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LASER-INDUCED CHEMICAL (IR LASER RADIATION) REACTION OF BCl_3 AND METHANE

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Laser-induced chemical reactions in systems, one of whose components is BCl_3, are comparatively well studied [1-4], firstly, owing to the proximity of the active vibration frequency of absorption of the BCl_3 molecule (ν_3 = 956 cm^{-1} for $^{11}BCl_3$, ν_3 = 995 cm^{-1} for $^{10}BCl_3$) to the radiation frequency of CO_2 IR lasers, and secondly, owing to the relative ease of carrying out the reaction with BCl_3. Several authors [5-8] noted the complexity of interpretation of the experimental results, due to the necessity of allowing for anharmonicity, the role of processes of V—V and V—T relaxation, and the character of the primary elementary photochemical act; there is not even a common view on the nature of threshold phenomena in laser-induced chemical reactions of this kind [8]. Moreover, since the difference between the vibrational and translational temperatures is unknown a priori, the ratio of thermal and photochemical reaction mechanisms is estimated indirectly, as a rule, from the results of analysis of the reaction products. At the same time, there is nothing in the literature

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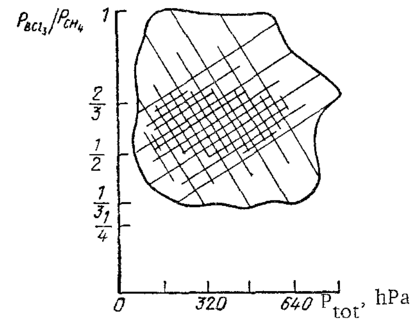

Fig. 1. Curve of intensity of emission versus ratio of partial pressures of BCl_3 and CH_4 and their total pressure. Density of lines is proportional to luminescence intensity.

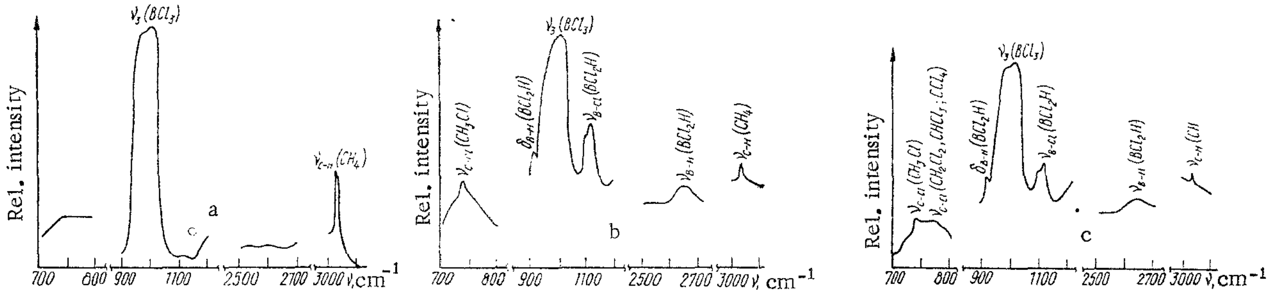

Fig. 2. IR spectra of BCl_3–CH_4 mixture ($P_{BCl_3}:P_{CH_4}$) = 1:2; P_{tot} = 160 hPa: a) before irradiation by continuous CO_2-laser radiation; b) after 10-min irradiation by continuous CO_2-laser radiation; c) after 20-min irradiation by continuous CO_2-laser radiation.

about the behavior of a mixture of BCl_3 and CH_4 subjected to continuous radiation from a CO_2 laser. The present study is concerned with clearing up the above questions for this system.

In our investigations the radiation source was a continuously acting CO_2 laser of ~40 W power. The radiation was directed into a stainless-steel cell 100 mm long and 25 mm in inner diameter, which had two mutually perpendicular channels. The entrance and exit windows were made of KRS-5 with a thin protective coating, whereas the side windows consisted of optical silica. The products were analyzed in a UR-20 spectrometer; moreover, chemical and x-ray structural analyses were performed.

Our irradiation of the BCl_3–CH_4 gas mixture with continuous CO_2-laser radiation, periodic luminescence is visually observed having a light-pulse repetition period of the order of a minute. An emission, having nearly the same spectral composition, is described in [1] as the result of subjecting a mixture of boron trichloride and hydrogen to radiation from a pulsed CO_2 laser.

The investigations were conducted over a rather broad interval of total pressure of reactants in the system and ratios of BCl_3 and CH_4 partial pressures (Fig. 1). It is evident from Fig. 1 that emission is observed in a certain region of total pressure and ratios of BCl_3 and CH_4 partial pressures. At $P_{tot} < 80$ hPa emission was not detected, apparently owing to its low intensity, whereas at $P_{tot} \gtrsim 1200$ hPa it was not observed, because there was no reaction.

After irradiation of the BCl_3–CH_4 mixture with continuous CO_2-laser radiation, the following reaction products were identified by their IR spectra; methyl chloride CH_3Cl (characteristic absorption band $\nu_{C-Cl} = 732\ cm^{-1}$ [9]) and dichloromonoborane $HBCl_2$ (characteristic absorption bands: ν_{B-H} doublet with center at 2617 cm^{-1}; ν^{as}_{B-Cl}, doublet at 1110 cm^{-1} for $^{10}BCl_3$ and 1085 cm^{-1} for $^{11}BCl_3$; $\nu_{B-H} = 890\ cm^{-1}$ [10]). As an example the IR spectrum of the original $BCl_3 + CH_4$ mixture at P_{tot} = 160 hPa and P_{BCl_3}/P_{CH_4} = 1:2 is shown in Fig. 2a along with the IR spectrum of the same mixture after irradiation for 10 min with continuous CO_2-laser radiation (Fig. 2b). On further irradiation of the mixture for 10 min the intensity of the ν_{C-Cl} band in CH_3Cl (732 cm^{-1}) is decreased, and a band appears in the 740-795 cm^{-1} region (Fig. 2c). The band shift is evidently due to the formation of chloro derivatives of methane having higher chlorine content [9]. Further irradiation of the mixture has no effect on the IR spectrum.

Our experiments at various values of P_{tot} and P_{BCl_3}/P_{CH_4}, within the limits of the cross-hatched area (Fig. 1), showed that changing these parameters does not affect the course of the process at all: In all cases the same bands appear in the IR spectrum. Moreover, a solid black product formed on the cell walls, which proved to be finely divided carbon according to the results of chemical (for boron and carbon) and x-ray structural analyses.

The absence of any sign of laser-induced chemical reaction of BCl_3 and CH_4 at higher pressures up to ∿1000 hPa (absence of emission, absence of new bands in the IR spectra, and absence of a black product) attests in favor of the selective photochemical, and not thermal, nature of this laser-induced chemical reaction at low pressures. One may also suppose that the reaction of BCl_3 and CH_4 does not go by the radical mechanism proposed, e.g., for the laser-induced chemical reaction of SF_6 and SO_2 [11]. In this case the first step would have to be dissociation of BCl_3 into $BCl_2^{\bullet}$ and $Cl^{\bullet}$ radicals with formation mainly of such products as B_2Cl_4, BCl_2CH_3, and HCl, which are not found in the IR spectra of products of the laser-induced chemical reaction of BCl_3 and CH_4.

Based on the reaction products detected, a more logical mechanism is that proposed in [12] for the reaction $BCl_3^* + H_2 \rightarrow HBCl_2 + HCl$, which is determined not by dissociation of BCl_3 with subsequent radical reactions, but by direct reaction with participation of the vibrationally excited molecule BCl_3^*. In this case the course of the reaction between BCl_3 and CH_4 subjected to continuous CO_2-laser radiation may be represented by the following scheme:

$$\text{a) } BCl_3 + nh\nu \rightarrow BCl_3^*,$$

$$\text{b) } BCl_3^* + CH_4 \rightarrow BCl_2H + CH_3Cl,$$

$$\text{c) } BCl_3^* + CH_3Cl \rightarrow BCl_2H + CH_2Cl_2,$$

$$\text{d) } BCl_3^* + CH_2Cl_2 \rightarrow BCl_2H + CHCl_3,$$

$$\text{e) } BCl_3^* + CH_3Cl \rightarrow BCl_2H + CCl_4.$$

Besides this reaction mechanism, vibrationally excited BCl_3 molecules, undergoing "rigid" collisions with CH_4 molecules and transmitting accumulated vibrational energy to them, may cause decomposition of the CH_4 molecule into carbon and hydrogen: $BCl_3^* + CH_4 \rightarrow BCl_3 + C + 2H_2$.

It is not yet possible to specify the character of primary photochemical act (a) in more detail. One can only advance two hypotheses, based, on the one hand, on data [13] on the shift of the ν_{B-Cl} vibration frequency toward longer wavelengths when the BCl_3 molecules are subjected to intense IR radiation, and on the other, on our own experimental results, consisting in the fact that, in the presence of a small amount of oxygen in the reaction cell, neither photochemical conversions nor luminescence occur (according to IR spectral data). From the fact, that luminescence intensity increases with the degree of photochemical conversion, on the other, one may conclude that vibrational excitation of the molecule or its intermediate reaction products substantially affects the electronic structure of the molecule on account of electronic-vibrational interaction. By virtue of this the original photochemical act may consist in the formation of both BCl_3^+ and electronic-vibrational excited states of this molecule.

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ADSORPTION OF WATER VAPOR ON SILICA WITH A PROGRAMMED TEMPERATURE INCREASE

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The most popular methods for determination of heats of adsorption of substances on the surface of solids are their calculation from isotherms and measurement by calorimetric methods. In the present communication, we propose a method for determination of heats of adsorption according to integrated kinetic curves of the relation of the amount of the adsorbed substance to temperature obtained during linear heating of the adsorbent—adsorbate system.

Let us consider a closed solid-surface—gas (or vapor) system whose temperature increases according to a linear law. Let us assume that the change in the concentration of the adsorbed substance with time is proportional to the difference between its equilibrium and actual values

$$dn/dT = k_a (n_e - n) C,$$

where $k_a = k_0 \exp(-ERT)$ is the rate constant of adsorption, k_0 is the preexponential factor, E is the activation energy of adsorption, n_e is the equilibrium amount of the adsorbed substance with respect to the mass of the adsorbent, and C is the concentration of the substance in the gas phase. Let the equilibrium concentration within the entire range of the preassigned temperatures and concentrations of the substance in the gas phase be described by Henry's equation

$$n_e = \lambda K C,$$

where λ is the ratio of the volume occupied by the gas to the mass of the adsorbent, and $K = A\exp(Q/RT)$ is the equilibrium constant (Q is the heat of adsorption, and A is a constant including the entropy factor). Going to the coordinate with respect to temperature ($T = T_0 + bt$, where b is the heating rate), we obtain

$$dn/dT = \frac{k_a}{b} (\lambda K C - n) C. \tag{1}$$

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