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Evidence for the State Dependence of Primary Photodecomposition Processes on the Reaction of Ethyl Chloride at 163.3nm[a]

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Introduction

In this communication we report the study of the state dependence of primary photodecomposition modes on ethyl chloride in vacuum ultraviolet (VUV) region. The study of energy dependence and state dependence of primary reaction modes becomes an active research area in recent years:[1] The importance of the research of these fields are mainly due to the possible control of the reaction pathway and of the selective excitation of the molecules by varying an incident light energy.[1,2]

Recent studies on the photochemistry of alkyl halides have suggested that the primary reaction modes of these compounds are wavelength dependent. When the halide molecules absorb the light in VUV region, they show two distinctively different excitation patterns, *i.e.,* a Rydberg state and a σ^* state. Rydberg state molecules decompose further by the molecular HX elimination process[3-6] while those of σ^* state demonstrate C-X bond fission reaction process.

Though ampoule data on these fields have been accumulated last two decades from various research groups, they have not reached to any definite conclusion whether the excited state or the total energy content of molecules plays the major role on the reaction scheme. The difficulties have been inheritted from two major draw backs. Firstly, the works of ethyl halides other than ethyl bromide have been performed rather short wavelength region,[6-9] *e.g.*, 104.8-106.7 nm, 123.6 nm and 147 nm, and lacking the information in longer wavelength region. Secondly, even the work on ethyl bromide which has covered 104.8-193.1 nm region[10-15] has also suffered due to its strong diffusive nature of its absorption band.[4] We now report the state dependence on the VUV photolysis of ethyl chloride at 163.3 nm.

The reaction system and the experimental procedure have been described previously.[12,13] The light source was an electrodeless discharge bromine atom lamp[16] operated by KIVA MPG-4M microwave generator. The lamp had a 1.2 cm O.D. x 10 cm L. side arm located 27 cm from the front window (2 mm thickness x 2.5 cm diameter optically flat Suprasil quartz) to control the vapor pressure of bromine utilizing dry ice/acetone slush bath. The spectral purity of the lamp at 163.3 nm was checked routinely by 0.3 m GCA/McPherson 218 vacuum monochromator and was found less than 0.1 nm of its band width.

The extinction coefficient of ethyl chloride at 163.3 nm was measured using a photo-absorption cell charged with known pressure of the sample between the lamp and the monochromator. The coefficient at this wavelength was determined to be $\varepsilon=(1/PL)\ln(I_0/I_1)=19.6\pm2.3$ $cm^{-1}atm^{-1}$ with 95% confidence level.

Reaction products were analyzed using HP5880A gas chromatograph (GC) equipped with twin hydrogen flame ionization detectors (FID) and HP5985B GC/Mass spectrometer. The quantitative analyses of the reaction products were done by comparison of the retention times and the peak areas of the products with those of the authentic samples and confirmed by the GC/MS. The separation of the products, *i.e.*, CH_4, C_2H_6, C_3H_8, C_2H_3Cl and n-C_4H_{10}, was done using 0.31 cm O.D. x 250 cm L. stainless steel column packed with 100/150 mesh Porasil B.

Ethyl chloride (stated purity>99.5%) was obtained from Matheson and was purified by a trap-to-trap distillation technique at liquid nitrogen temperature. The final purity was checked by GC until no traceable impurities were detected. All other authentic samples (Matheson) were also purified using the same technique.

The major reaction product was found to be C_2H_6 with minor products of CH_4, C_3H_8, C_2H_3Cl and n-C_4H_{10}. The reaction product quantum yields of these compounds are listed in Table 1 and are displayed in Figure 2 as a function of the reactant pressure. Quite contrary to this finding at 163.3 nm, the previous works of ethyl halides at shorter wavelengths[3,4,7] have shown the competitive primary reaction modes between the HX

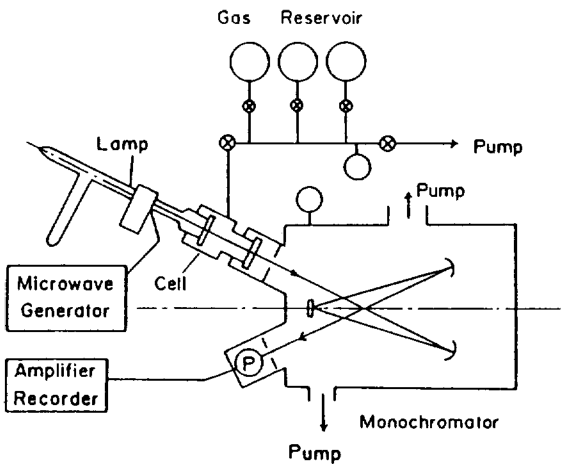

Figure 1. Schematic Diagram of Extinction Coefficient Measuring System at Vacuum UV Region.

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TABLE 1: Product Quantum Yields of 163.3 nm Photolysis of C_2H_5Cl

Run No.	P (C_2H_5Cl) (Torr)	Product Quantum Yield				
		CH_4	C_2H_6	C_3H_8	n-C_4H_{10}	C_2H_3Cl
1	1.0	0.013	0.075	0.002	—	0.012
2	2.0	0.009	0.111	0.002	0.009	0.021
3	3.0	0.010	0.136	0.002	0.010	0.031
4	5.0	0.014	0.228	0.003	0.016	0.049
5	7.0	0.014	0.271	0.002	0.018	0.049
6	9.0	0.010	0.269	0.002	0.032	0.059
7	9.9	0.017	0.302	0.004	0.024	0.059
8	11.4	0.013	0.375	0.002	0.033	0.074
9	13.0	0.023	0.410	0.009	0.032	0.079
10	16.8	0.020	0.432	—	0.033	0.083
11	20.0	0.019	0.576	0.003	0.030	0.089
12	7.1 + 0.2 NO	0.000	0.000	0.000	0.000	—
13	7.6 + 1.5 NO	—	0.000	0.000	0.000	—

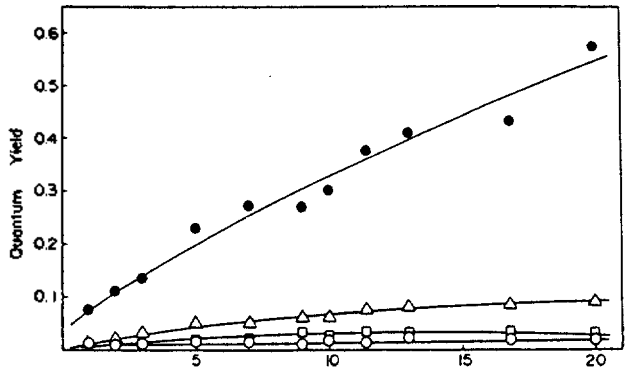

Figure 2. Variation of Quantum Yields of Reaction Products with Reactant Pressure in 163.3 nm Photolysis of C_2H_5Cl: ●, C_2H_6; △, C_2H_3Cl; □, n-C_4H_{10}; ○, CH_4.

molecular elimination and the C-X bond fission. In the case of ethyl bromide, the competitive nature has been observed even at 193.1 nm with the variations of the ratio only.[12, 14] In the present work, however, the HCl molecular elimination product, *i.e.*, C_2H_4, was not detected within the pressure range of 1.0 to 100 torr. By comparing the present work at 163.3 nm and the previous works at 104.8-106.7 nm,[9] 123.6 nm,[9] and 147 nm,[7] the wavelength dependence of the primary reaction modes of ethyl chloride may be deduced and can be described by two distinctively different mechanisms, *i.e.*, one≤147 nm and the other≥163 nm.

$$C_2H_5Cl+h\nu \xrightarrow{\lambda \leq 147\,nm} C_2H_5Cl^{\dagger}(1) \longrightarrow C_2H_4+HCl$$

$$C_2H_5Cl^{\dagger}(2) \longrightarrow C_2H_5+Cl$$

$$C_2H_5Cl^{\dagger}(1)+M \rightarrow C_2H_5Cl^{\dagger}(2)$$

and

$$C_2H_5Cl+h\nu \xrightarrow{\lambda \geq 163.3\,nm} C_2H_5Cl^{\dagger} \longrightarrow C_2H_5+Cl$$

At the wavelength less than or equal to 147 nm, C_2H_5Cl excites to Rydberg state which is correspond to n→(n+1)P (D band) transition.[17] Rydberg state of C_2H_5Cl proceeds further the molecular elimination or converts to the lower electronic excited state by collision with third body and then proceeds C-X bond fission. The possibility of the radical formation from Rydberg state has been also included in the mechanism on the basis of the observation of the radical product at zero pressure extrapolation. The results at 163.3 nm as shown in Table 1, however, indicate that the reaction proceeds only by the radical process since the radical scavenger NO suppreses the product quantum yield effectively. Since the absorption band of C_2H_5Cl at 163.3 nm is correspond to n→σ* (A band) transition,[17] the result suggests that the excited state of C_2H_5Cl by n→σ* transition proceeds to C-Cl bond repture and the energy transfer between the electronic and the vibrational states is not so effective in this system. From the foregoing discussion, the reaction mechanism of the secondary process in this system is suggested by,

$$C_2H_5+C_2H_5+M \longrightarrow n\text{-}C_4H_{10}+M$$

$$C_2H_5+C_2H_5Cl \longrightarrow C_2H_6+C_2H_4Cl$$

$$C_2H_4Cl+C_2H_4Cl+ \longrightarrow C_2H_3Cl+C_2H_5Cl.$$

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