INFRARED LASER SPECIFIC REACTIONS OF BORON COMPOUNDS. CO_2 LASER CONTROL OF THE EXCHANGE REACTIONS $B(CH_3)_n Br_m + HBr \rightarrow B(CH_3)_{n-1} Br_{m+1} + CH_4$

H.R. BACHMANN, H. NÖTH, R. RINCK

Institut für Anorganische Chemie der Universität München 8000 Munich 2, Germany

and

K.L. KOMPA

Max-Planck-Institut für Plasmaphysik, Euratom Association, 8046 Garching/Munich, Germany

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Laser specific product formation has been achieved in the exchange reactions of HBr with boron trimethyl $B(CH_3)_3$ and the mixed boron methyl bromides $B(CH_3)_2Br$ and $B(CH_3)Br_2$. The non-thermal nature of these reactions was shown by the line specific action of the CO₂ laser radiation and by an in-situ temperature probe.

1. Introduction

In a previous communication it has been demonstrated [1] that the diborane decomposition produced by CO_2 laser irradiation differs markedly from the conventional pyrolysis of B_2H_6 . In the present paper we report on the reactions of various boron methyl compounds with hydrogen bromide which under the influence of line selected CO_2 radiation also proceed in a non-thermal manner.

In an infrared laser-controlled reaction one attempts to bring molecules to a selected state of vibrational excitation from which reaction occurs with a collision efficiency higher than that of any other collisional process in the system. If such a reaction channel exists the question arises whether the rate of vibrational heating can compete with the rates of the various relaxation processes [2,3]. In a rough approach this competition may be discussed in terms of scheme (1):



It is assumed here that the energy is channelled into the reactive state N_v through absorption and vibrational exchange processes with characteristic times $\tau_{\rm q}$ and $\tau_{\rm vv}$ whose combined effects determine $\tau_{\rm exc}$. To reduce relaxation and thermal reaction it is necessary that $\tau_{\rm exc} < \tau_{\rm vRT}$. Accordingly a small photon flux, $\tau_{\rm vv} < \tau_{\rm vRT} < \tau_{\rm q}$ will only heat the system, more or less preserving the total thermodynamic equilibrium. With an increase in the laser field intensity, $\tau_{\rm vv} < \tau_{\rm q}$ $< \tau_{\rm vRT}$, the equilibrium is broken between rotation/ translation and vibration of the molecule. Finally with very high photon fluxes, $\tau_q < \tau_{vv} < \tau_{vRT}$, it is conceivable that the heating be restricted to only one bond resonant with the laser field. We believe that we have achieved laser-specific product formation in the following set of exchange reactions:

$$B(CH_3)_3 + HBr \rightarrow B(CH_3)_2Br + CH_4, \qquad (2)$$

laser 970.5 cm⁻¹, thermal activation 150–180°C;

$$B(CH_3)_2 Br + HBr \rightarrow BCH_3 Br_2 + CH_4,$$

$$Iaser 1039.4 \text{ cm}^{-1}, \text{ thermal activation} > 250^{\circ}\text{C};$$
(3)

$$BCH_{3}Br_{2} + HBr \rightarrow BBr_{3} + CH_{4},$$

$$Has = 970.5 \text{ or } 1039.4 \text{ cm}^{-1}, \text{ thermal activation} > 450^{\circ}C.$$
(4)

As shown, these reactions can also proceed with thermal activation. The reactions, however, do not occur to a measurable extent below the temperature limits indicated [4]. To give proof of the non-thermal nature of the laser-induced reactions a direct temperature probe was used. This technique employs a second reaction system present in the gas which is itself not excited by resonance absorption of the laser light but whose temperature characteristics are known. Thus, if reaction occurs in this admixture the degree of thermal heating by the laser radiation can be estimated. Such an indiator reaction is to be preferred particularly in cases where large temperature gradients exist due to inhonogeneous absorption of the laser light in the volume. n such cases the maximum temperature can be measred as opposed to other techniques where only averge temperatures are obtained [5]. The desired laser nduced reaction may be called non-thermal if its therolysis temperature is above that of the indicator and the indicator shows no reaction. The application of is principle to the sequence of reactions (2), (3), (4)ith temperatures $T_2 < T_3 < T_4$ is rather straightforard. It is to be demonstrated then that e.g. reaction 1) can be forced to occur in the presence of the reacints of (3) which remain unreacted at the same time.

Experimental

The apparatus used in these experiments has been lly described previously [1]. The gas cells (22 cm^3) lume, l = 60 mm which were fitted with teflon lves and KCl windows were evacuated and filled by eans of an all-glass vacuum line. Care was taken in

aligning the cells on the beam axis and to avoid any absorption and reflection by the cell walls. The radiation not absorbed by the gas was monitored with a conventional power meter. Absorptions were above 90% at the beginning of each run. The products were examined infrared and mass spectrometrically. The methylbromo borane compounds were prepared by the reaction of tin tetramethyl with stoichiometric amounts of boron tribromide [6] and were purified by bulb to bulb distillation. The trimethylborane was obtained through the reaction of $(CH_3)_3 Al_2 Cl_3$ with $(n - C_4 H_0 O)_3 B$ [7]. Unless mentioned otherwise the pressures chosen were 150 torr of the boron compound plus 450 torr of HBr. The materials conversion was rather substantial and up to 120 torr of product were formed under the conditions explained below. If $B(CH_3)_3$ alone was exposed to the laser no reaction was found to occur.

3. Results

To show the validity of the temperature probe technique the following experiment was done first. A mixture of BCH₃Br₂ (100 torr), HBr (200 torr) and $B(CH_3)_7$ Br as a temperature indicator (20 torr) was exposed to the radiation of the R(12), 00^01-10^00 CO_2 laser line (60 min, 4.5 W). This line at 970.55 cm⁻¹ is absorbed by the BBr₂ antisymmetric stretching vibration (b_1) of BCH₃Br₂^{\top} while all the other gases are transparent at this wavelength. As expected BBr3 was formed (fig. 1) according to reaction (4). The concentration of the indicator gas $B(CH_3)_2B_1$ was not changed to any appreciable extent showing that the translational temperature during the reaction did stay below 250°C. Since the thermal reaction (4) requires temperatures even $> 450^{\circ}$ C the non-thermal nature of this reaction was obvious. In this reaction the action of the laser radiation has some features of a catalyst[®], since it lowers the gas temperature required for the main reaction and so inhibits the side reaction. Of course, the laser does not lower the activation energy of the main reaction but it channels the energy into the desirable reactant mode. Thus a successful in-situ temperature probe experiment shows that IR laser radiation is

The assignment of the vibration band follows ref. [8].

Catalysts for the protolysis of trialkyl boranes were recently described by Köster et al. [9].



Fig. 1. (a) Absorption of a mixture of 100 torr BCH₃Br₂, 200 torr HBr and 20 torr of $B(CH_3)_2Br$ (BBr₃ is present as an impurity). (b) The same mixture after 60 min exposure to CO₂ laser emission (4.5 W, R(12) $00^0 1-10^0 0$). As indicated by the increased BBr₃ and decreased BCH₃Br₂ absorption about 5 torr of BBr₃ have been produced [reaction (4)] while the concentration of the temperature indicator $B(CH_3)_2Br$ is nearly unchanged.

capable of stimulating chemical reactions selectively. Such selective reactions could be of interest in industrial processes where one component of a mixture is to be converted into a certain product by the laser while other components remain unaltered.

From the work of Wiberg and Buchheit [4] it is known that the three methyl groups in $B(CH_3)_3$ can be substituted stepwise by bromine through reaction with hydrogen bromide if the mixture is heated to $150-180^{\circ}C$, $> 250^{\circ}C$ and $> 450^{\circ}C$ [see reactions (2)--(4)]. The same reactions can be brought about on irradiation with suitable CO_2 laser lines. This, however, requires tuning to different lines for the different reaction steps.

To study reaction (2) the R(12) line 00^01-10^00 , 970.55 cm⁻¹ was used to excite a fundamental vibration of $B(CH_3)_3$ which is assigned to a CH_3 rocking motion [8]. In a mixture of $B(CH_3)_3$ and HBr only $B(CH_3)_2Br$ is formed but no $B(CH_3)Br_2$ or BBr_3 . We thus conclude that the gas kinetic temperature was below 250°C, the temperature required for reaction (3) to occur. The absorbed radiation power was between 7.2 and 6 W over a period of 30 min.

For reactions (3) and (4) somewhat lower absorbed laser powers (< 5.5 W, 30 min) were sufficient to produce similar reactive changes. Since the thermolysis



Fig. 2. Infrared absorption spectra in the range of the CO₂ laser emission of B(CH₃)₃ and of the various reaction mixtures studied. Spectra were recorded under the following conditions: Slit width $\Delta v = 1.8 \text{ cm}^{-1}$ at 1000 cm⁻¹, scanning speed $v = 20 \text{ cm}^{-1} \text{ min}^{-1}$, reference dry air.

temperatures of (3) and (4) are even higher than for (2) this lends additional support to the assumption of a non-thermal reaction. For reaction (3) the P(28) CO_2 laser line $OO^0 1-O2^0 0$, 1039.37 cm⁻¹ was selected while for (4) both lines R(12) $OO^0 1-IO^0 0$ and P(28) $00^0 1-02^0 0$ could be used, the R(12) line, however, being preferably used in most runs. In these experiments either the reaction mixtures from the preceding run or freshly prepared mixtures were employed with no noticeable difference in the results. If DBr is used in addition to HBr, CH₃D is produced. Fig. 2 shows the infrared absorption of B(CH₃)₃ in the range of interest together with the changes in the absorption in the sequence of reactions (2), (3), and (4). In between these reactions the gas mixtures were not changed. The spectra correspond to a superposition of the respective bromo methyl boranes with very little impurity absorption.

In conclusion it has been shown that the temperature rise produced by the absorption of certain CO_2 laser lines in the various reaction mixtures studied cannot solely account for the observed chemical reactions. It is thus believed that specific vibrational heating of a particular reactant is important in promoting the reactions.

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