Infrared Spectroscopic Studies on Photolysis of Ethyl Iodide in Solid Parahydrogen

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The photolysis of ethyl iodide in solid parahydrogen leads to the formation of ethyl radical, ethylene, and ethane upon near-UV illumination at about 5 K which are characterized by vibrational spectroscopy. The mechanism of the formation of the products is elucidated consistently. Two kinds of ethylene are discriminated spectroscopically which show distinctly different temporal behaviors during illumination and standing under dark. One of them is attributed to a complex between ethylene and iodine atom. The present work demonstrates that the cage effect is insignificant in the solid parahydrogen matrix, and a variety of elementary reactions of *in situ* photolysis can be studied in detail in contrast to conventional rare gas matrices.

Introduction

Photochemistry and photophysics of alkyl iodides have been subjected to a number of investigations as reviewed in our previous study on methyl iodide.[1] In the previous work we had shown that solid parahydrogen is a useful matrix for characterizing photoproducts by infrared absorption spectroscopy.[1,2] The matrix allows photofragments to be separated and trapped, giving highly resolved vibrational spectra.[1,2] This is in contrast to conventional rare gas and other matrices where *in situ* photolysis of the alkyl iodides “all failed undoubtedly due to the cage effect”.[3] Thus, Pacansky *et al.*, e.g., had to use a special precursor, $C_2H_5COO-OOCC_2H_5$, to obtain ethyl radical by *in situ* photolysis in an argon matrix.[4−6] Apparently, the spacer molecule of the CO_2 byproduct prevented two ethyl radicals from recombining.

This difference between the parahydrogen and conventional matrices can be ascribed to the extreme softness, shown by the very high isothermal compressibility,[7] and to the exceedingly high thermal conductivity,[8] both being special properties of a quantum solid. The softness originating from the large amplitude of the zero point lattice vibration allows easy separation of the alkyl radical and iodine atom, while the high thermal conductivity facilitates rapid cooling to stabilize the separated photofragments. These properties can be used for characterizing elementary reactions which is otherwise difficult. An equally important advantage of the parahydrogen matrix is that the spectroscopic resolution can be much higher than in other matrices, as reviewed by Oka[9] and as shown in our studies on molecules such as CH_4,[10] CD_3H,[11] and methyl radical.[12]

In this work we report a photolytic study on ethyl iodide as a natural extension of the previous work on methyl iodide to broaden the understanding of reactions occurring in the cryogenic matrix at about 5 K. Aided by gas phase studies[13−16] three products, ethyl radical, ethylene, and ethane, are identified by infrared spectroscopy. An unexpected finding is the formation of two spectroscopically different ethylenes. One of them shows remarkable spectral changes under illumination and dark standing. The whole reaction scheme is elucidated consistently.

Experimental Section

The experimental procedure is described in our previous work[1,2] with the exception that methyl iodide is replaced with ethyl iodide from Nacalai Tesque, Inc., and KBr and BaF_2 are used for beam splitter and optical windows, respectively. A brief description of the procedure is given below. Parahydrogen gas containing less than 0.1% orthohydrogen was mixed with 0.008% ethyl iodide at room temperatures and then introduced to a copper cell attached to the base of a cryostat kept at 8.2−8.3 K. An optically transparent solid sample was grown in the cell by continuously flowing the gas into the cell for about 1 h. The optical measurement was carried out at about 5 K, using the same Nicolet FTIR spectrometer of a resolution of 0.25 cm^{-1} and the MCT detector as before.

Spectral Assignment

Figures 1−3 demonstrate the spectral regions where changes were observed upon UV illumination (spectra II−IV), subsequent standing under dark (spectrum V), reillumination (spectrum VI), and annealing at 8.0 K for 5 min and recooling to 5.0 K (spectrum VII). Spectrum I is for the sample before illumination. The seven spectra in Figures 1−3 are chosen representatively, to avoid congestion, from a number of spectra recorded. Figure 3 shows the three spectral regions to be ascribed to ethylene. The spectra are expanded to demonstrate detailed differences between two kinds of ethylene discussed later.

Figure 4 shows the temporal change of the integrated spectral intensity of the species designated in the figure. The intensities are normalized to the strongest absorption for each of the 14 measurements. The lines drawn in the figure are for clarity only and not fitted to any known curve. The spectra in Figures 1−3 and the plots in Figure 4 are for a typical experiment in which ethyl iodide was almost exhausted and ethyl radical and ethylene attained their maxima at the end of the first period of illumination (Figure 4). If the illumination was continued beyond this point, the yield of the radical declined. The scattering of the plots in Figure 4 was due to the spectral overlap and the difficulty of separation of spectral signals from the background. The spectral assignment was made by referring to the literature and by internal consistency among the observed spectra.

Ethyl Iodide. Spectra I in Figures 1−3 are, of course, due to the intact ethyl iodide. Reference to the gas phase spectrum leads to the following correspondence between the present and the literature values in parentheses,[15] all in units of cm^{-1}: Figure 1, 3021.9 (3025), 2988.0 (2989), 2982.4 (2987), 2967.9 (2973); Figure 2, 1218.3 (1208), 1208.3 (1201); Figure 3, 955.5 (957). In addition, we detected ethyl iodide peaks at 2926.5 (2932),

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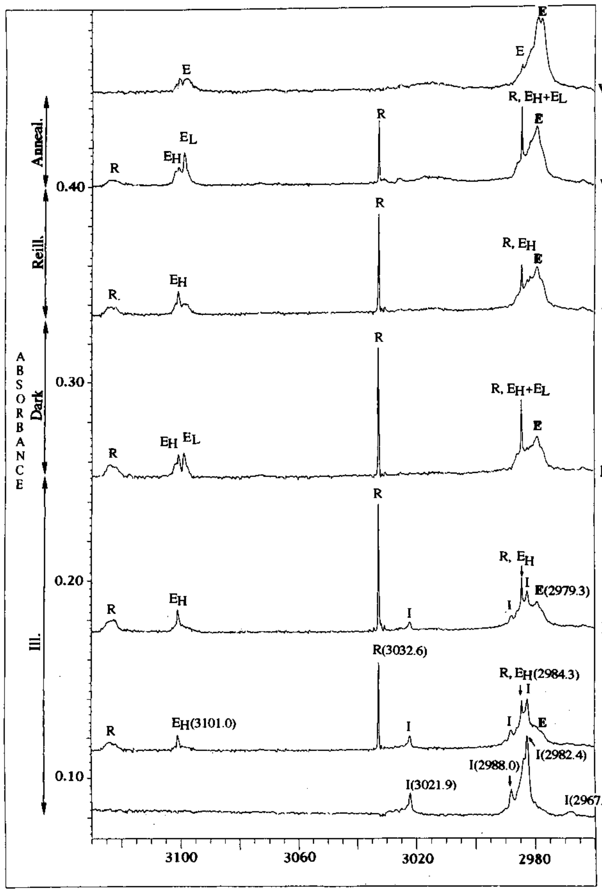

Figure 1. Infrared absorption spectra of ethyl iodide in solid parahydrogen, 2960−3130 cm^{-1}. The seven spectra are chosen representatively from the total fourteen spectra. Spectrum I is as deposited, II is the same as I after 155 min UV illumination, III is after 270 min UV illumination, and IV is after 420 min UV illumination. Spectrum V is the same as IV after 6 h standing under dark. Spectrum VI is the same as V after 180 min UV reillumination. Spectrum VII is the same as VI after the sample was annealed at 8.0 K for 5 min and then recooled to 4.99 K. The temperature of spectral measurement varied from 4.99 to 5.27 K, but the fluctuation within this range did not affect the spectra quality. The scale of the ordinate is common to all of the spectra which are shifted arbitrarily for legibility. The spectral assignment (cm^{-1}) is as follows (see text); ethyl iodide (I), 3021.9, 2988.0, 2982.4, 2967.9; ethyl radical (R), 3122.8, 3032.6, 2984.3; the high-frequency ethylene (E$_H$), 3101.0, 2984.2; the low-frequency ethylene (E$_L$), 3099.1, 2984.2; and ethane (**E**), 2979.3.

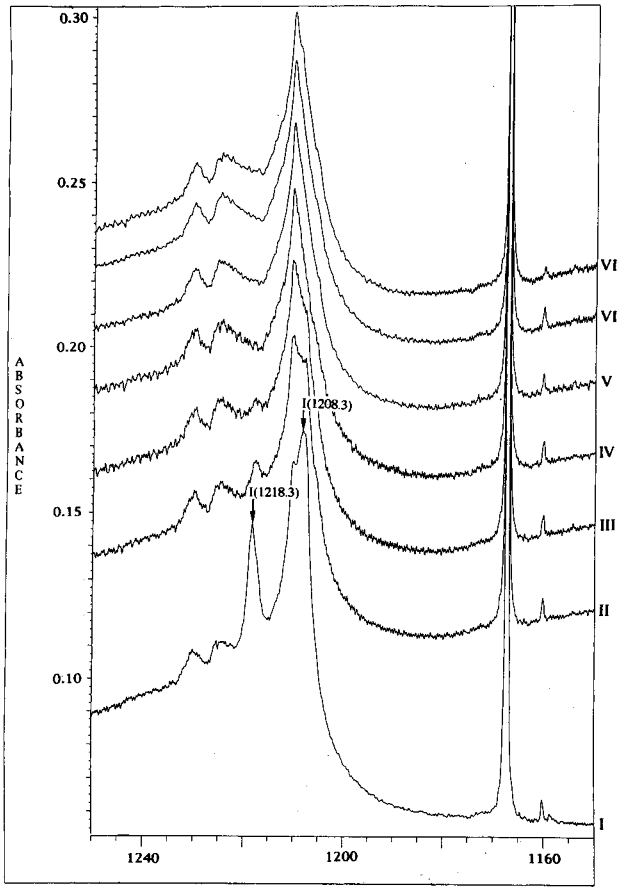

Figure 2. Infrared absorption spectra of ethyl iodide in solid parahydrogen, 1150−1250 cm^{-1}. See the caption for Figure 1. In spectrum I, ethyl iodide (1218.3, 1208.3 cm^{-1}). The sharp peak at 1167.3 cm^{-1} and the huge absorption at ~1250 cm^{-1} through ~1165 cm^{-1} in spectra I−VII are due to the intrinsic absorption of the matrix (see the text).

1450.2 (1462), 1446.9 and 1445.9 (1447), 1381.4 and 1380.0 (1385), and 1046.6 (1049), but the spectra are not shown to save space.

The intensity of the absorption of ethyl iodide decreased in an approximately exponential way upon illumination, as seen from the plots in Figure 4. Only well-separated and relatively intense peaks were selected for plotting (see caption of Figure 4).

A remark on Figure 2 showing the absorption of not only ethyl iodide but also parahydrogen may be appropriate at this moment. Except for the rapidly decaying absorption of ethyl iodide peaking at 1218.3 and 1208.3 cm^{-1}, the absorption between about 1250 and about 1165 cm^{-1} remains constant through the light and dark periods. The sharp peak at 1167.3 cm^{-1} is ascribed to the zero-phonon band of the solid parahydrogen corresponding to the U-band of the freely rotating hydrogen molecule, *i.e.*, due to the transition of $v' = 0, J' = 4 \leftarrow v'' = 0, J'' = 0$. The rest of the absorption is the accompanying phonon band.[9] For the present work the absorption serves merely as the background of the absorption of ethyl iodide.

Ethyl Radical. Guided by the proximity to the literature frequencies[4−6,17] and by inference from our study on methyl radical which showed a tendency for the radical to disappear on annealing,[1] we obtained the following correspondence between the present and the literature frequencies (cm^{-1}) in parentheses:[6,17] Figure 1 (spectra II−VI), 3122.8 (3112)[6] and (3114),[17] 3032.6 (3033)[6] and (3036),[17] and 2984.3 (2987).[6]

Among the above three the one at 2984.3 cm^{-1} seems to nearly coincide, by accident, with the absorption of ethylene at 2984.2 cm^{-1}.

Outside the wavenumber region in Figure 1, weak absorption peaks were detected at 2879.1, 2812.1, and 2716.5 cm^{-1} whose temporal behavior is similar to that of the above three peaks as shown in Figure 4. In ref 6 seven more peaks are reported at 2920, 2842, 1440, 1366, 1175, 1138, and 540 cm^{-1}; similarly, in ref 17 eight, at 2844, 1442, 1383, 1369, 1185, 1133, 1025, and 532 cm^{-1}. Since the lowest attainable frequency in the present work is 910 cm^{-1}, we cannot compare the reported 540 [6] and 532 [17] cm^{-1} with the present work. As for the remaining six[6] and seven,[17] we failed to detect the corresponding peaks. A reinvestigation of spectroscopic assignment of the radical is now under way.[18]

Ethylene. Ethyl radical in the gas phase photodecomposes to ethylene and hydrogen atom upon near-UV illumination.[13,14] Thus, we expect the formation of ethylene in the present work also. For reference, we measured the absorption spectrum of ethylene in parahydrogen (0.004%, 4.90 K). The complete

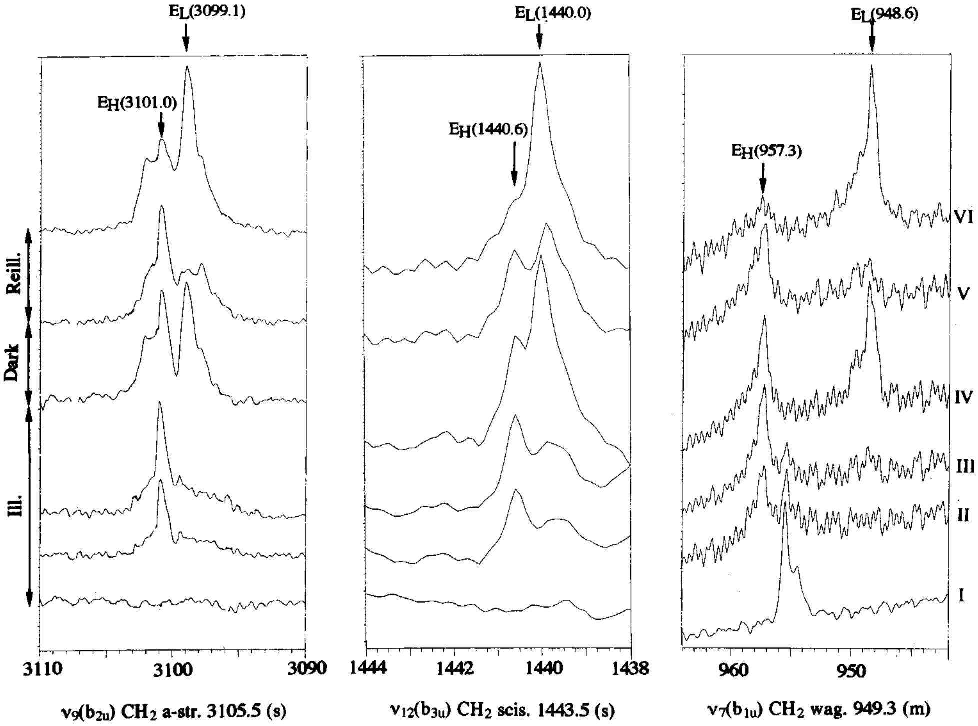

Figure 3. Infrared absorption spectra reproduced for the three regions of ethylene. See the caption for Figure 1 for the spectral numbers I−VI. Peaks at 3101.0, 1440.6, and 957.3 cm^{-1} are assigned to the high-frequency ethylene, while those at 3099.1, 1440.0, and 948.6 cm^{-1} are to the low-frequency ethylene. The quickly decaying peak at 955.5 cm^{-1} in spectra I−III is due to ethyl iodide.

isolation of ethylene in the solid parahydrogen matrix was not yet been attained, but strong peaks were observed at 3098, 2981.8, 1442−1435, and 958 cm^{-1}. These can be compared with the gaseous frequencies of 3106 (ν_9 (b$_{2u}$) CH$_2$ a-str), 2989 (ν_{11} (b$_{3u}$) CH$_2$ s-str), 1444 (ν_{12} (b$_{3u}$) CH$_2$ sciss), and 949 (ν_7 (b$_{1u}$) CH$_2$ wag) cm^{-1}.[19]

With these reference data and with the consideration that the absorption of the stable ethylene should not vanish as easily as radicals on annealing, we ascribe the following observed absorption to ethylene: Figure 1 (spectra II−VI), ~3103 to ~3096 and 2984.2; Figure 3 (spectra II−VI), ~3103 to ~3096 peaking at 3101.0 (E$_H$), 3099.1 (E$_L$), ~1441 to ~1439 peaking at 1440.6 (E$_H$) and 1440.0 (E$_L$), ~960 to ~945 peaking at 957.3 (E$_H$) and 948.6 (E$_L$).

The suffixes H and L stand for "high" and "low" frequencies and represent two families of absorption peaks to be ascribed in the next section to two complexes of ethylene. Despite the closeness of the frequencies of the two ethylenes their temporal behavior is distinctly different, as shown in Figure 4. This apparent peculiarity will also be discussed in the next section.

Ethane. Figure 1 shows that the broad absorption at about 2980 cm^{-1} continues to grow in spectra II−VII, indicating that the absorption is due to a stable photoproduct. Since the most probable candidate is ethane, the spectrum of ethane in parahydrogen was measured to obtain a matching peak at about 2980 cm^{-1}. In this spectral range of 2980 ± 10 cm^{-1} we have already assigned peaks to ethyl iodide (2988.0, 2982.4 cm^{-1}), ethyl radical (2984.3 cm^{-1}), and ethylene (2984.2 cm^{-1}). However, since the absorption due to ethyl iodide decays quickly as shown in Figure 4 and since the absorption of ethyl radical and ethylene is sharp compared with the growing broad absorption attributed to ethane, the temporal change of the growing absorption at 2979.3 cm^{-1} is easily recognized and plotted in Figure 4.

Reaction Mechanism

The observed spectral changes were analyzed separately in the order of the first period of continual illumination, the subsequent standing under dark, the reillumination, and the final thermal annealing.

First Illumination Period. The reactant ethyl iodide decays exponentially whereas the radical grows approximately in an exponential fashion, as shown in Figure 4. This suggests reaction 1.

$$C_2H_5I + h\nu \rightarrow \cdot C_2H_5 + \cdot I \qquad (1)$$

Ethyl radical is known to absorb near-UV light,[20] and "conclusive evidence" for the methyl C−H bond cleavage of the radical is reported for the photolysis with 248 nm photons.[14] Therefore, the following reaction will take place while reaction 1 is in progress.

$$\cdot C_2H_5 + h\nu \rightarrow \cdot H + CH_2{=}CH_2 \qquad (2)$$

Because of the absorption of two photons in succession, the production of the ethylene from reactions 1 and 2 should be slow at the beginning. Comparison of the lower two panels in Figure 4 immediately suggests that the ethylene classified as the low-frequency ethylene is identified as such ethylene. It is noted that this ethylene should accompany the iodine atom produced by reaction 1.

Before the discussion on the reaction mechanism is continued, a preparatory pause is placed here for further discussion: The spectral line shape of ethyl iodide in spectrum I (Figures 1−3) suggests incomplete isolation of the iodide in the matrix. In particular, the absorption peaking at 955.5 cm^{-1} in Figure 3 shows a "tail" toward lower frequencies which indicates the presence of clusters of the iodide. The size of the clusters is likely small, as the absorption of crystalline ethyl iodide in the *p*-H$_2$ matrix is significantly red-shifted and broad with a typical

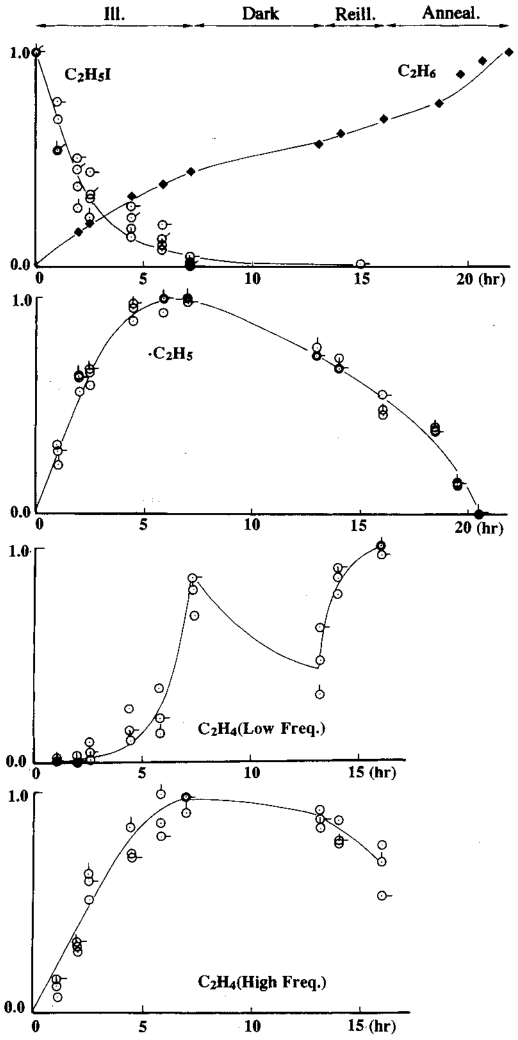

Figure 4. Temporal changes of the absorption intensity for ethyl iodide, ethane, ethyl radical, the low-frequency ethylene, and the high-frequency ethylene. The integrated intensities are normalized to the strongest absorption for each peak. The horizontal arrows atop are common to all four panels. They indicate the first period of continual illumination, the subsequent period under dark, the subsequent period of reillumination, and the period of annealing to 6.0, 7.0, 8.0, and 9.0 K, each for 5 min standing and then recooling to ~5.0 K. The various symbols for plotting represent absorption peaks of the five species as follows. Top panel for ethyl iodide and ethane: Open circles, ethyl iodide at 3021.9 cm^{-1}; open circles with horizontal bar, sum of the ethyl iodide peaks at 1381.4 and 1380.0 cm^{-1}; open circles with vertical bar, ethyl iodide at 1218.3 cm^{-1}; open circles with slant bar, ethyl iodide at 955.5 cm^{-1}; solid squares, ethane at 2979.3 cm^{-1}. Second panel for ethyl radical: Open circles, 3122.8 cm^{-1}; open circles with horizontal bar, 3032.6 cm^{-1}; open circles with vertical bar, 2879.2 cm^{-1}. Third panel for the low-frequency ethylene: Open circles, 3099.1 cm^{-1}; open circles with horizontal bar, 1440.0 cm^{-1}; open circles with vertical bar, 948.6 cm^{-1}. Bottom panel for the high-frequency ethylene: Open circles, 3101.0 cm^{-1}; open circles with horizontal bar, 1440.6 cm^{-1}; open circles with vertical bar, 957.3 cm^{-1}.

bandwidth of 10−20 cm^{-1} at full width at half-maximum (fwhm, data not shown). Meanwhile, the photolysis of ethyl iodide dimers in molecular beams was reported by Donaldson *et al.*,[16] showing that the dimer yields an iodine molecule by a one photon process, as in the case of methyl iodide cited in our previous work.[1] They proposed a concerted reaction for alkyl iodide dimers

$$(RI)_2 + h\nu \rightarrow 2\cdot R \text{ and/or } R_2 + I_2 \qquad (3)$$

In fact, both methyl radical and ethane were detected in our previous study on methyl iodide in solid parahydrogen in conformity with reaction 3 which suggests the presence of the dimer in the parahydrogen matrix.[1,2]

Thus, a simple analogy from the molecular beam experiment would predict the formation of ethyl radical ($^{\bullet}R$) and butane (R_2) in the ethyl iodide/*p*-H_2 system of the present study. However, no absorption due to butane[21] was detected despite a thorough survey of the spectrum. Instead, the absorption of ethane and the high-frequency ethylene increased monotonously (see Figures 1 and 4). Therefore, in the ethyl iodide/*p*-H_2 system, disproportionation rather than dimerization seems to be favored; that is, the product corresponding to R_2 in reaction 3 is equal to the products of reaction 4.

$$2\cdot C_2H_5 \rightarrow CH_2{=}CH_2 + C_2H_6 \qquad (4)$$

For dimerization to occur, two heavy C_2 units must approach each other, whereas for disproportionation only the hydrogen atom transfer is required which may be preferred by tunneling in the solid parahydrogen at about 5 K. The ethylene produced by reaction 4 should accompany ethane and iodine molecules produced molecularly by reaction corresponding to (3). On this basis the low- and high-frequency ethylenes are regarded as two different charge transfer complexes of ethylene with the iodine atom and molecule, respectively. However, since the absorption of both ethylenes is close to that in the gas phase[19] as well as in argon[22] and xenon[23] matrices, the perturbation due to the accompanying iodine atom for the low-frequency ethylene and that due to the accompanying iodine and ethane molecules for the high-frequency ethylene must be small. Nevertheless, we expect a larger interaction for the low-frequency ethylene in view of the well-known complexation between π electronic systems and a halogen atom.[24] In other words, the high-frequency ethylene is more like the free ethylene and the low-frequency ethylene is more affected by the open-shell iodine atom. Since the absolute absorbance of both ethylenes will not be significantly different, the appearance of both of them to the same order of magnitude (see Figures 1 and 3) implies that their yields are similar. This, in turn, implies that the precursors of both ethylenes, that is, monomeric and dimeric ethyl iodide, are present to the same order of magnitude in the system.

Dark Period. Figure 4 demonstrates that ethyl iodide is almost exhausted at the beginning of the dark period when the yield of ethane is still less than about 45% of that at the end of the annealing period. Since the iodide should be the seminal source for ethane whatever the intermediate reaction path is, the C_2 unit originally in the iodide must be transferred to ethyl radical and ethylene also, which would eventually yield the additional ethane. Unfortunately, the lack of information on the absolute absorbance of each entity prevents stoichiometric analysis, but the qualitative features of the marked, moderate, and very little, if any, decreases of the low-frequency ethylene, ethyl radical, and the high-frequency ethylene, respectively, are obvious. In particular, the low-frequency ethylene decays rapidly in the dark period and recovers quickly in the subsequent reillumination period. This feature is shown in Figure 3 for the three spectral regions of ethylene. From Figure 3 it is easy to see the parallel behavior of the low- and high-frequency ethylenes among the three spectral regions.

The rapid decay and the quick recovery of the absorption of the low-frequency ethylene in the dark and the reillumination periods, respectively, implies that the ethylene is transformed into a photosensitive species during the dark period, which resumes the low-frequency ethylene upon reillumination. Since we assume that the iodine-atom-complexed low-frequency ethylene is produced by reactions 1 and 2, the ethylene unit may react, during the dark period, with a hydrogen atom photogenerated by reaction 2 as follows.

$$CH_2{=}CH_2 + {\cdot}H \rightarrow {\cdot}C_2H_5 \qquad (5)$$

According to reaction 5 ethyl radical should increase with the decrease of the low-frequency ethylene. However, Figure 4 shows the decrease of the absorbance of ethyl radical during the dark period. Figure 4 also demonstrates a continuous increase of ethane and a slight decrease of the high-frequency ethylene under dark. In order to elucidate these results the following mechanism is proposed on the basis of the reported migration of hydrogen atom in solid parahydrogen at 4.2 K:[25] Some of the hydrogen atoms photogenerated by reaction 2 may escape into the bulk, where some of them recombine to hydrogen molecule and some encounter ethyl radical to result in reaction 6.

$${\cdot}C_2H_5 + {\cdot}H \rightarrow C_2H_6 \qquad (6)$$

The hydrogen atom may also encounter the high-frequency ethylene produced by reaction 4 to cause the same reaction as 5. However, reaction 6 would proceed more easily than reaction 5 because the former is a barrier free reaction. If the absolute absorbance of ethyl radical is large, the decrease of observed absorbance of ethyl radical due to reaction 6 may surmount the increase due to reaction 5 which proceeds with a barrier. Since the hydrogen atom produced by reactions 1 and 2 will find near-lying ethylene of reaction 2 more easily than far-lying ethylene of reaction 4, the low-frequency ethylene will decrease more easily than the high-frequency ethylene. The fast and slow decreases of the low- and high-frequency ethylenes during the dark period may reflect this difference of the reaction efficiency.

Reillumination Period. The quick recovery of the low-frequency ethylene shown in Figure 4 (see also Figure 3) is attributed to reaction 2 coupled with reaction 1, resulting in the complex between ethylene and iodine atom. After the consumption of ethyl iodide the absorption of 253.7 nm photons by the ethyl radical in reaction 2 becomes efficient, which causes the excitation of the radical to a 3s Rydberg state.[20] The recovery of the low-frequency ethylene should be related to the noticeably accelerated decrease of ethyl radical (compare the second and third panels of Figure 4). The continued increase of ethane in the top panel of Figure 4 is attributable to reaction 6, which should proceed irrespective of the light and dark periods.

As for the high-frequency ethylene, which has survived until the end of the dark period, it starts to decrease appreciably as is seen from Figure 4 (see also Figure 3). Simultaneously, the low-frequency ethylene continues to increase overpassing the maximum in spectrum IV of Figure 3. Since the low-frequency ethylene originating from monomeric ethyl iodide in reaction 1 is not available limitlessly, the continued increase of the low-frequency ethylene from spectrum V to VI of Figure 3 must be associated with other remaining C_2 carriers, that is, the high-frequency ethylene. With the depletion of ethyl iodide and ethyl radical, both absorbing 253.7 nm photons, the absorption by iodine molecule produced from the molecular reaction corresponding to 3 will become more and more significant. The absorption of iodine molecule is well-known to cause photolysis into two iodine atoms.[26] The iodine atom will find the nearby ethylene from reaction 4, *i.e.*, the high-frequency ethylene, and will form a complex between the ethylene and the iodine atom, which is nothing other than the low-frequency ethylene. This mechanism explains the increase of the low-frequency ethylene as shown in spectrum VI of Figure 3.

Annealing Period. The continued increase of ethane and the rapid decay of ethyl radical in Figure 4 may be understood if reaction 6 is favored at the elevated temperatures, which is plausible. Since there is no sign of the regeneration of ethyl iodide and the appearance of absorption of butane,[21] neither the reverse reaction of 1 nor the dimerization of the radical takes place. As for the two ethylenes in the annealing period, broadening and distortion of the spectrum prevent meaningful plotting in Figure 4 so that they are omitted.

Concluding Remarks

As in the previous work on methyl iodide, photoreactions and thermal reactions in the ethyl iodide system are pursued by observing the vibrational spectroscopic changes. The system is relatively simple, involving only ethyl iodide, ethyl radical, ethane, and ethylene. Yet, new findings are obtained such as the formation of two kinds of ethylene and the reactions involving the migrating hydrogen atom. These reactions may have relevance to molecular evolution on hydrogen covered cold surfaces of dusts in interstellar space. The cryogenic reactions may also be enticing to theoretical chemists for the study of tunneling reaction. An important advantage of the solid parahydrogen matrix is that we are free from the cage effect inherent in conventional rare gas matrices. This allows the study of *in situ* photolytic reactions in detail by means of vibrational spectroscopy. Utilizing this advantage, we are aiming at improving the versatility of matrix isolation spectroscopy.

A remaining problem is that no absorption was detected in the region where hydrogen iodide in several matrices is reported to absorb, i.e., 2255−2230 cm^{-1} in argon,[27,28] 2240−2210 cm^{-1} in krypton,[28] and 2238 cm^{-1} in nitrogen.[28] In this context a statement is noted that "the absorbance of monomer HI appears to be significantly weaker than the absorbance of HI that forms a hydrogen bond to another molecule. It is therefore difficult to observe monomer HI in a matrix without significant dimer absorptions."[27]

Another comment will be made on reaction 5; Klein and Scheer did not mention anything about the prototype reaction 5 in their classic work on reactions between various alkenes and hydrogen atom at temperatures above 77 K, which may be allusive to the absence of appreciable reaction between ethylene and hydrogen atom under their experimental conditions.[29] However, the environment in the present work is considerably different from that of the previous workers so that there may not be serious conflict between the two studies.

Finally, we note the difference of the behavior of methyl radical in the previously studied methyl iodide/p-H_2 system[1,2] versus the behavior of ethyl radical in the present system. The methyl radical in the methyl iodide/p-H_2 system did not show noticeable decay under dark during the experimental time scale, which is in contrast to the present system. Further comparative studies on the two systems are now under way.

In the present work, dedicated to Professor Saburo Nagakura, we put emphasis on dynamical aspects of electronically excited ethyl iodide. There remain, however, several points worthy of further investigation on the present system from the viewpoint of vibrational spectroscopy. These include (1) the elucidation of the aforementioned incomplete agreement of the vibrational spectrum of ethyl radical between the present work and the literature,[6,17] (2) the broad radical absorption at 3122.8 in contrast to the very sharp ones at 3032.6, 2984.3, 2879.1, 2812.1, and 2716.5 cm^{-1} as well as the broadness of ethane absorption, and (3) the conspicuously large spectral shift between the low- and the high-frequency ethylenes at 948.6 vs 957.3 cm^{-1} assigned to an in-plane C−H scissoring mode of the ethylenic unit in the complex, to name a few.

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