

## LASER PYROLYSIS OF CH<sub>3</sub>Br

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Laser pyrolysis of CH<sub>3</sub>Br by a strong laser irradiation was studied in this work. Besides a fine needle of solid carbon was deposited at the surface on the substrate, HBr and CH<sub>4</sub> were found as gaseous products with a ratio of 2:1. Small amount of C<sub>2</sub>H<sub>2</sub> was also detected. The variation in the pressures of CH<sub>3</sub>Br, HBr and CH<sub>4</sub> were measured by Raman spectroscopy. It indicated that the decomposition of CH<sub>3</sub>Br was first order with respect to CH<sub>3</sub>Br. The reaction mechanism of the laser pyrolysis was suggested as follows: After gaining enough energy at the hot spot, CH<sub>3</sub>Br was pyrolyzed to produce HBr and CH<sub>2</sub> which then reacted with CH<sub>3</sub>Br to form CH<sub>4</sub> and solid carbon.

KEY WORDS: Laser pyrolysis, CH<sub>3</sub>Br.

### INTRODUCTION

It is well known that laser light can be focused into a small spot with a diameter in an order of 10  $\mu\text{m}$ . The enormous intensity of light can induce a high temperature such as 1000 or even 2000 K on a surface. At that hot spot, chemical vapor can be pyrolyzed into fragments and solid may deposit on surface. This is laser induced pyrolysis or laser pyrolysis.

The laser induced chemical vapor deposition was studied by Barananskas, Mammana, Klinger and Greene in 1980.<sup>1</sup> Polycrystalline Si was formed. Laser pyrolysis of C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub> has been studied by Leyendecker, Bauerle, Geittner and Lydtin by the radiation with a wavelength of 488 nm for an argon ion laser.<sup>2-4</sup> The deposited carbon was polycrystalline in the forms of layers and cylindrical rods. The deposition of Si from SiH<sub>4</sub> was studied by Bauerle, Irsigler, Leyendecker, Noll and Wanger in 1982.<sup>5</sup> Fine needle and very narrow thin film of polycrystalline Si deposited. The deposition of Ni spots by laser pyrolysis was also reported.<sup>6,7</sup> Hwang and Chang obtained polycrystalline Si in the form of fine needle or cylindrical rod from the vapor of Si(CH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> by the 488 nm laser irradiation from an argon ion laser.<sup>8,9</sup> Various amount of C codeposited with Si.<sup>10</sup> Many works on this laser pyrolysis had been carried out since 1980 and had been summarized by Bauerle.<sup>11</sup> Recently, laser pyrolysis of polyphenylene- and polyamidocarboranes<sup>12</sup> and trichlorosilane have been reported.<sup>13</sup>

Laser pyrolysis of CH<sub>3</sub>Br was carried out in a reaction cell with different pressures in this work. A hot spot was induced by the strong irradiation with a wavelength of 488 nm from an argon ion laser. Fine needle and thin film of carbon deposited on the surface of a glass substrate. The chemistry involved in the laser pyrolysis should

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be important and interesting. It was studied in the system of  $\text{Si}(\text{CH}_3)_2\text{Cl}_2$ .<sup>10</sup> In this work,  $\text{CH}_4$  and  $\text{HBr}$  were found to be the major gaseous products with little  $\text{C}_2\text{H}_2$ . The reaction rate constants were obtained from the variation in the pressures of  $\text{CH}_3\text{Br}$ ,  $\text{HBr}$  and  $\text{CH}_4$  which were measured by Raman spectroscopy during the laser pyrolysis. A reaction mechanism of the laser pyrolysis of  $\text{CH}_3\text{Br}$  at the hot spot was suggested. After diffused and adsorbed to the hot spot,  $\text{CH}_3\text{Br}$  gained enough energy and decomposed to  $\text{HBr}$  and  $\text{CH}_2$ .  $\text{CH}_2$  at the surface reacted with  $\text{CH}_3\text{Br}$  to form  $\text{CH}_4$  and solid carbon.

## EXPERIMENTAL

The reaction cell was made from a Pyrex tubing with a diameter of 2.5 cm and a length of 7 cm. It had two sections: one for the reaction and the other for the spectrum measurement. Several chips of thin glass plate were placed in the reaction section as the substrate for the laser pyrolysis to occur. Raman spectra were measured in the spectrum measurement section. Two sections were separated by a small diameter tubing in order to keep the mists formed during the pyrolysis in the reaction section from diffusing into the spectrum measurement section. Reagent grade of  $\text{CH}_3\text{Br}$  from Tokyo Kasei was used without further purification.

The reaction cell was filled with  $\text{CH}_3\text{Br}$  to a proper pressure and sealed off. High power laser radiation from a Coherent Innova 100-15 argon ion laser was focused at the surface of the substrate in the reaction section. If the focus of the laser radiation was sharp, a hot spot could be induced on the surface of the substrate. Intense emission in orange colour from the hot spot was a good indication for the laser pyrolysis. Black solid deposited at the focal point on the surface of the substrate.

When the laser beam was focused at the center of the cell, no laser pyrolysis could be induced. Therefore, the Raman spectrum were measured with the laser beam focused at the center of the cell in the spectrum measurement section. The scattered light was collected and focused into a Spex model 1403 double spectrometer. After dispersion, the scattered light was detected by a cooled RCA C31034A photomultiplier, processed through an SSR photon counting system and recorded. The pressure of each component was obtained by the intensity of the corresponding Raman band through a calibration factor.

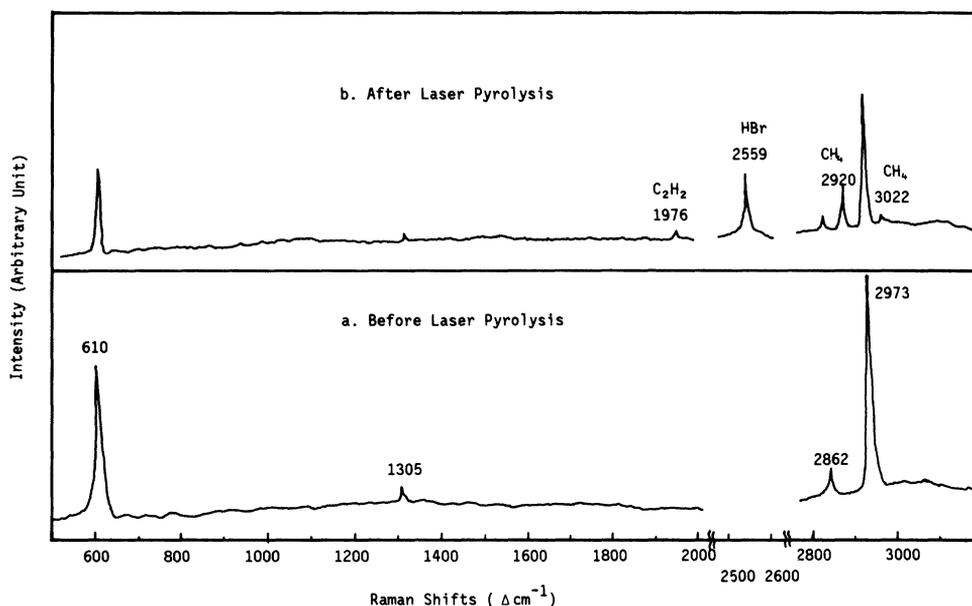
## RESULTS AND DISCUSSION

When the high power laser beam was focused sharply at the surface of a substrate in the reaction section, bright emission of light in orange colour could be observed. If this emitted light was focused into a spectrometer, a continuous spectrum of black body radiation could be obtained.<sup>8</sup> A black solid began to deposit and grew along the direction of the laser beam as a fine needle. The diameter of the black solid was less than 0.5 mm. It depended on the laser power: the higher the laser power was, the larger was the diameter. The black solid was soft and fragile. Its Raman spectrum

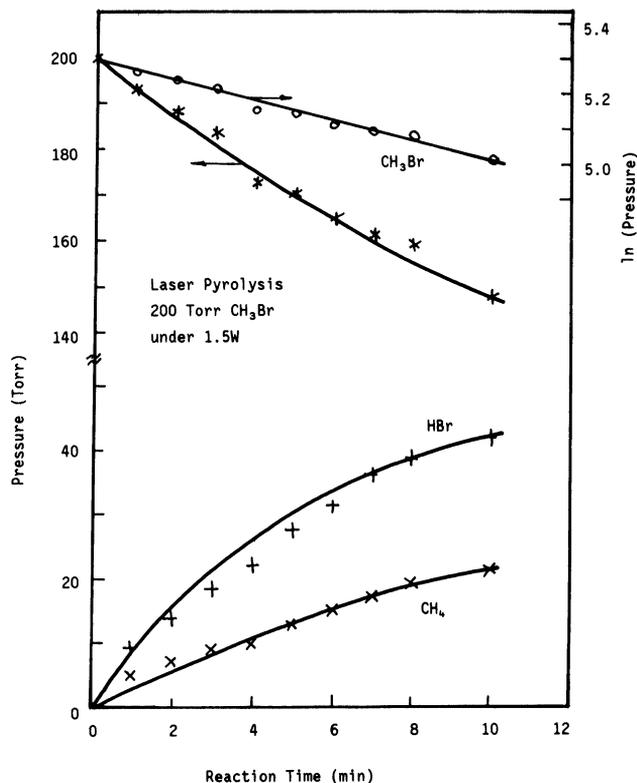
was tried to measured but only a weak and broad band around 1550 cm<sup>-1</sup> was found in the range from 1000 to 2000 cm<sup>-1</sup>. It might be aggregate of carbon. Accompanied with the deposition, mists formed, circulated in the reaction section and deposited on the wall as a byproduct during the pyrolysis. In a 10 min pyrolysis, the amount of the mists produced was little. No further study on them was carried out. When the laser beam was focused at the center of the tube, no chemical reaction occurred. This was an evidence for the chemical reaction occurred at the hot spot.

(a) *The Measurement of Partial Pressure*

If the laser beam was focused in the center of the spectrum measurement section, no laser pyrolysis would happen. In this case, Raman spectrum of the mixed gases in the cell could be measured. Figure 1 shows the Raman spectra taken before and after the laser pyrolysis in the ranges from 500 to 2000, 2450 to 2650 and 2800 to 3200 cm<sup>-1</sup> with a band pass of the spectrometer of 16 cm<sup>-1</sup>. The excitation power was 1 W of the 488 nm laser radiation. The pressure of CH<sub>3</sub>Br in the cell was 200 torr. Figure 1(a) is the spectrum taken before laser pyrolysis. Strong Raman bands appeared at 610, 1305, 2862 and 2973 cm<sup>-1</sup>. They belong to CH<sub>3</sub>Br as reported.<sup>14</sup> Figure 1(b) shows the Raman bands observed after 15 min of laser pyrolysis by 2 W of 488 nm laser irradiation in a test run. Besides the Raman bands of CH<sub>3</sub>Br, bands at 2559, 2920, 3028 and 1976 cm<sup>-1</sup> were recorded. They indicated the presence of HBr



**Figure 1** The Raman spectra (a) before and (b) after the laser pyrolysis of 200 torr of CH<sub>3</sub>Br with 2 W of 488 nm laser radiation for 30 min in a test run.



**Figure 2** The variation in pressures of CH<sub>3</sub>Br, HBr and CH<sub>4</sub> during the laser pyrolysis of 200 torr of CH<sub>3</sub>Br by 1.5 W of 488 nm laser radiation for 10 min. The pressure of CH<sub>3</sub>Br was plotted in both linear and logarithm scales.

(2559 cm<sup>-1</sup>), CH<sub>4</sub> (2920 and 3028 cm<sup>-1</sup>) and C<sub>2</sub>H<sub>2</sub> (1976 cm<sup>-1</sup>). The amount of C<sub>2</sub>H<sub>2</sub> was very little or even not measurable in some experiments. In this work, the amounts of HBr and CH<sub>4</sub> were measured with the reactant CH<sub>3</sub>Br.

The laser pyrolysis of CH<sub>3</sub>Br for 10 minutes in a cell filled with 200 torr of CH<sub>3</sub>Br by a laser radiation of 1.5 W was given as an example to illustrate the variation in the pressures of CH<sub>3</sub>Br, HBr and CH<sub>4</sub>. Raman spectrum was taken after every minute of laser pyrolysis. Before the measurement of the spectrum, it had to wait for about 20 minutes to let the mists condense in order to avoid the Mie scattering from mists. The intensities of the three bands at 2973, 2559 and 2920 cm<sup>-1</sup> were measured. After calibration, the pressures of CH<sub>3</sub>Br, CH<sub>4</sub> and HBr were obtained and plotted in Figure 2. The decrease in the pressure of CH<sub>3</sub>Br was not linear, however its logarithm was. This indicated that the decomposition of CH<sub>3</sub>Br was first order with respect to CH<sub>3</sub>Br. The increases in the pressures of CH<sub>4</sub> and HBr were not linear either. They increased fast first and then slowed down. The pressure of CH<sub>4</sub> was only about half of that of HBr. This indicates that one CH<sub>4</sub> was produced with two HBr.

*(b) Reaction Mechanism*

Meissner and Schumacher had studied the thermal pyrolysis of CH<sub>3</sub>Br in a closed system.<sup>15</sup> Around 500°C, gaseous HBr and CH<sub>4</sub> were obtained, with a ratio of 2:1 and solid carbon deposited. Following reaction mechanism was suggested<sup>15</sup>

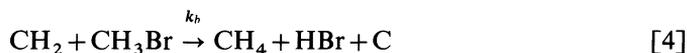


Their results was similar to ours.

It was also reported that CH<sub>3</sub> and Br were produced first by breaking the C–Br bond in pyrolysis.<sup>16</sup> C–Br band is weak in CH<sub>3</sub>Br. However, the activation energy and the enthalpy change for the product of CH<sub>3</sub> and Br were much higher than that of CH<sub>2</sub> and HBr. Furthermore, Br is very active and it may subtract a H immediately from CH<sub>3</sub> to form CH<sub>2</sub> and HBr. Definitely, Br should be produced first and might involve in a H subtract reaction. However, the time scale for the existence of Br should be extremely short. In this work, the time scale was very long, hence the reactions which Br involved in were not included in the reaction mechanism. Therefore, we suggested that the reaction mechanism should be initiated by the following reaction as Meissner and Schumacher suggested<sup>15</sup>



Because CH<sub>2</sub> radical is very active, the probability for two CH<sub>2</sub> to react with each other should be scarce. The reaction between CH<sub>2</sub> and CH<sub>3</sub>Br should be dominant. We suggested that following reaction should be



where  $k_a$  and  $k_b$  were the reaction rate constants for Reactions [3] and [4], respectively. Following two reactions between two CH<sub>2</sub> should be less probable or even absent because the lifetime of CH<sub>2</sub> was short and CH<sub>3</sub>Br was dominant at the hot spot.



The overall reaction could be represented by following equation

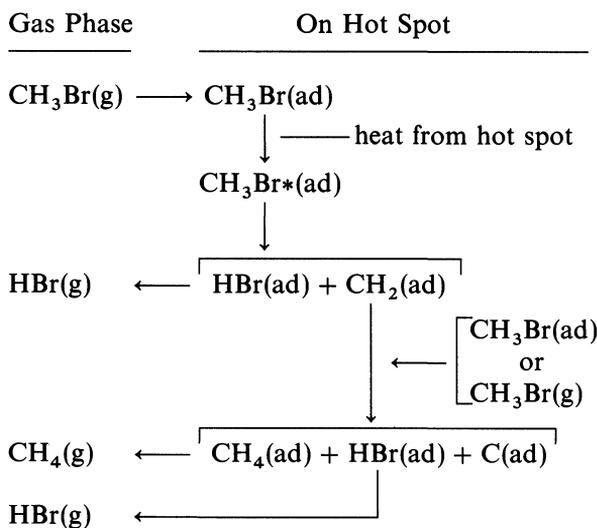


The laser pyrolysis might process as follows:

1. The intense laser irradiation induced a hot spot at the surface of the substrate. The temperature could be very high.
2. CH<sub>3</sub>Br molecule diffused to the hot spot and was adsorbed on it.
3. Adsorbed CH<sub>3</sub>Br gained enough energy at the hot spot and decomposed to HBr and CH<sub>2</sub>.
4. CH<sub>2</sub> could react with CH<sub>3</sub>Br to form CH<sub>4</sub>, HBr and C.

5.  $\text{CH}_2$  might also react with each other on the hot spot and form  $\text{CH}_4$  and C or  $\text{C}_2\text{H}_2$  and  $\text{H}_2$ . Both reactions might be negligible.
6. HBr and  $\text{CH}_4$  desorbed from the hot spot.
7. C deposited on the hot spot. It might be amorphous.

The laser pyrolysis could be summarized as Scheme I.



Scheme I

### (c) Temperature Estimation

The temperature at the hot spot should be important. However, it was not measured in this work. It could be estimated by a formula given by Baranauskas, Mammana, Klinger and Greene as follows<sup>1</sup>

$$T = 0.96Qr/K \quad (1)$$

where  $Q$  is the intensity density of the radiation ( $\text{W}/\text{mm}^2$ ),  $r$  is the radius of the illuminated area (mm) and  $K$  is thermal conductivity of the substrate ( $\text{W}/\text{mm}^\circ\text{C}$ ). In this work, the radius of the laser beam at the focusing point was about  $40\ \mu\text{m}$ . The intensity density was about  $2500\ \text{W}/\text{mm}^2$  for a laser beam with a power of 2 W.  $K$  should be measured directly from the sample. In this work, no attempt was made to measure it. For graphite, it was 95 or 0.104 for a hard solid or powder, respectively.<sup>17</sup> For our sample, it was an aggregate of powders. 0.1 might be a good trial. The temperature at the hot spot could be calculated to be  $960^\circ\text{C}$ . Of course, the error might be large due to the uncertainty in thermal conductivity. In our case, the calculated temperature was in the range from  $480$  to  $2160^\circ\text{C}$  for the laser power from 1 to 4.5 W, respectively. This estimation was reasonable at low laser power. For high laser power, the estimated temperature seemed too high.

The standard enthalpy change for Reaction [3] was estimated to be 390 kJ based on the standard enthalpies of formation for CH<sub>3</sub>Br, CH<sub>2</sub> and HBr which are  $-35.1$ ,  $391.7$  and  $-36.4$  kJ/mol, respectively.<sup>18</sup> This amount of energy could be obtained from the hot spot. The standard enthalpy change for reaction [4] was  $-468$  kJ based on the standard enthalpy of formation of CH<sub>4</sub>  $-74.7$  kJ/mol.<sup>18</sup> For Reaction [5] the standard enthalpy change was about  $-858$  kJ. Both Reactions [4] and [5] were exothermic.

(d) *Reaction Rate Law*

We used  $P$  for the pressure of the gaseous species in our system although the reactions occurred on the hot spot. Here, only Reactions [3] and [4] were considered. The rate equations for the decomposition reaction of CH<sub>3</sub>Br and the formation rate equations of HBr and CH<sub>4</sub> at the hot spot during the laser pyrolysis were as follows:

$$-\frac{dP(\text{CH}_3\text{Br})}{dt} = k_a P(\text{CH}_3\text{Br}) + k_b P(\text{CH}_2)P(\text{CH}_3\text{Br}) \quad (2)$$

$$\frac{dP(\text{HBr})}{dt} = k_a P(\text{CH}_3\text{Br}) + k_b P(\text{CH}_2)P(\text{CH}_2\text{Br}) \quad (3)$$

$$\frac{dP(\text{CH}_4)}{dt} = k_b P(\text{CH}_2)P(\text{CH}_3\text{Br}) \quad (4)$$

The amount of CH<sub>2</sub> could be obtained from steady state hypothesis. It was

$$\frac{dP(\text{CH}_2)}{dt} = -k_b P(\text{CH}_2)P(\text{CH}_3\text{Br}) + k_a P(\text{CH}_3\text{Br}) = 0 \quad (5)$$

Hence

$$P(\text{CH}_2) = \frac{k_a}{k_b} P(\text{CH}_3\text{Br}) \quad (6)$$

By substituting  $P(\text{CH}_2)$  into Eqs. (2), (3) and (4) and after integrating, we could obtain following rate equations for CH<sub>3</sub>Br, HBr and CH<sub>4</sub>

$$\ln P(\text{CH}_3\text{Br}) = \ln P(\text{CH}_3\text{Br})_0 - 2k_a t \quad (7)$$

$$P(\text{HBr}) = P(\text{CH}_3\text{Br})_0 [1 - \exp(-2k_a t)] \quad (8)$$

$$P(\text{CH}_4) = P(\text{CH}_3\text{Br})_0 [1 - \exp(-k_a t)] \quad (9)$$

where  $P(\text{CH}_3\text{Br})_0$  was the initial pressure of CH<sub>3</sub>Br. All the rate equations were expressed in terms of  $k_a$ .  $k_b$  could not be obtained unfortunately, because steady state hypothesis related  $k_a$  and  $k_b$ .

(e) *Measured Reaction Rate Constants*

In this work, the pressures of CH<sub>3</sub>Br, HBr and CH<sub>4</sub> were measured during the laser

**Table I** The reaction rate constants  $k$ ,  $k_1$  and  $k_2$  obtained from the variation in the pressures of  $\text{CH}_3\text{Br}$ ,  $\text{HBr}$  and  $\text{CH}_4$  in the laser pyrolysis of  $\text{CH}_3\text{Br}$  at a pressure of 100, 200 and 300 torr by various laser powers at a wavelength of 488 nm.

		Laser powers ( $W$ )							
		1.0	1.5	2.0	2.5	3.0	3.5	4.0	4
		(a) 100 torr $\text{CH}_3\text{Br}$							
$k^*$	none**	none	none	none	0.0041	0.0058	0.0081	0.0094	
$k_1$	none	none	none	none	0.0041	0.0056	0.0080	0.0093	
$k_2$	none	none	none	none	0.0020	0.0029	0.0038	0.0047	
		(b) 200 torr $\text{CH}_3\text{Br}$							
$k$	none	0.0030	0.0044	0.0066	0.0074	0.0098	0.0116	0.0134	
$k_1$	none	0.0030	0.0043	0.0066	0.0074	0.0098	0.0115	0.0131	
$k_2$	none	0.0014	0.0022	0.0033	0.0037	0.0047	0.0055	0.0067	
		(c) 300 torr $\text{CH}_3\text{Br}$							
$k$	0.0020	0.0038	0.0056	0.0075					
$k_1$	0.0017	0.0038	0.0054	0.0075					
$k_2$	0.0009	0.0017	0.0025	0.0037					

\*  $k$ ,  $k_1$  and  $k_2$  are in units of  $\text{min}^{-1}$ .

\*\* none indicates no laser pyrolysis observed.

pyrolysis, therefore these data were used to fit in the following three equations by a least square fitting program.

$$\ln P(\text{CH}_3\text{Br}) = \ln P(\text{CH}_3\text{Br})_0 - kt \quad (10)$$

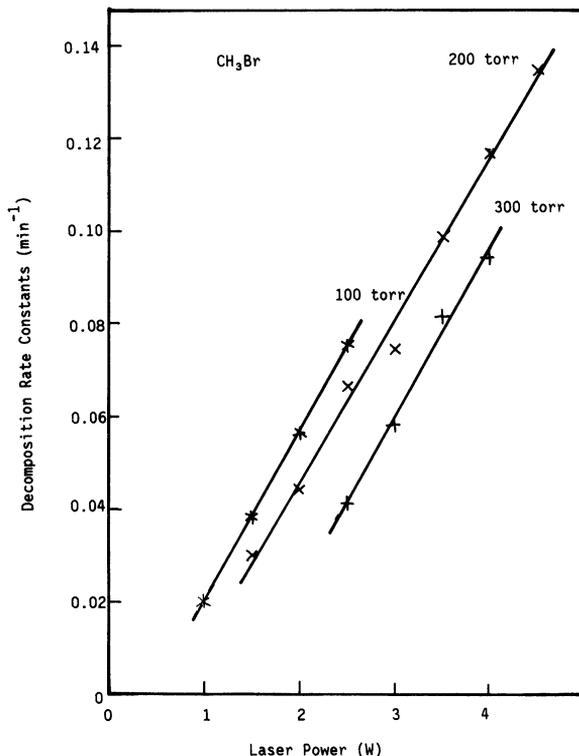
$$P(\text{HBr}) = P(\text{CH}_3\text{Br})_0 [1 - \exp(-k_1 t)] \quad (11)$$

$$P(\text{CH}_3) = P(\text{CH}_3\text{Br})_0 [1 - \exp(-k_2 t)] \quad (12)$$

Here, rate constants  $k$ ,  $k_1$  and  $k_2$  were used for the experimental values.  $k$  and  $k_1$  should be equal to  $2k_a$  and  $k_2$  to  $k_a$  if the reaction mechanism (Reactions [3] and [4]) were strictly followed.

In this work, laser pyrolysis of  $\text{CH}_3\text{Br}$  at 100, 200 and 300 torr were studied. The power of laser radiation at a wavelength of 488 nm was from 1 to 4.5 W. The results of the reaction rate constants of  $k$ ,  $k_1$  and  $k_2$  are summarized in Table I.  $k$  was found in the range of 0.02 to  $0.134 \text{ min}^{-1}$ .  $k_1$  was found to be a little less than the values of the corresponding  $k$ . They should be the same because each  $\text{CH}_3\text{Br}$  should produce one  $\text{HBr}$  in this laser pyrolysis. The differences of  $k_1$  from  $k$  were within 4% except the case for 300 torr of  $\text{CH}_3\text{Br}$  under 1.0 W of laser radiation.  $k_2$  was found in the range from 0.009 to  $0.067 \text{ min}^{-1}$ . They were also a little less than the half of the values of  $k$ . The differences of  $k_2$  from  $k/2$  were large but within 7% except the cases for 300 torr of  $\text{CH}_3\text{Br}$  under 1.0, 1.5 and 2.0 W of laser radiation. This discrepancy indicated that some other paths, e.g., to form  $\text{C}_2\text{H}_2$ , might occur but were not important.

Figures 3, 4 and 5 show the plots of the rate constants  $k$ ,  $k_1$  and  $k_2$  based on the data listed in Table I for various laser powers. These figures show that the plots of



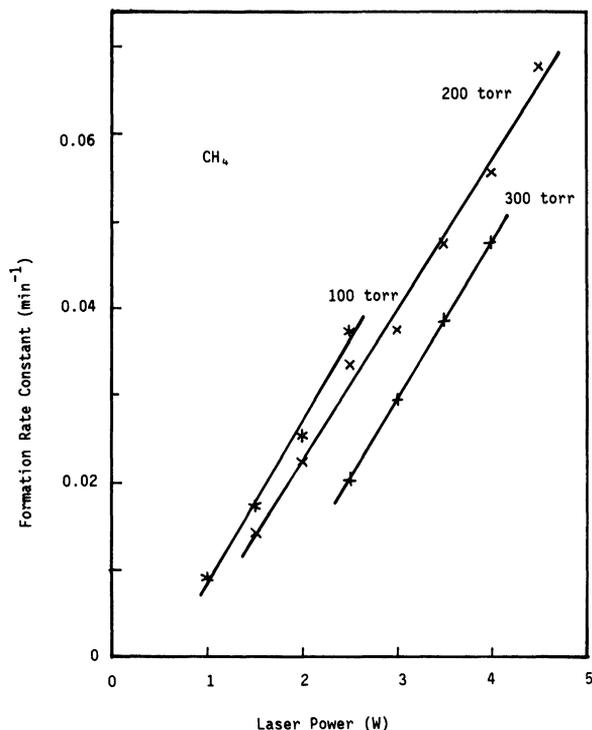
**Figure 3** The rate constants  $k$  obtained from CH<sub>3</sub>Br in the laser pyrolysis of 100, 200 and 300 torr of CH<sub>3</sub>Br by various power of laser irradiation.

the rate constants for a fixed pressure of CH<sub>3</sub>Br laid on a straight line and the lines for different pressures of CH<sub>3</sub>Br were parallel to each other. It also indicated that the rate constants would be larger for higher pressure of CH<sub>3</sub>Br and also for higher laser power.

Finally, if the power of laser radiation was too low, the emission from the hot spot was very weak. It indicated that the temperature at the hot spot could not reach high enough for the laser pyrolysis to proceed. On the other hand, if the pressure of CH<sub>3</sub>Br was too low, the amount of CH<sub>3</sub>Br diffused to the hot spot was limited and the laser pyrolysis became difficult to continue. In both cases, no black solid could deposit. These two factors were interrelated. No laser pyrolysis could be observed below 2.5, 1.5 and 1.0 W for the pressures of CH<sub>3</sub>Br at 100, 200 and 300 torr, respectively, as Table I shows.

#### (f) Laser Pyrolysis and Laser Photodissociation

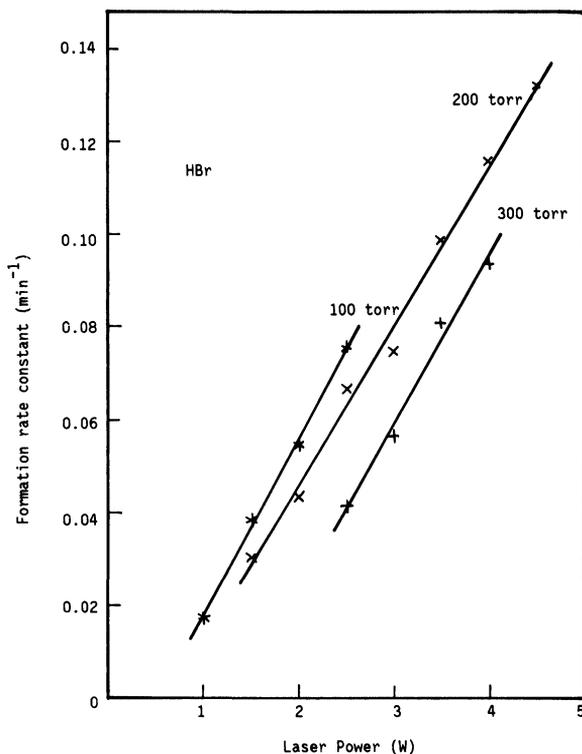
Laser induced pyrolysis and laser photodissociation are two different phenomena induced by intense laser radiation. In laser pyrolysis, a spot of high temperature is



**Figure 4** The rate constants  $k_1$  obtained from HBr in the laser pyrolysis of 100, 200 and 300 torr of  $\text{CH}_3\text{Br}$  by various power of laser irradiation.

induced by the high power of laser irradiation at the surface of a substrate and causes the decomposition of chemical vapor. Solid may deposit at the hot spot in various features. The hot spot is induced on the surface, therefore the solid formed should be a narrow film or a needle like solid. In this method, the power of the laser radiation is important. Therefore, argon ion laser is always used. In laser photodissociation, on the other hand, the vapor decomposes after the absorption of one or several photons. Because the photon has to be absorbed, the wavelength of the radiation is essential. It is always in UV or IR range. For UV radiation, the molecule is excited to an excited electronic state and then dissociates. For IR radiation, it should be a multiphoton process. The molecule is excited through vibrational rotational energy levels of the ground electronic state beyond the dissociation limit. Dissociation in the gas phase results formation of solid which may deposit on a large area on the substrate. both processes are important in industrial processes for CVD.

In this work, the laser beam should be focused sharply at the surface on the substrate. If the focusing was not sharp, the process could not happen. The process also depended on the laser power and not on the wavelength of the radiation.



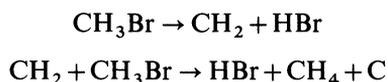
**Figure 5** The rate constants  $k_2$  obtained from CH<sub>4</sub> in the laser pyrolysis of 100, 200 and 300 torr of CH<sub>3</sub>Br by various power of laser irradiation.

Therefore, this was a laser pyrolysis process. One more evidence was the solid which was formed only on the hot spot not over a large area on the substrate.

## CONCLUSION

In this study, CH<sub>3</sub>Br was pyrolyzed by a strong laser irradiation with a wavelength of 488 nm. When the laser beam was focused sharply at the surface of the substrate, a black solid of carbon could deposit in the form of a needle with a diameter of less than 0.5 mm. The solid was soft and fragile. This is laser induced pyrolysis or laser pyrolysis because the hot spot was induced by the high power laser irradiation.

The chemistry of this laser pyrolysis should be important. In this work, HBr and CH<sub>4</sub> were found to be the main products. A little amount of C<sub>2</sub>H<sub>2</sub> was also recorded sometimes. The reaction mechanism for the laser pyrolysis was suggested as follows



The total reaction was



The rate constants for the dissociation of  $\text{CH}_3\text{Br}$  were obtained from the pressure variation of  $\text{CH}_3\text{Br}$  to be  $0.02$  to  $0.134 \text{ min}^{-1}$  for  $100$  to  $300$  torr of  $\text{CH}_3\text{Br}$  under the laser radiation of  $1$  to  $4.5 \text{ W}$ .

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