VIBRATIONAL EXCITATION EFFECTS ON SILANE REACTIVITY IN ITS REACTION WITH BROMINE ATOMS

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A rate increase of SiH_3Br formation in SiH_4 photobromination under irradiation by a cw CO_2 laser is reported. At low SiH_4 pressures (~ 1–2 Pa) the radiation effect is shown to be isotope-selective.

Зарегистрировано увеличение скорости образования SiH_3Br под действием излучения непрерывного CO_2 лазера на фотобромирование SiH_4. Показано, что при низких давлениях SiH_4 (~ 1–2 Па) действие излучения изотопически селективно.

The accelerating effect of cw CO_2 laser irradiation on methyl fluoride photobromination and the possibility to perform a carbon isotope selective reaction in this system were reported elsewhere /1–4/. It was of interest to verify the possibility to carry out similar processes for other molecules possessing absorption lines in the region of CO_2 laser generation, e.g. silane.

First, the photobromination of silane under UV light of various wavelengths was studied /5/. The rate constants of silane reaction with bromine atoms in the ground $(^2P_{3/2})$ and electronically excited $(^2P_{1/2})$ states were: $k = 3.2 \times 10^{-11} \exp(-21.8/RT)$ and 3×10^{-13} cm^3/s, respectively. These constants imply that the vibrational excitation of silane molecules can decrease the activation barrier of the reaction with $Br(^2P_{3/2})$ and thus accelerate it, whereas with $Br(^2P_{1/2})$ (no activation barrier) excitation cannot be effective.

The effect of vibrational excitation on silane photobromination was studied on a setup described elsewhere /1–4/. SiH_4 was excited by the radiation of the P(20) line of the $00°1 - 10°0$ transition (944.195 cm^{-1}) of the cw CO_2 laser (15–20 W

power). The reaction was performed in two different vessels. One was a 50 cm long quartz tube, (ID = 2 cm) with two NaCl end windows: to irradiate the vessel by filtered light of a DRSh-500 mercury lamp ($\lambda = 365$ nm) to dissociate Br_2 into atoms, and by the laser. The other reaction vessel was a 20 cm long quartz tube of the same diameter with NaCl windows stuck to the edges at a Brewster angle. The tube was placed between two mirrors (one with a pinhole) for focusing laser radiation which, reflected by the mirrors, was repeatedly passed through the reactor. Temperature measurements of the gas heated by the laser radiation permitted to determine the irradiation intensity inside the reactor which appeared to be four times higher than in a single pass laser beam reactor. UV light passed through the cylindrical surface of the reactor normally to the laser beam. The reaction vessel was connected to the ion source of an MX-1303 mass spectrometer via a 10 μ pinhole to permit the on-line analysis of the concentration of the reactants and products. The reaction rate was measured by the accumulation of SiH_3Br formed in the reaction $SiH_3 + Br_2 \rightarrow SiH_3Br + Br$ immediately following the slow step $Br + SiH_4 \rightarrow HBr + SiH_3$. The concentrations of $^{28}SiH_3Br$ were measured by the lines m/e 111 and 112 and 114 of the mass spectrum, respectively. The concentration of $^{29}SiH_3Br$ was determined by the line 113 corrected for contribution from $^{30}SiH_3Br$. The reaction was studied at room temperature and 0.8 to 0.6 Pa silane and 13 to 50 Pa bromine. To decrease the rate of vibrational relaxation of excited SiH_4 molecules on the walls, the reaction mixture was diluted with argon to 100–300 Pa.

In the single pass laser beam reactor the rate of laser induced $^{28}SiH_3Br$ formation increased by 20–30% independently of the absorbing gas pressure. To increase the effect and to investigate it, we performed our experiments in vessels with multipass laser beams which raised the reaction rate by a factor of 1.5–2. SiH_3Br accumulation curves for all silicon isotopes (28, 29 and 30) are illustrated in Fig. 1. The reaction was performed at 2.7 Pa silane, 54 Pa bromine and 270 Pa argon. It is seen that under laser irradiation the reaction rate increases for all silicon isotopes; however, the increase is more pronounced in the case of ^{29}Si. The analysis of the isotope composition of SiH_3Br at the degree of reaction close to saturation indicates that the amount of ^{28}Si and ^{30}Si differs insignificantly from natural and the amount of ^{29}Si grows. The concentration of rare 29 and 30 isotopes in the reaction product SiH_3Br vs. the SiH_4 pressure is illustrated in Fig. 2. A decrease in the isotope effect with increasing pressure indicates an important role of excitation energy transfer between isotopic molecules in this pressure range. The fact that SiH_3Br is enriched in ^{29}Si means that the P(20) line of the CO_2 laser is absorbed by $^{29}SiH_4$ molecules. However, an increase in the reaction rate for $^{28}SiH_4$ cannot be attributed solely to energy transfer from excited $^{29}SiH_4$, since it does not vary
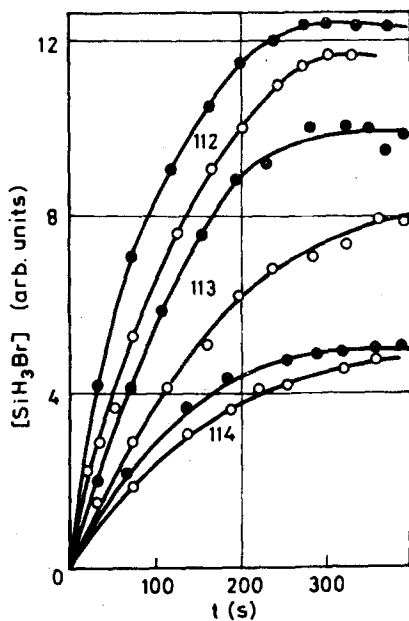
SiH$_3$Br accumulation. ^{30}SiH$_3$^{81}Br $-$ m/e 114, ^{29}SiH$_3$^{81}Br $-$ m/e 113, ^{28}SiH$_3$^{81}Br $-$ m/e (10 : 1 demagnification), light dots $-$ without laser; dark dots $-$ with laser
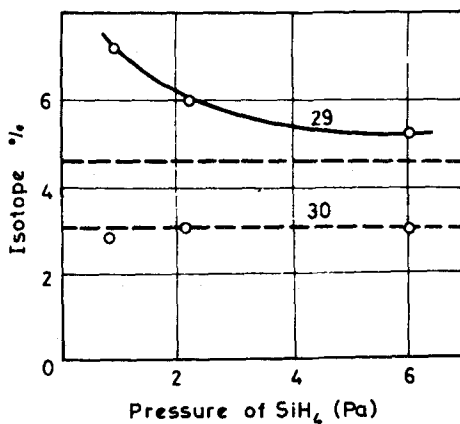

Fig. 2. Silicon isotope composition (29, 30) of SiH$_3$Br vs. SiH$_4$ pressure. Dashed lines correspond to the natural abundance of silicon isotopes 29 and 30

with decreasing silane pressure. This means that the CO_2 laser radiation is also absorbed by $^{28}SiH_4$ molecules although with a lower coefficient compared with $^{29}SiH_4$.

From the dependence of isotope effect on SiH_4 pressure, the rate constant of vibrational energy transfer between isotopic molecules can be estimated. The pressure at which the isotope effect reduces by one half corresponds to the equality of the rates of $V - V$ and $V - T$ relaxations. The experimental rate constant of $V - T$ relaxation of silane with argon determined according to laser induced IR luminescence is 6×10^{-14} cm^3/s.

Taking into account the excited SiH_4 relaxation on the walls by the diffusion mechanism, the rate of $V - T$ relaxation is 3×10^3 1/s at an argon pressure of 133 Pa (3×10^{16} 1/cm^3). The rate of vibrational energy transfer, which is equal to this value, is obtained if the transfer rate constant is 6.7×10^{-12} cm^3/s at an SiH^4 pressure of 2 Pa (4.5×10^{14} 1/cm^3).

To estimate the stationary concentration of vibrationally excited molecules generated under laser irradiation, the SiH_4 absorption cross section was measured at the P(20) line of the CO_2 laser. At low pressures it equals 3×10^{-19} cm^2. After the admission of an inert gas, it increases sharply to 1×10^{-18} cm^2 at 2000 Pa argon. This means that the P(20) line gets to a wing of the SiH_4 absorption line. According to the measured absorption cross section and the $V - T$ relaxation rate, the excess concentration of excited molecules must be 6–12% of the total number of SiH_4 molecules at 50–100 W power of IR irradiation and 200 Pa argon pressure. The thermal equilibrium concentration of vibrationally excited molecules is 5.4% at room temperature.

The concentration of vibrationally excited molecules under these conditions is 2–3 times higher than the equilibrium value, the reaction rate being twice as high. Hence, under steady-state conditions, not less than half the rate of the reaction $Br + SiH_4 \rightarrow HBr + SiH_3$ is determined by the reaction of vibrationally excited SiH_4 molecules.

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