radicals by C—C bond fission of the electronically excited ethyl bromide state through Rydberg transitions from the $\sigma(\text{C—C})$ and pseudo- $\pi(\text{CH}_3)$ orbitals to the carbon 3s and 3p orbitals [14]. From these observations and previous studies [3 - 6, 10], we propose two different electronically excited states in the primary process.

Collisional cross-over between these two electronic excited states, as observed at other wavelengths [1 - 6], is ruled out in this system for two reasons. First, on the assumption that the collision diameter for ethyl bromide is 0.51 nm [15], the calculated collision rate ω can be estimated as $9.14 \times 10^6 P \text{ s}^{-1}$ (where P (Torr) is the pressure) at the total pressure P during the experiment. The required pressure for effective collision of $E-E$ energy transfer is then about 250 Torr at the estimated lifetime of $4 \times 10^{-10} \text{ s}$ [16] for $\text{C}_2\text{H}_5\text{Br}^{\dagger(1)}$. This value is much too high considering the present experimental conditions. Second, the concentration ratio $\text{C}_2\text{H}_5\text{Br}^{\dagger(1)}/\text{C}_2\text{H}_5\text{Br}^{\dagger(2)}$ of the excited states averaged 2.1 (see below) with no pressure dependence observed experimentally as shown in Table 2, runs 1 - 12. On the basis of this rationale two simultaneous excitations in the 121.6 nm photolysis are suggested. The nature of the primary processes may then be summarized as





The total quantum yield in Fig. 1 above 10 Torr exhibited a tendency to decrease. This observation may be interpreted in terms of the collisional quenching phenomenon of the electronically excited parent molecules in the pressure region of interest as suggested by Atkinson and Thrush [17] from their photolysis study of cycloheptatriene as a function of irradiation wavelength. Since the sole source of C_2H_6 is from the radical process, the quenching rate can be estimated using $\phi(\text{C}_2\text{H}_6)$ data at various pressures and is found to be $1.43 \times 10^{-3} \text{ Torr}^{-1}$, whereas for the non-scavengeable C_2H_4 it probably contains two major pressure effects. The first effect, the electronic quenching of the excited ethyl bromide on increasing the pressure, is the reducing tendency to produce vibrationally hot C_2H_4 molecules. These hot C_2H_4 molecules may undergo further decomposition or may be stabilized by collision. The second effect, the vibrational quenching of the hot C_2H_4 molecule by collisional deactivation, probably enhances the production ratio of stable C_2H_4 molecules in competition between stable C_2H_4 and C_2H_2 production. Since these two are opposite effects to $\phi(\text{C}_2\text{H}_4)$, utilizing the quenching rate calculated from $\phi(\text{C}_2\text{H}_6)$ data and assuming the same electronic quenching rate for both cases, we were able to explain the pressure effect of $\phi(\text{C}_2\text{H}_4)$ and to estimate, in turn, the deactivation rate of C_2H_4 which was $8.2 \times 10^{-4} \text{ Torr}^{-1}$.

4.1. Molecular elimination processes

On the assumption of $235.2 \text{ kcal mol}^{-1}$ for the external photon energy and 20 kcal mol^{-1} for the heat of formation for reaction (3) at room temperature, the excess remaining energy of the system becomes $215.2 \text{ kcal mol}^{-1}$ and this energy may be distributed between C_2H_4 and HBr . A statistical energy partitioning model [18, 19] in the photodissociation predicts that $143.5 \text{ kcal mol}^{-1}$ goes to C_2H_4 , $11.9 \text{ kcal mol}^{-1}$ goes to the HBr molecule and $59.8 \text{ kcal mol}^{-1}$ goes to the relative rotational and translational motions. The experimental observation, however, did not agree with the prediction in which the most vibrationally hot C_2H_4 molecules are expected to undergo further decomposition since their energy content exceeds the critical energy of the decomposition reaction of 80 kcal mol^{-1} . Further supporting evidence has been found in low pressure studies. The extrapolated value for the production of C_2H_2 at low pressure was about 25%, indicating that the energy distributions to the primary photodecomposition products are rather broad and only a small portion of C_2H_4 molecules are distributed above 80 kcal mol^{-1} . From the foregoing discussion it is concluded that the statistical model does not apply to the energy partitioning in the photodissociation reaction of ethyl bromide. For 147 nm photolysis [3], where $174.3 \text{ kcal mol}^{-1}$ of excess energy is available to distribute between C_2H_4 and HBr , the secondary product C_2H_2 appeared for the first time as an upper wavelength limit in the vacuum UV photolysis of the

ethyl bromide system. Hence a large portion of excess energy must be transferred to HBr, and then the hot HBr molecule decomposes further into hydrogen and bromine atoms and/or some of these can be collisionally stabilized by other molecules. Thus, when we consider that the HBr molecule takes a dissociation energy ($E_0 = 89.4 \text{ kcal mol}^{-1}$) out of the excess energy as a first priority, the average vibrational energy of hot C_2H_4 is assumed to be about 66 kcal mol^{-1} in addition to translational and rotational energy of $5/18$ of the total excess energy.

Since the plot of $\phi(\text{C}_2\text{H}_4)/\phi(\text{C}_2\text{H}_2)$ against the reactant pressure in the presence of NO in Fig. 3 reflects the competition between stabilization and decomposition and increases with increasing reactant pressure, the fate of the vibrationally excited C_2H_4 may be collisionally quenched to the ground state or decomposed to C_2H_2 . The deviation from the linearity of the plot may be strong evidence that hot C_2H_4 molecules show an energy distribution curve over a broad energy range. From the low pressure limit value of $\phi(\text{C}_2\text{H}_4)/\phi(\text{C}_2\text{H}_2)$, we assume that the portion of molecules with energy above the threshold energy for decomposition is 25% of the total energy distribution. These competition reactions may then be presented by the reactions

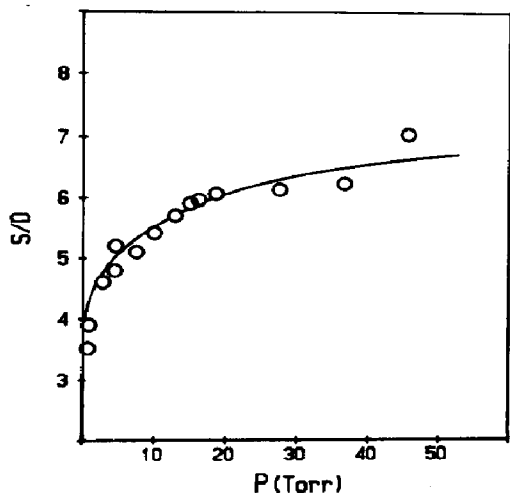


Fig. 3. Plot of $\phi_{\text{C}_2\text{H}_4}/\phi_{\text{C}_2\text{H}_2}$ vs. reactant pressure.

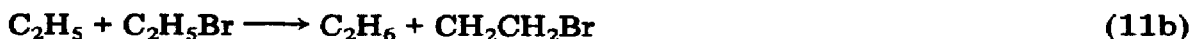
4.2. Radical formation processes

The complete disappearance of C_2H_6 , CH_3CHBr_2 , CH_4 and a small portion of C_2H_4 in the presence of NO confirms that these products are probably formed from radical precursors. C_2H_6 can be formed only by radical formation and its quantum yield increases up to a reactant pressure of 10 Torr, as shown in Fig. 2. Therefore, we suggest the hydrogen abstraction reaction by the C_2H_5 radical from the ethyl bromide molecule as the source of C_2H_6 . In addition, since Table 2, runs 13 - 20, show that the addition of CF_4 reduces the production of C_2H_6 significantly and hence reduces the probable collision chances between C_2H_5 and ethyl bromide, hot C_2H_5 radicals may react readily by this path even if the estimated activation energy of the reaction



is somewhat high, *i.e.* 11 kcal mol⁻¹ [18].

In the reaction of the C_2H_5 radical with the ethyl bromide molecule, two types of C_2H_4Br radicals can be produced, depending on whether the C_2H_5 radical attacks the α or the β hydrogen in ethyl bromide as shown in the reactions



Since CH_3CHBr is favoured by 3 kcal mol⁻¹ over CH_2CH_2Br from thermochemical data [21], the contribution of the CH_2CH_2Br radical will be negligible. This prediction is consistent with our result in which CH_3CHBr_2 was produced, together with about 30% less than the stoichiometric amount of scavengeable C_2H_4 , from the disproportionation reaction of CH_3CHBr radical combination by the reaction



Although the major portion of CH_3CHBr_2 is probably formed in reaction (12), there must be another additional source of CH_3CHBr_2 on the basis of its quantum yield value ($\phi = 0.07$ at an ethyl bromide pressure of 5 Torr). As the second source of CH_3CHBr_2 , the combination of CH_3CHBr and bromine radicals is the generally accepted termination reaction in the photolysis [10, 22] and pyrolysis [23] of ethyl bromide by the reaction



The qualitative detection of a small amount of HBr by mass spectrometry may originate from secondary reactions:



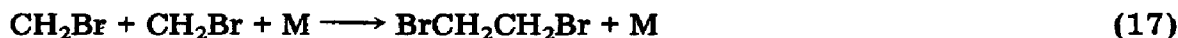
where the hydrogen and bromine atoms were formed in reaction (8). The heat of reaction (15), *i.e.* -17 kcal mol⁻¹, obtained from thermochemical

data for the chemical species shows that this reaction is thermodynamically favourable [24].

The complete disappearance of CH_4 in the presence of NO confirms that this product is also formed from radical precursors. Since the CH_3 radical is probably formed through the Rydberg transition competitively with the production of non-scavengeable C_2H_4 by the HBr elimination process, the probability of $\text{C}-\text{C}$ bond fission, for which $\Delta H = 88 \text{ kcal mol}^{-1}$, is far less than that for HBr molecular elimination, for which $\Delta H = 20 \text{ kcal mol}^{-1}$, in terms of thermochemical considerations. CH_4 can only be formed by hydrogen abstraction of the CH_3 radical produced in the reaction

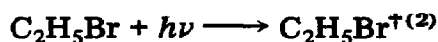
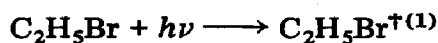


since it did not appear when a quantity of CF_4 was present in the system. The type of $\text{C}_2\text{H}_4\text{Br}$ radical must be CH_3CHBr by the same reason as reaction (11). The CH_2Br radical produced in reaction (4) can be involved in a wall termination step as a heat sink. The reaction



has been observed by detecting the trace amount of $\text{BrCH}_2\text{CH}_2\text{Br}$ by GC.

From the foregoing discussions, two markedly different electronically excited states were proposed in this system:



Decomposition of the first excited state, $\text{C}_2\text{H}_5\text{Br}^{\dagger(1)}$, produces non-scavengeable C_2H_4 , C_2H_2 and scavengeable CH_4 and decomposition of the second state, $\text{C}_2\text{H}_5\text{Br}^{\dagger(2)}$, produces C_2H_6 in the primary process. It can be shown by

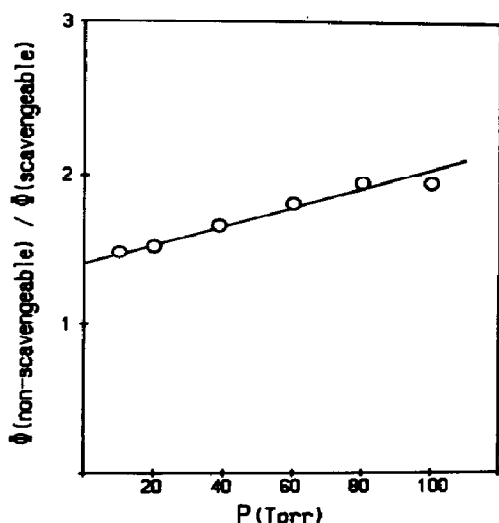


Fig. 4. Plot of $\phi(\text{non-scavengeable})/\phi(\text{scavengeable})$ vs. pressure of CF_4 .

application of the usual stationary state approximation that

$$\frac{\phi_1^\circ}{\phi_2^\circ} = \frac{\phi(\text{C}_2\text{H}_4)(\text{non-scavengeable}) + \phi(\text{C}_2\text{H}_2) + \phi(\text{CH}_4)}{\phi(\text{C}_2\text{H}_6)}$$

where ϕ_1° and ϕ_2° represent the primary quantum yields of the first and the second electronically excited states respectively and $\phi(\text{C}_2\text{H}_4)(\text{non-scavengeable})$ represents the product quantum yield of the non-scavengeable portion of C_2H_4 . From the data of Table 2 we obtain $\phi_1^\circ/\phi_2^\circ = 2.1$, extrapolating to zero pressure. From the intercept of the plot in Fig. 4 we also determined that the competition ratio of the molecular elimination to the radical formation mode is 1.42 in this system.

5. Conclusion

The vacuum UV photolysis of ethyl bromide using the 121.6 nm hydrogen atom transition line ($2\text{P}^0 \rightarrow 2\text{S}$) has demonstrated the competitive decomposition mode of 58.7% molecular elimination and 41.3% radical formation. These observations coincide with our earlier work in which the major mode of primary process shifts from the radical process to molecular elimination with increasing photon energy of the light source in the vacuum UV region.

From this study it is suggested that the ethyl bromide molecule can be excited simultaneously to one of two electronically excited states, *i.e.* $\text{C}_2\text{H}_5\text{Br}^{\dagger(1)}$ or $\text{C}_2\text{H}_5\text{Br}^{\dagger(2)}$, competitively with a discrete ratio by absorbing a photon. The first excited state, $\text{C}_2\text{H}_5\text{Br}^{\dagger(1)}$, produces hot C_2H_4 by HBr molecular elimination and the CH_3 radical by C—C bond fission and the second excited state, $\text{C}_2\text{H}_5\text{Br}^{\dagger(2)}$, decomposes to C_2H_5 and bromine radicals by C—Br bond fission. As a secondary process, the hot C_2H_4 molecule decomposes to C_2H_2 and/or is collisionally quenched to the ground state. The production of CH_3CHBr_2 and that of scavengeable C_2H_4 have been interpreted as due mainly to the termination processes.

Acknowledgment

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