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Photoinduced reactions of methyl radical in solid parahydrogen

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Photolysis of methyl iodide in solid parahydrogen $(p-H_2)$ at about 5 K is studied with ultraviolet light at 253.7 and 184.9 nm. It is found that the light at 253.7 nm produces only methyl radical, whereas the light at 184.9 nm yields both methyl radical and methane. The mechanism of the formation of the photoproducts is elucidated by analyzing the temporal behavior of the observed vibrational absorption. It is concluded that methyl radical in the ground state does not react with $p-H_2$ molecules appreciably but that the radical in the electronic excited state of $\tilde{B}({}^2A'_1)$, accessible by reabsorption of 184.9 nm photons by the radical, decomposes to a singlet methylene CH₂ $\tilde{a}({}^1A_1)$ and a hydrogen atom (2S) and that the singlet methylene reacts with a $p-H_2$ molecule to give methane. © 1998 American Institute of Physics. [S0021-9606(98)00139-1]

I. INTRODUCTION

Solid parahydrogen $(p-H_2)$ is a useful matrix in matrixisolation spectroscopy because it allows both high-resolution rotation-vibration spectroscopy in favorable cases¹⁻⁶ and kinetic studies of photolysis of embedded molecules.^{3,7-10} In a series of our work on alkyl iodides in the p-H₂ matrix, we have shown that the iodide is easily photolyzed to alkyl radicals and an iodine atom. This is in remarkable contrast to the conventional rigid rare gas matrices. In the latter matrices, the cage effect prevents the photofragments from being separated.¹¹⁻¹⁴ The advantageous feature of the mitigation of the cage effect in the p-H₂ matrix is attributed to the fact that solid $p-H_2$ forming a hexagonal close packed crystal is a quantum solid having the following properties: (1) a large lattice constant, (2) a large amplitude of the zero-point lattice vibration, and (3) a large thermal conductivity.³ Due to the properties of (1) and (2), solid $p-H_2$ can be regarded as a spacious and soft lattice for foreign molecules, and due to (3), the excess energy imparted to nascent photofragments is quickly removed and the fragments are rapidly frozen to be protected from geminate recombination.

On account of these properties, we have been successful in photolyzing methyl iodide in the p-H₂ matrix to obtain methyl radical for its rotation–vibration spectral analysis.^{3,7,8} In these studies, using a low pressure mercury lamp, however, we obtained methane and ethane, in addition to methyl radical. As for the mechanism of the formation of ethane, a consistent explanation was put forth by referring to the result of laser photolysis of methyl iodide in molecular cluster beams, which invokes the involvement of methyl iodide dimers.^{3,7,15–17} However, as to the production of methane, there remained an ambiguity and we conjectured two possibilities.⁸ The present work is intended to settle the argument on the formation mechanism of methane by examining the dependence of the formation of methane upon the wavelength of ultraviolet (UV) light used for the photolysis.

II. EXPERIMENT

The experimental procedure is the same as in our previous work^{7,8} and is elaborated in a review article.³ Briefly, normal hydrogen gas was converted to p-H₂ which contained about 0.01% residual orthohydrogen. The converted gas was mixed with $\sim 0.02\%$ CH₃I at room temperature. The mixed gas was introduced into a cylindrical copper cell of dimensions 5 to 10 cm long and 2 cm in diameter attached with BaF₂ windows at both ends of the cylinder. The temperature of the cell was kept at 8.1±0.2 K during the introduction of the sample gas for some 1.5 h. The temperature during the crystal growth was slightly lower than the previous work^{7,8} in order to avoid the formation of iodide cluster in solid p-H₂ as much as possible.^{6,7} Then, the temperature was slowly lowered to 4.5±0.1 K and kept at the same temperature throughout the experiment. A low pressure 20 W mercury lamp was used for the photolysis, which emitted UV light at 253.7 and 184.9 nm and weak lines in the visible region. To effect the selective photolysis at 253.7 nm, a cutoff filter Toshiba UV-25 was used. Since the filter transmitted wavelengths longer than 200, light at 184.9 was completely cut while light at 253.7 nm was transmitted by about 60%. For the exclusive photolysis at 184.9 nm, a narrowband filter Acton Research Corporation 185-N-ID was used which transmitted wavelengths between 169 and 220 nm. The transmission at 184.9 nm was approximately 18.3%. The infrared absorption of samples was observed using a Nicolet Magna 750 Fourier-transform infrared (FTIR) spectrometer with a resolution of 0.25 cm^{-1} in combination with a KBr beam splitter and a liquid nitrogen cooled mercury cadmium telluride [MCT (HgCdTe)] detector. The experimental procedure for the photolysis of deuterated methyl iodide (CD₃I) was the same as that for CH₃I.

III. EXPERIMENT RESULTS

Figure 1 shows part of the FTIR spectrum of methyl iodide in solid p-H₂ before (lower panel) and after UV irradiation (upper panel). The figure is reproduced from our pre-

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FIG. 1. Infrared absorption spectra of methyl iodide in solid p-H₂ in the spectral region of 2900–3200 cm⁻¹. Bottom: the sample as deposited and recorded before UV irradiation. Top: after a four-hour UV (253.7+184.9 nm) irradiation without filters. The symbols I, R, M, and E stand for methyl iodide, methyl radical, methane, and ethane, respectively.

vious paper.⁷ The sample was irradiated for 240 min with full light from the low pressure mercury lamp described in the preceding section. The absorption bands are assigned as methyl iodide (I), methyl radical (R), methane (M), and ethane (E).^{7,8} It is seen that methyl iodide is photolyzed completely to yield the three products. The mechanism of the formation of ethane has been accounted for as a one-photon concerted process of methyl iodide dimer⁷ and will not be repeated in the present work. Instead, we will focus on the mechanism of the formation of methane which was argued rather arbitrarily in the previous work.⁸ It is found that the absorption of the radical scarcely decays, if at all, in the dark for a few days at about 4.5 K (see below, Fig. 4). Therefore, the reaction of methyl radical in the electronic ground state, $CH_3+H_2\rightarrow CH_4+H$, cannot be responsible for the remarkable appearance of methane upon the four-hour irradiation shown in Fig. 1. Thus, the observed methane must have been produced by some photochemical process.

In order to uncover the photochemical process, photolysis with selective wavelengths was carried out. Traces (a)-(c) in Fig. 2 show the spectra of CH_3I in solid $p-H_2$ upon the irradiation with a filter UV-25, which cuts 184.9 light but transmits 253.7 nm light, while traces (d) and (e) show the spectral change with an additional irradiation through the narrow-band filter, which transmits only 184.9 nm light. Although the spectral data in Fig. 2 are rather noisy due to the attenuation of the photon flux and the absorption of atmospheric water, it is evident that in traces (a)-(c) the absorption of methyl iodide at approximately 2960–2975 cm⁻¹ diminishes continuously and that the absorption of methyl radical at around 3171 cm⁻¹ appears, but that the absorption of methane at about 3026 cm⁻¹ does not. However, as is seen in traces (d) and (e), the succeeding irradiation with 184.9 nm light induces the appearance of methane at about 3026 cm^{-1} .

We carried out another series of experiments in which a $CH_3I/p-H_2$ system was irradiated exclusively by 184.9 nm light by use of a narrow-band filter. As a result, it was found that methyl radical was formed from the beginning of the irradiation as in the case of the irradiation with 253.7 nm



FIG. 2. Infrared absorption spectra of methyl iodide in solid p-H₂ at about 4.5 K in the spectral region of 2900–3200 cm⁻¹. Spectrum (a): the sample as deposited and recorded before UV irradiation. Spectrum (b): after a 120 min UV (253.7 nm) irradiation through a cutoff filter, UV-25. Spectrum (c): after a 240 min UV (253.7 nm) irradiation with the same filter as (b). Spectrum (d): after the 240 min UV (253.7 nm) irradiation and a 90 min UV (184.9 nm) irradiation through a narrow-band filter, 185-N-D. Spectrum (e): after the 240 min UV (253.7 nm) irradiation and a 170 min UV (184.9 nm) irradiation. The symbols I, M, and R stand for methyl iodide, methane, and methyl radical, respectively.

light, while methane appeared retardedly at later stages of the irradiation. Figure 3 shows the integrated absorption intensities of the degenerate C–H bending vibration (ν_4) of methyl iodide, methyl radical, and methane as a function of time of



FIG. 3. Temporal behavior of the degenerate C–H bending vibration (ν_4) of methyl iodide at 1244.6–1251.2 (circles), methyl radical at 1401.4–1403.0 (triangles), and methane at 1306.7–1308.6 cm⁻¹ (squares) upon irradiation of 184.9 nm photons. The curves are the theoretical intensities I_1 (CH₃I), I_2 (CH₃), and I_3 (CH₄) in the text.

the irradiation with 184.9 nm light. The scale of the ordinate is normalized to the intensity of the iodide at t=0 and the relative intensities of methyl radical and methane are amplified by a factor of ten for better legibility. It is seen that the curve for methyl radical is slightly convexed while the curve for methane concaved. The analysis of the curves in Fig. 3 will be made in the next section.

IV. DISCUSSION OF THE REACTION MECHANISM

A. Mechanism consistent with experiment

The results in the preceding section indicate that with the 253.7 nm irradiation only methyl radical is formed while with the 184.9 nm irradiation both methyl radical and methane are produced. We propose the following mechanism of reactions (I)–(III) to be consistent with the experiment.

UV light at both 253.7 and 184.9 nm produces methyl radical with an excess energy $(CH_3^{\#})$, but the radical is deactivated to its ground state as in reaction (I). Since methyl radical absorbs at wavelengths shorter than 216 nm, to be exited to a 3*s* Rydberg state $(\tilde{B}\ ^2A_1')$, ^{18,19} the deactivated radical reabsorbs light at 184.9 but not at 253.7 nm as in reaction (II). The excited radical in the \tilde{B} state dissociates into a singlet methylene ($\tilde{a}\ ^1A_1$) and a hydrogen atom (2S), the former executing the insertion reaction with a hydrogen molecule as in reaction (III),

$$CH_3I + h\nu(253.7 \text{ nm}, 184.9 \text{ nm}) \rightarrow CH_3^{\#} + I \rightarrow CH_3 + I, \quad (I)$$

$$CH_3 + h\nu(184.9 \text{ nm}) \rightarrow CH_3^* (\tilde{B}^2A_1') \rightarrow CH_2(\tilde{a}^1A_1) + H,$$
(II)

$$CH_2(\tilde{a}^{-1}A_1) + H_2 \rightarrow CH_4.$$
(III)

The second step of reaction (II) is put forth because a subpicosecond dynamics study of the radical in the \overline{B} state has disclosed a rapid dissociation into $CH_2(\tilde{a}^{-1}A_1)$ and H^{20} . Lee and his co-workers also investigated photodissociation of methyl radical at 193.3 nm using photofragment translational spectroscopy and demonstrated unambiguously that the methyl radical in the \tilde{B} state dissociates into the singlet methylene $(\tilde{a}^{-1}A_1)$ and a hydrogen atom $({}^2S)$ in conformity with reaction (II).²¹ The barrier height of this dissociation in the \tilde{B} state is estimated to be 2200 cm⁻¹.²⁰ Since the photon energy of 184.9 nm light (\cong 54 100 cm⁻¹) is sufficiently larger than the dissociation barrier height of 48 500 cm⁻ measured from the ground state of methyl radical, there should be an ample energetic allowance for the whole sequence of reaction (II). As for reaction (III), a theoretical calculation predicts no barrier against the reaction,²² so that reaction (III) is considered to be complete.

According to reactions (I)–(III), the temporal change of the concentration of iodide [CH₃I], methyl radical [CH₃], and methane [CH₄] under the irradiation with 184.9 nm light should conform to the following kinetic equations, where *t* is the irradiation time and k_1 and k_2 are the apparent rate constants of photodissociation of methyl iodide and methyl radical, respectively. It is presumed that the 184.9 nm light is absorbed by the iodide and the radical proportionally to their concentrations,

$$\frac{d[\mathrm{CH}_{3}\mathrm{I}]}{dt} = -k_{1}[\mathrm{CH}_{3}\mathrm{I}],\tag{1}$$

$$\frac{d[CH_3]}{dt} = k_1[CH_3I] - k_2[CH_3],$$
(2)

$$\frac{d[\mathrm{CH}_4]}{dt} = k_2[\mathrm{CH}_3]. \tag{3}$$

Under the initial condition of $[CH_3]_{t=0}=0$, and $[CH_4]_{t=0}=0$, the above equations can be solved immediately. As a result, the time dependence of the intensities I(X) of the three species X are obtained as in Eqs. (4)–(6), where I_1 , I_2 , and I_3 are the constants proportional to the oscillator strengths of CH₃I, CH₃, and CH₄, respectively,

$$I(CH_3I) = I_1 e^{-k_1 t}, \tag{4}$$

$$I(CH_3) = I_2 \frac{k_1}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right),$$
(5)

$$I(CH_4) = I_3 \left(1 - \frac{k_2}{k_2 - k_1} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right).$$
(6)

The three curves in Fig. 3 are drawn by the least-squares procedure with the best fitting parameters of $I_1 = 1.000 \pm 0.002$, $I_2 = 0.255 \pm 0.012$, $I_3 = 0.220 \pm 0.003$, $k_1 = (2.30 \pm 0.03) \times 10^{-4} \text{ min}^{-1}$, and $k_2 = (5.47 \pm 0.69) \times 10^{-4} \text{ min}^{-1}$.

We may go a little further with the parameters obtained above: Since the parameters $I_1 - I_3$ are proportional to the oscillator strengths f(X) of the observed band of the three species, we have the relation $I_1:I_2:I_3 \cong f(CH_3I, \nu_4):$ $f(CH_3, \nu_4):f(CH_4, \nu_4) = 1.00:0.26:0.22$. The apparent rate constants k_1 and k_2 should be proportional to the product of the absorption coefficient ε and the quantum yield η of photolysis in reactions (I) and (II) at 184.9 nm. Thus, we have $\varepsilon(CH_3I)\eta(CH_3I):\varepsilon(CH_3)\eta(CH_3) = 2.3:5.5$.

In order to strengthen the credence of the above mechanism we will examine other conceivable mechanisms (1)-(5) in the next section, all of which will be disproved in the end.

B. Mechanisms inconsistent with experiment

1. Reaction of kinetic methyl radical with hydrogen molecule

One may conceive that the kinetic methyl radicals $CH_3^{\#}$ in reaction (I) undergo the collision-induced reaction (IV),

$$CH_3^{\#} + H_2 \rightarrow CH_4 + H.$$
 (IV)

However, the failure of the appearance of methane in traces (a)-(c) in Fig. 1 means that 253.7 nm light cannot yield methane by this mechanism, the reason for which is accounted for as follows.

The kinetic (translational) energy of methyl radical produced by reaction (I) is estimated to be crudely 15 000 cm⁻¹ for the case of 253.7 nm light.²³ Since the activation energy of the thermal reaction between methyl radical and hydrogen molecule is known to be about 3700 cm⁻¹,²⁴ which is by far smaller than the above kinetic energy of the methyl radical, the collision-induced reaction (IV) is energetically allowed. Therefore, the failure of the formation of methane at 253.7 nm indicates that the conversion from the translational en-

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ergy of $CH_3^{\#}$ to the internal energy for the large-amplitude motion to accomplish reaction (IV) is inefficient. The translational energy of the methyl radical seems, in actuality, to be transferred to the phonon of solid hydrogen. The presumed rapid dissipation of the excess energy to phonon is probably due to the distinctly high thermal conductivity of solid *p*-H₂.³

Similarly to the case of the irradiation with 253.7 nm light, the collisional reaction (IV) does not occur for 184.9 nm light either: reaction (IV) would take place in competition with the deactivation of $CH_3^{\#}$ [the second step of reaction (I)]. If we assume that reaction (IV) is the major process to yield methane, the concentrations of methyl radical and methane should obey Eqs. (7) and (8), where α is the efficiency of the deactivation of the kinetic methyl radical,

$$\frac{d[\mathrm{CH}_3]}{dt} = \alpha k_1 [\mathrm{CH}_3 \mathrm{I}],\tag{7}$$

$$\frac{d[\mathrm{CH}_4]}{dt} = (1-\alpha)k_1[\mathrm{CH}_3\mathrm{I}].$$
(8)

Therefore, the temporal dependence of the absorption intensities of methyl radical and methane should be given by Eqs. (9) and (10), respectively,

$$I(CH_3) = I_2 \alpha (1 - e^{-k_1 t}), \tag{9}$$

$$I(CH_4) = I_3(1 - \alpha)(1 - e^{-k_1 t}).$$
(10)

However, Fig. 3 shows that methane behaves differently from the above prediction. Thus, although the kinetic energy imparted to the methyl radical upon the irradiation with 184.9 nm light is even higher than in the case of the irradiation with 253.7 nm light, reaction (IV) does not account for the experimental result. The excess kinetic energy in both cases of 253.7 and 184.9 nm light is regarded as to be dissipated to the matrix in vein.

2. Direct production of CH₂ from CH₃I upon UV irradiation

In the literature it is suggested that methyl iodide excited to the *C* state,¹⁸ which is accessible by the 184.9 nm light, may decompose as in reaction (V),²⁵

$$CH_3I + h\nu(184.9 \text{ nm}) \rightarrow CH_2(\tilde{a}^{-1}A_1) + HI.$$
 (V)

If reaction (V) were important in the present work, the singlet methylene produced by reaction (V) could give methane by reaction (III). However, it is difficult to assume that reaction (V), which is a minor process in the gas phase photolysis,²⁵ becomes major in the p-H₂ matrix in the present work. If the direct dissociation of the iodide into the singlet methylene is the major process to form methane, it is easily shown that the time dependence of the intensity of methane should be of the same form as that in Eq. (10), which is not in accord with the temporal profile in Fig. 3. Moreover, there was detected no significant absorption attributable to HI to be produced by reaction (V). Therefore, we conclude that reaction (V) should not be the main reaction in solid p-H₂.



FIG. 4. Temporal behavior of the integrated intensities of methyl radical and methane under dark at 4.5 K. The symbols of the plot represent the intensities of methyl radical at 3169.8–3172.2 (ν_3) (Δ) and at 1401.4–1403.0 (ν_4) (\blacktriangle), and the intensities of methane at 3024.2–3027.0 (ν_3) (\diamond) and at 1304.4–1308.7 cm⁻¹ (ν_4) (\blacklozenge). The scale of the ordinate is in arbitrary common units.

3. Hydrogen abstraction from H_2 by electronically excited CH_3

The abstraction of a hydrogen atom from a hydrogen molecule by the excited radical in the \tilde{B} state is also conceivable for the production of methane as in reaction (VI),

$$CH_3^*(B^2A_1') + H_2 \rightarrow CH_4 + H.$$
(VI)

However, the possibility of reaction (VI) can be ruled out by a parallel study of the photolysis of a $CD_3I/p-H_2$ system: In this system, if the reaction corresponding to reaction (VI) took place, the formation of CD_3H should be expected, while if reactions corresponding to reactions (II) and (III) are important in the $CD_3I/p-H_2$ system, the formation of CD_2H_2 should be dominant. As a result of (unfiltered) UV irradiation of a $CD_3I/p-H_2$ system, absorption lines are found at 2979 and 3017 cm⁻¹ which are definitely attributable to the asymmetrical stretching mode (v_3) of CD_2H_2 ,²⁶ but no absorption due to CD_3H appeared in the region of 2980–3005 with a maximum at 2995 cm⁻¹.¹⁰ Thus, we conclude that in the photolyzed $CD_3I/p-H_2$ system, reactions corresponding to reactions (I)–(III) take place but the reaction corresponding to reaction (VI) does not.

At this moment we should like to substantiate the statement in Sec. III that the reaction of methyl radical in the electronic ground state does not react with hydrogen molecules: Fig. 4 shows the integrated intensities of the degenerate C-H stretching (ν_3) and bending (ν_4) vibrations of methyl radical and methane recorded intermittently for the sample kept in the dark at the same temperature of 4.5 K as the temperature for recording the data in Fig. 3. The ordinate of Fig. 4 is in arbitrary units but is common to all the four absorption bands. It is seen from Fig. 4 that the change of the absorption intensities with the standing time is very little, if any, and we consider that reaction (VII) below for the methyl radical in the electronic ground state does not proceed appreciably under the present experimental conditions,

$$CH_3(\tilde{X}^2A_2'') + H_2 \rightarrow CH_4 + H.$$
(VII)

In connection with reaction (VII), we should like to digress a little further and to draw attention to our separate paper dealing with the *dark* reactions of CD_3 with $p-H_2$ and of CH₃ with p-H₂ molecules at about 5 K.¹⁰ To our surprise, CD₃ in the dark does react definitely with H₂ to produce CD₃H absorbing at 2980-3005 with a maximum at 2995 cm^{-1} , which is diametrically different from CH₃ in reaction (VII). This seemingly puzzling result, however, has been consistently elucidated¹⁰ and it does not conflict with the present work. A brief elucidation for the difference of the dark reactions of CH₃ and CD₃ will be reproduced below. The dark reaction (VIII) in the photolyzed $CD_3I/p-H_2$ is found to be slightly exothermic, whereas the dark reaction (VII) in the $CH_3I/p-H_2$ system is barely endothermic when the zero-point vibrational energies of the reactants and the products are taken into account,¹⁰

$$CD_3+H_2 \rightarrow CD_3H+H,$$
 (VIII)

This subtle difference between the two systems accounts consistently for the observed result. At about 5 K the tunneling chemical reaction in reaction (VIII) continues to proceed whereas reaction (VII) does not appreciably.

4. Reaction of triplet CH₂ with hydrogen molecules

If the nascent methylene produced by reaction (II) were trapped metastably in the p-H₂ matrix before reaction (III) completes, the singlet methylene would relax to its ground triplet state as in reaction (IX),

$$\operatorname{CH}_{2}(\tilde{a}^{-1}A_{1}) \to \operatorname{CH}_{2}(\tilde{X}^{-3}A_{1}).$$
(IX)

The triplet methylene thus produced might also react with a hydrogen molecule. In this case, however, the conservation of the electron spin quantum number demands that the abstraction in reaction (X) should be the major process but that no methane should be produced,

$$CH_2(X^{3}A_1) + H_2 \rightarrow CH_3 + H.$$
(X)

Thus, the singlet methylene in reaction (II) is considered to react with hydrogen molecules to form methane prior to its relaxation to the ground state triplet methylene. Furthermore, if part of the singlet methylene failed to complete reaction (III), it would relax to the ground state triplet methylene, which should exhibit the well-known absorption of the triplet methylene at 963.10 cm⁻¹ reported for the gas phase.^{27–31} We did not observe such a transition at all.

5. Commitment of migratory H atoms

The stability of the absorption of the polyatomic photoproducts CH_3 and CH_4 as illustrated in Fig. 4 means that they are immobile in solid at $p-H_2$ 4.5 K. However, the hydrogen atom produced by reaction (II) may migrate in the bulk. If it encounters methyl radical, methane would be formed. However, the stability of the radical mentioned above implies that such a process cannot be dominant.

By ruling out the possibilities (1)-(5) above, the credence of the mechanism of reactions (I)-(III) is reinforced.

Although the present work is concerned with photochemistry in solid p-H₂ at cryogenetic temperatures, the work contributes, hopefully, to the understanding of the photochemistry of methyl radical in hydrogenous systems in the gas phase as well.

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