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The role of a catalyst in the isotopically excited laser photochemistry

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Laser photochemistry of BCl_3/H_2 using catalysis was carried out experimentally. The $10.55 \mu\text{m}$ radiation from a high power (GW/cm^2) TEA CO_2 pulse laser was used to selectively excite the $^{11}\text{BCl}_3$ molecules. Using Ti catalyst the reaction products analyzed were $^{10}\text{B}^{11}\text{BH}_2\text{Cl}_4$, $^{11}\text{B}^{11}\text{BH}_2\text{Cl}_4$, and HCl , whereas those were $^{10}\text{B}^{10}\text{BCl}_4$, $^{11}\text{B}^{10}\text{BCl}_4$, and HCl when Pb metal powder was employed, i.e., $^{10}\text{B}^{10}\text{BH}_2\text{Cl}_4$ and $^{10}\text{B}^{10}\text{BCl}_4$ molecules were not generated in our experiment. Moreover, it was found that the $^{10}\text{BCl}_3$ concentration in the unreacted BCl_3 gas increased from 20% to 37% after 360 laser pulses, but the isotopic enrichment was not obtained for the reaction products. The mechanisms for the observed catalytic laser photochemistry are proposed.

I. INTRODUCTION

Thermal chemistry of BCl_3/H_2 in the presence of a catalyst was found^{1,2} to produce various compound mixtures such as B_2H_6 , $\text{B}_2\text{H}_5\text{Cl}$, BHCl_2 , etc. On the contrary, Rockwood and Hudson³ reported that laser photochemistry of BCl_3 and H_2 is characterized by a non-thermal reaction yielding exclusively pure BHCl_2 . Recently, a high efficiency laser photochemical isotopic enrichment of boron was achieved by Lin *et al.*⁴ using a mixture of $\text{BCl}_3/\text{H}_2/\text{Ti}$, where Ti metal powder functions as a catalyst. However, the exact mechanism for the effect of a catalyst in the laser photochemistry was not yet established.

In this paper we extended the study further using Ti (a strong hydrogen chemisorption metal) as well as Pb (a weak hydrogen chemisorption metal-physical adsorption) as catalysts. Moreover, it is known³ that the multiphoton dissociation of BCl_3 molecules depends strongly on the laser power density used; we thus chose to employ a focused CO_2 laser beam (GW/cm^2) in the present experiment instead of an unfocused laser beam (MW/cm^2) which was used in our earlier work.⁴ Emphasis is given on the detailed analysis of the catalytic laser photochemical products. The experimental implications are twofold: (1) The specific hydrogen chemisorption on the Ti metal surface permits us to generate for the first time a new class of halogenated diboranes $\text{B}_2\text{H}_2\text{Cl}_4$; (2) a catalyst can speed up the photochemical reaction rate and, at the same time, decrease the probability of energy transfer processes between isotopes. This allows us to perform the laser isotope separation of boron using a relatively high sample pressure which is very important for a large scale production of isotopes.

II. EXPERIMENTAL

BCl_3 and H_2 used were the Matheson gas products, and Ti and Pb metal powders were obtained from the British Drug House Ltd. and the Carlo Erba do Brasil, S. A., respectively. The chemicals were used without further purification because no other impurities were detected except that small quantities of HCl molecules

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were found to contaminate the BCl_3 sample. The experimental systems such as the specifications of sample cell and of vacuum line were essentially the same as described previously.⁴⁻⁸

Static mixtures of BCl_3 (13 mm Hg), H_2 (25 mm Hg), and ~ 1 g Ti (or Pb) were irradiated at room temperature using a CO_2 TEA pulse laser of Molelectron Corporation, model T250. The pulse laser was operated with a repetition rate of 3 Hz by a trigger generator. A SD 20 grating sine drive was used to isolate the $10.55 \mu\text{m}$ radiation [$P(16)$ line of the $00^0_1-10^0_0$ transition] of the CO_2 laser which was employed to selectively excite the ν_3 mode of $^{11}\text{BCl}_3$ molecules. The laser frequency was calibrated by a CO_2 spectrum analyzer of Optical Engineering Inc., model 16-A. The laser beam was focused into the center of the reaction cell using a GaAs lens ($f=5$ cm). To minimize the laser heating effect the focal spot was adjusted to "near" but not "on" the metal surface. The laser peak power at the focal point is $\sim \text{GW}/\text{cm}^2$.

The catalytic laser photochemical reaction products were then analyzed by a Finnigan model 1015C quadrupole mass spectrometer. A standard computer program was used to simulate the isotopic mass spectral pattern for the parent molecules as well as for the fragmented molecules. The spectral assignment was confirmed by the perfect agreement between the computed and the observed mass spectrum.

III. RESULTS

A. General observations

Pure BCl_3 ,^{9,10} mixtures of $\text{BCl}_3/\text{H}_2\text{S}^{11,12}$ and mixtures of BCl_3/H_2 ^{3,13,14} were shown to give chemiluminescence when the systems were subjected to an intense ir laser radiation. Evidently, the observed visible luminescences were found to originate from the excited molecules or radicals through a radiative deactivation process. In our experiment we noticed that the surface of the metal powder was shivering upon the laser pulse but no visible fluorescence was seen. In fact, we should have observed the chemiluminescence since the sample pressure and the laser power density we used were similar to those reported previously.⁹⁻¹⁴ Our negative observations in fluorescence might indicate that the cata-

lyst has indeed speeded up the laser photochemical reaction rate in which the excited molecules or radicals readily reacted to form the stable ground state compounds before they had a chance to deactivate and give emission.

B. Spectral assignments

Figure 1 shows the observed (top) and computed (bottom) mass spectra for the laser photochemistry of BCl_3 and H_2 using Ti (right) and Pb (left) as catalysts. The spectrum is normalized with respect to the largest product H^{35}Cl ($m/e = 36$). The spectral intensities for peaks after $m/e = 50$ are amplified by 20.

1. System $\text{BCl}_3/\text{H}_2/\text{Ti}$

Mass spectrum for the system $\text{BCl}_3/\text{H}_2/\text{Ti}$ consists peaks at $m/e = 2 = \text{H}_2$; $m/e = 35$ and $37 = {}^{35}\text{Cl}$ and ${}^{37}\text{Cl}$, respectively; $m/e = 36$ and $38 = \text{H}^{35}\text{Cl}$ and H^{37}Cl , respectively; $m/e = 94-98$ (group I), $m/e = 128-133$ (group II), and $m/e = 163-170$ (group III). Each group is made of an isotopically distributed spectral pattern. If one compares the spectral groups I, II, and III, one notices that the difference among them is $m/e = 35$, which corresponds to a difference in one chlorine atom. Clearly, if one can correctly assign the spectral peaks for group III, then the assignments for the groups I and II would become trivial. One recognizes that the mass spectrum of group III constitutes an isotopically distributed contour of both boron and chlorine isotopes. Masses $m/e = 163-170$ can be attributed to either B_2Cl_4 or $\text{B}_2\text{H}_2\text{Cl}_4$. If the B_2Cl_4 molecules are assigned, we should observe an intense peak at mass $m/e = 162$ which originates from the molecule ${}^{11}\text{B}_2{}^{35}\text{Cl}_4$. However, no spectral peak at $m/e = 162$ appeared, instead, we observed an intense

peak at $m/e = 164$, indicating that the $\text{B}_2\text{H}_2\text{Cl}_4$ molecule is the right assignment for the spectra of group III.

Two assignments are possible for the spectra of groups II and I: (1) One can assign them as the fragmentation of $\text{B}_2\text{H}_2\text{Cl}_4$, i. e., group II = $\text{B}_2\text{H}_2\text{Cl}_3$ and group I = $\text{B}_2\text{H}_2\text{Cl}_2$; (2) they can be assigned as independent reaction products. i. e., $\text{B}_2\text{H}_3\text{Cl}_3$ and $\text{B}_2\text{H}_4\text{Cl}_2$ correspond to group II and I, respectively. If the second assignment is forwarded, then we should see an intense mass spectral peak at mass $m/e = 130 = {}^{11}\text{B}_2\text{H}_3{}^{35}\text{Cl}_3$ for the group II and at mass $m/e = 96 = {}^{11}\text{B}_2\text{H}_4{}^{35}\text{Cl}_2$ for the group I. The fact that we observed intense peaks at mass $m/e = 129$ and $m/e = 94$ for group II and I, respectively, indicates that the mass spectra of groups II and I are the fragmentations of the molecules $\text{B}_2\text{H}_2\text{Cl}_4$. The appearance of the chlorine atom in the mass spectrum at masses $m/e = 35$ and 37 is a further support for our assignment.

2. System $\text{BCl}_3/\text{H}_2/\text{Pb}$

The left-hand side spectrum of Fig. 1 contains masses $m/e = 2, 35-38, 80-85$, and $115-120$. The $m/e = 2$ is clearly due to the H_2 molecules, and $m/e = 35$ and 37 can be assigned to the atoms ${}^{35}\text{Cl}$ and ${}^{37}\text{Cl}$, respectively. The $m/e = 36$ and 38 should correspond to the molecules H^{35}Cl and H^{37}Cl , respectively. The bunch of spectra at masses $m/e = 115-120$ are no doubt originated from the unreacted BCl_3 molecules. The spectral group at masses $m/e = 80-85$ can be attributed to either BCl_2 or BHCl_2 . If the molecule BHCl_2 is assigned, one should observe an intense peak at $m/e = 82$ which would correspond to ${}^{11}\text{BH}^{35}\text{Cl}_2$. However, an intense mass spectral peak is found to appear at mass $m/e = 81$ which is the ${}^{11}\text{B}^{35}\text{Cl}_2$ radical.

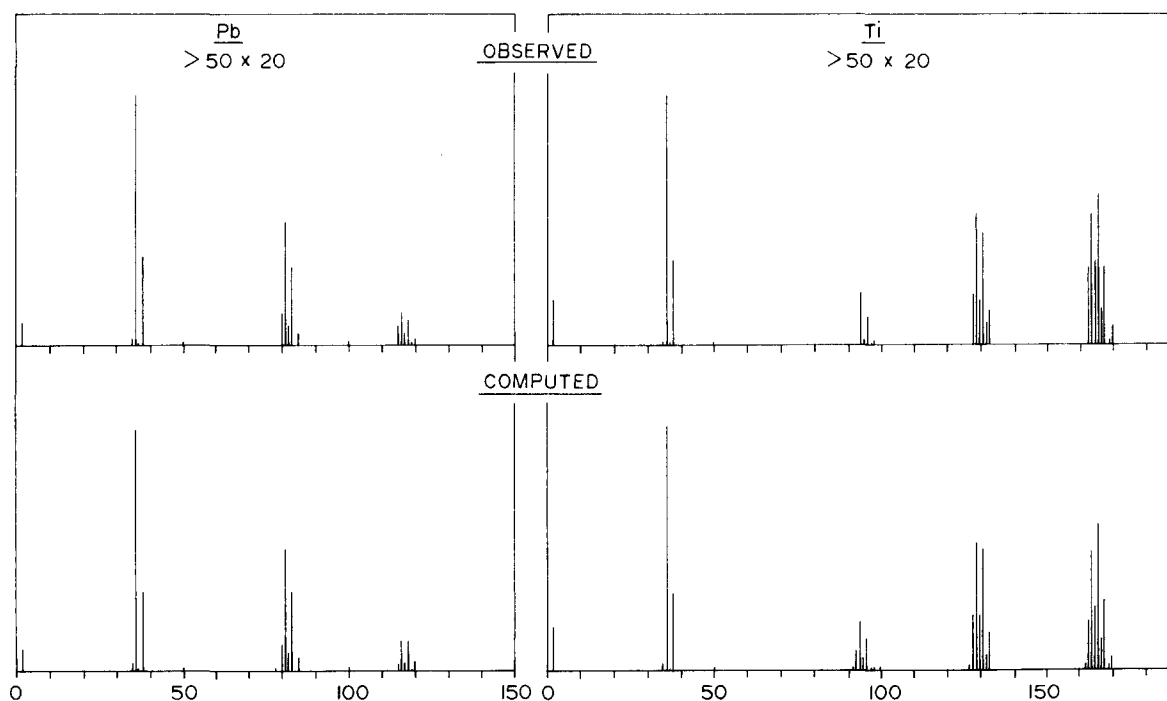


FIG. 1. Top: the observed mass spectra for the catalytic laser photochemistry of BCl_3 (13 torr) and H_2 (25 torr) after 360 laser pulses using Ti (right) and Pb (left) as catalysts. Bottom: the corresponding computer simulated mass spectra using the natural abundance of boron and chlorine.

TABLE I. Observed and computed isotopic ratio of boron for the catalytic laser photochemical products of BCl_3/H_2 .

Compounds	m/e ($^{10}\text{B} : ^{11}\text{B}$)	Relative intensity ^a	
		Observed	Simulated
B^{35}Cl_3	115:116	1:1.5	1:4.3
$\text{B}^{35}\text{Cl}_2\text{}^{37}\text{Cl}$	117:118	1:2.0	1:4.2
$\text{B}^{35}\text{Cl}^{37}\text{Cl}_2$	119:120	1:2.0	1:4.6
B^{35}Cl_2	80:81	1:3.8	1:4.3
$\text{B}^{35}\text{Cl}^{37}\text{Cl}$	82:83	1:4.0	1:4.3
$\text{B}^{11}\text{BH}_2\text{}^{35}\text{Cl}_4$	163:164	1:2.6	1:2.6
$\text{B}^{11}\text{BH}_2\text{}^{35}\text{Cl}_3\text{}^{37}\text{Cl}$	165:166	1:1.8	1:2.1
$\text{B}^{11}\text{BH}_2\text{}^{35}\text{Cl}_2\text{}^{37}\text{Cl}_2$	167:168	1:2.0	1:2.2
$\text{B}^{11}\text{BH}_2\text{}^{35}\text{Cl}^{37}\text{Cl}_3$	169:170	1:1.5	1:2.0
$\text{B}^{11}\text{BH}_2\text{}^{35}\text{Cl}_3$	128:129	1:2.5	1:2.3
$\text{B}^{11}\text{BH}_2\text{}^{35}\text{Cl}_2\text{}^{37}\text{Cl}$	130:131	1:2.4	1:2.2
$\text{B}^{11}\text{BH}_2\text{}^{35}\text{Cl}^{37}\text{Cl}_2$	132:133	1:1.6	1:2.2
$\text{B}^{11}\text{BH}_2\text{}^{35}\text{Cl}^{37}\text{Cl}$	95:96	1:3	1:2.3
$\text{B}^{11}\text{BH}_2\text{}^{37}\text{Cl}_2$	97:98	1:1.8	1:2.0

^aEstimated accuracy ± 0.2 .

A question immediately arises whether the appearance of BCl_2 radicals is due to the fragmentations of the unreacted gas BCl_3 or the reaction products B_2Cl_4 . The mass spectra of boron trichloride and diboron tetrachloride were studied by Dibeler and Walken.¹⁵ They found that the bond dissociation energy for $\text{BCl}_2\text{-Cl}$ is 4.78 eV, whereas that for $\text{BCl}_2\text{-BCl}_2$ is only 3.80 eV. Moreover, they indicated that the principal peaks for the mass spectrum of B_2Cl_4 molecules were BCl_2 and the spectral intensity of $I_{\text{BCl}_2} > I_{\text{BCl}_3}$ was observed in the mass spectrum of pure BCl_3 . In our experiment the recorded mass spectrum for the system $\text{BCl}_3/\text{H}_2/\text{Pb}$ gives the intensity ratio of $I_{\text{BCl}_2} : I_{\text{BCl}_3} = 3 : 1$. The results suggest that the observed group spectra at $m/e = 80\text{-}85$ are indeed the fragmentations of the catalytic laser photochemical reaction product B_2Cl_4 .

C. Isotopic enrichment of boron

In the spectral assignment we have noticed that the BCl_3 gas was completely used up in the mixtures of 13 torr BCl_3 , 25 torr H_2 , and ~ 1 g Ti after 360 laser pulses. In order to know the isotopic enrichment of boron for BCl_3 in this system we carried out an experiment using a shorter irradiation time. We found that the observed isotopically distributed mass spectral pattern for the unreacted BCl_3 gas of the $\text{BCl}_3/\text{H}_2/\text{Ti}$ system after 180 laser pulses is essentially the same as that observed for the system $\text{BCl}_3/\text{H}_2/\text{Pb}$ after 360 laser pulses. Therefore, we will only show the isotopic enrichment of boron for the later case.

Table I gives the experimentally observed and computer calculated $^{10}\text{B}/^{11}\text{B}$ for the compounds BCl_3 , BCl_2 , $\text{B}_2\text{H}_2\text{Cl}_4$, $\text{B}_2\text{H}_2\text{Cl}_3$, and $\text{B}_2\text{H}_2\text{Cl}_2$. The computed values

are carried out according to the natural abundance of boron. The results show that the intensity ratio of $I_{^{10}\text{BCl}_3} : I_{^{11}\text{BCl}_3}$ is observed as 1 : 1.8, whereas that of the computed value is 1 : 4.4. This means that the $^{10}\text{BCl}_3$ concentration of the unreacted BCl_3 gas has increased from 20% (the $^{10}\text{BCl}_3$ concentration of our initial sample) to 37%, i. e., we have doubled the $^{10}\text{BCl}_3$ concentration in our experiment. In the case of reaction products the experimentally observed values of $I_{^{10}\text{B}} : I_{^{11}\text{B}}$ are 1 : 3.9, 1 : 2.0, 1 : 2.2, and 1 : 2.4, respectively, for the molecules BCl_2 , $\text{B}_2\text{H}_2\text{Cl}_4$, $\text{B}_2\text{H}_2\text{Cl}_3$, and $\text{B}_2\text{H}_2\text{Cl}_2$.

The corresponding computer simulated values for the molecules above are 1 : 4.3, 1 : 2.2, 1 : 2.2, and 1 : 2.2, respectively. The perfect agreement between the observed and computed isotopic ratio of boron for the catalytic laser photochemical products of BCl_3/H_2 suggests the following facts: (1) The boron isotopic enrichment was not observed for the reaction products; (2) the spectral assignment of m/e 163–170 and 80–85 to the molecules $\text{B}_2\text{H}_2\text{Cl}_4$ and BCl_2 , respectively, is further confirmed; (3) the radicals $\text{B}_2\text{H}_2\text{Cl}_3$ and $\text{B}_2\text{H}_2\text{Cl}_2$ are indeed the fragmentations of $\text{B}_2\text{H}_2\text{Cl}_4$ molecules. It is worthwhile to mention that when one sums up the unreacted gases and the reaction products one finds that the observed natural abundance of boron is different from that of the computed. This indicates that one of the boron isotopes (^{11}B in our case) is absorbed on or even diffused into the metal catalyst. The identification of the metal catalyst using the ESCA technique is now in progress.

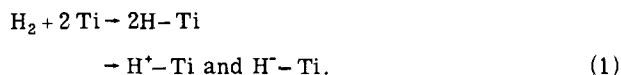
IV. MECHANISMS

We know that the reaction products for the catalytic laser photochemistry of $\text{BCl}_3/\text{H}_2/\text{Ti}$ and $\text{BCl}_3/\text{H}_2/\text{Pb}$ were identified as $\text{B}_2\text{H}_2\text{Cl}_4$ and B_2Cl_4 , respectively. However, Rockwood and Hudson³ indicated that the BHCl_2 is the only product for the CO_2 laser photochemistry of BCl_3 and H_2 . The difference between our experiments and those of the Rockwood *et al.*³ can be seen as follows: (1) $\text{B}_2\text{H}_2\text{Cl}_4$ and B_2Cl_4 molecules are readily generated on the surface of the metal catalysts; (2) the production of BHCl_2 may require a higher concentration mixture of BCl_3 and H_2 . It was found³ that a 1 : 1 ratio of BCl_3 to H_2 at a total pressure of 40 torr (which is similar to our sample mixtures) can produce 3 torr of HBCl_2 after 180 laser pulses. In addition, the reaction products of $\text{B}_2\text{H}_2\text{Cl}_4$ and B_2Cl_4 were not detected in our catalysis free system. These results eliminate the second possible explanation.

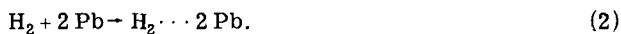
By comparing the top-right and the bottom-right mass spectra of Fig. 1 one sees that the mass peaks of m/e 162, 127, and 92 were not observed experimentally. This indicates that the possible boron isotopic combinations for the reaction products of the $\text{BCl}_3/\text{H}_2/\text{Ti}$ system are $^{10}\text{B}^{11}\text{BH}_2\text{Cl}_4$ and $^{11}\text{B}^{11}\text{BH}_2\text{Cl}_4$, i. e., $^{10}\text{B}^{10}\text{BH}_2\text{Cl}_4$ was not produced. Although the products $^{10}\text{B}^{11}\text{BCl}_4$ and $^{11}\text{B}^{11}\text{BCl}_4$ were not seen directly in the mass spectrum of the $\text{BCl}_3/\text{H}_2/\text{Pb}$ system, we believe that the observed $^{10}\text{BCl}_2$ radical is due to the fragmentation of $^{10}\text{B}^{11}\text{BCl}_4$ but not of $^{10}\text{B}^{10}\text{BCl}_4$. Furthermore, the isotopic enrichment of boron is only observed for the unreacted BCl_3 gas but not for the reaction products. Thus, one

can draw the following conclusions: (1) Laser excitation step of $^{11}\text{BCl}_3$ to give $^{11}\text{BCl}_2$ radical is selective but the following reaction step of $^{11}\text{BCl}_2$ radical with molecules BCl_3 and H_2 is not; (2) the formation of $\text{B}_2\text{H}_2\text{Cl}_4$ and B_2Cl_4 through a combination of two $^{11}\text{BCl}_2$ radicals did not occur.

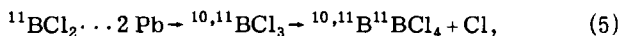
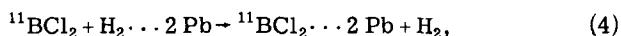
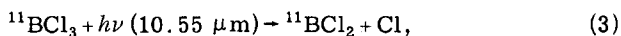
It is known¹⁶ that the adsorption of H_2 on the metal surface of Ti is a chemisorption process, whereas that on the Pb metal surface is a physical adsorption. Since chemisorption is essentially a chemical reaction, the strength of adsorption (or the heat of adsorption $-\Delta H_a$) for the adsorption of hydrogen on Ti may be sufficient to dissociate the H-H bond into two adsorbed hydrogen atoms (or hydrogen ions). The chemisorption of a hydrogen molecule on the Ti catalyst can be represented as



On the other hand, the potential energy curve for the process of physical adsorption is characterized by a shallow minimum. This means that the heat of physical adsorption for the hydrogen molecule on the Pb metal surface is small, i. e., the physically adsorbed hydrogen is readily desorbed. The representation of a molecule of hydrogen physically adsorbed on a Pb surface is

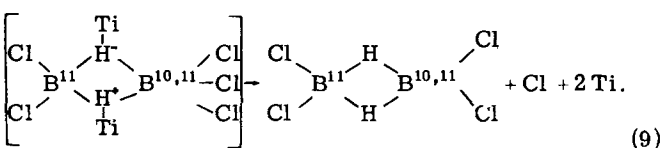
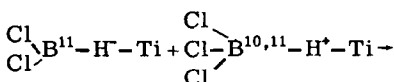
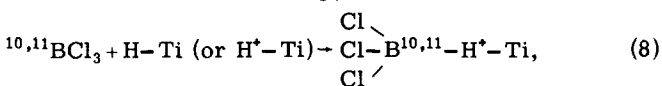
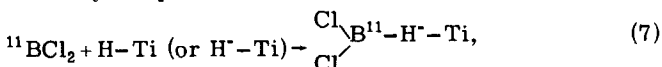


From the discussions above the mechanisms for the laser photochemistry of BCl_3 and H_2 on the Pb metal surface may be proposed as follows:



Reaction (3) is a selective multiple photon dissociation of $^{11}\text{BCl}_3$ to give $^{11}\text{BCl}_2$ radicals. When the kinetically energized $^{11}\text{BCl}_2$ radical approaches the Pb metal surface the kinetic energy carried by the radical would presumably be enough to desorb the H_2 as shown in reaction (4). Reaction (5) shows that the isotopically selective $^{11}\text{BCl}_2$ radicals react nonselectively with BCl_3 molecules which give the nonselective reaction products.

The possible reaction mechanisms for the case of $\text{BCl}_3/\text{H}_2/\text{Ti}$ are also initiated by the reaction (3) followed by the processes



The Cl radical will then react with H_2 and produce HCl following the reaction (6). One can see that the kinetic energy of $^{11}\text{BCl}_2$ is not large enough to break the H-Ti bond. Instead of a desorption of H_2 (H atom), a Lewis acid-base reaction occurs on the Ti surface for the species $^{11}\text{BCl}_2$, $^{10}\text{BCl}_3$, and $^{11}\text{BCl}_3$ as shown in Reactions (7) and (8). The exact configuration for the formation of bridge compounds $^{10}\text{B}^{11}\text{BH}_2\text{Cl}_4$ and $^{11}\text{B}^{11}\text{BH}_2\text{Cl}_4$ is not known. Presumably, the characteristic metal surface of Ti allows a transition state of Reaction (9) to form.

V. REMARKS

We have illustrated that catalysis can make the laser photochemistry go fast and allow one to generate a new class of compounds which was impossible to produce by a thermal reaction or by a catalysis free photochemical process. The effect of a catalyst on the laser photochemistry should depend not only on the different heterogeneous catalysts used but also on the state of a catalyst prepared such as the metal size, and face, etc. A thorough understanding of the effect is certainly very important in the field of laser photochemical industrialization.¹⁷

Up to the present time the high efficiency laser isotope separations were all achieved¹⁸ under very low sample pressure, in an order of 0.5–2 torr. This is due to the fact that the energy transfer processes through collisional channel become faster at higher sample pressure. The fast energy transfer from one isotope to the other results in a loss of the isotopic selectivity and limits the production of isotopes still in the laboratory scale. On the contrary, we have doubled the $^{10}\text{BCl}_3$ concentration for a sample mixture of 1 : 2 ratio of BCl_3 to H_2 at a total pressure of 38 torr after 180 laser pulses. Clearly, this is because the effect of catalysis speeds up the chemical reaction rate and also relatively decreases the energy transfer rate. At this point we would like to mention that the same technique is applicable for the other light elements as well as for the heavy elements ^{235}U and ^{238}U .¹⁹

ACKNOWLEDGMENTS

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