

STUDIES OF THE REACTIONS OF $\text{Br}(^2\text{P}_{3/2})$
AND $\text{Br}(^2\text{P}_{1/2})$ WITH SiH_4

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Photobromination of SiH_4 under uv-irradiation at various wavelengths has been studied. Rate constants for the elementary reactions $\text{Br}(^2\text{P}_{3/2}) + \text{SiH}_4 \rightarrow \text{HBr} + \text{SiH}_3$ ($k = 3.2 \times 10^{-11} \exp(-21.8 \pm 2.5)/RT$, cm^3/s) and $\text{Br}^*(^2\text{P}_{1/2}) + \text{SiH}_4 \rightarrow \text{HBr} + \text{SiH}_3$ ($k^* = (3 \pm 1) \times 10^{-13} \text{cm}^3/\text{s}$) have been determined in the temperature range from 300 to 415 K.

Исследована реакция фотобромирования под действием УФ-света различных длин волн. Определены константы скорости элементарных реакций $\text{Br}(^2\text{P}_{3/2}) + \text{SiH}_4 \rightarrow \text{HBr} + \text{SiH}_3$, $k = 3,2 \times 10^{-11} \exp(-21,8 \pm 2,5)/RT$ $\text{см}^3/\text{сек}$ и $\text{Br}^*(^2\text{P}_{1/2}) + \text{SiH}_4 \rightarrow \text{HBr} + \text{SiH}_3$, $k^* = (3 \pm 1) \times 10^{-13} \text{см}^3/\text{сек}$ в интервале температур 300–415 К.

Studies of CH_3F photobromination indicate that electronic excitation of bromine atoms to the $^2\text{P}_{1/2}$ state reduces the activation energy of their reaction with CH_3F by the magnitude of the excitation energy (44 kJ/mol) with a simultaneous decrease by three orders of magnitude of the preexponential factor /1, 2/. This was explained in terms of a nonadiabatic reaction mechanism of the excited bromine atom /3/. Activation energy for the reaction of unexcited Br atom with CH_3F (61 kJ/mol) is higher than its excitation energy. Therefore, it is of interest to study the role of electronic excitation of Br atoms in reactions whose activation energies are lower than the excitation energy. Since the energy of Si-H bond dissociation in SiH_4 is lower than that of the C-H bond in CH_3F , this situation can be predicted for SiH_4 bromination.

SiH_4 photobromination was studied experimentally by known methods /1, 2/. The reaction rate was measured according to the decrease of SiH_4 concentration

continuously recorded by a mass spectrometer. To dissociate Br₂ into atoms, the light of a DRSh-500 lamp was used; 365 or 436 nm lines were filtered out of its spectrum. In the former case, Br₂ dissociated into two atoms in the ground (²P_{3/2}) state, in the latter case, it gave one atom each in the ground and the electronically excited (²P_{1/2}) states.

By analogy with CH₃F photobromination /1/, the effective rate constant of SiH₄ photobromination can be described as

$$-\frac{d[\text{SiH}_4]}{dt} = k_{\text{eff}} [\text{SiH}_4]$$

where

$$k_{\text{eff}} = 2I(\sigma_1 + \sigma_2) \frac{k}{k_r} (1 - \beta) N + I\sigma_2 \frac{k^* (1 - \beta)}{k'_d (1 - \beta) + k''_d \beta} \quad (1)$$

where I is the light intensity, σ_1 and σ_2 are the absorption cross-sections of $\Pi(I_u) \leftarrow X^1 \Sigma_g^+$ and $B^3 \Pi(O_u^+) \leftarrow X^1 \Sigma_g^+$ transitions, which lead to Br₂ dissociation into two Br(²P_{3/2}) atoms and Br(²P_{3/2}) + Br*(²P_{1/2}), k and k* are the rate constants of the reactions Br(²P_{3/2}) + SiH₄ → HBr + SiH₃ and Br*(²P_{1/2}) + SiH₄ → HBr + SiH₃, k_r is the rate constant of heterogeneous recombination of Br(²P_{3/2}) atoms on the walls of the reaction vessel, k'_d and k''_d are the rate constants of Br*(²P_{1/2}) deactivation on Br₂ and SiH₄, N = [Br₂] + [SiH₄], β = [SiH₄]/N.

As is seen from eq. (1), k_{eff} depends linearly on N, the slope of the straight line being proportional to the rate constant of the Br(²P_{3/2}) reaction with SiH₄ and the intercept is proportional to that of Br*(²P_{1/2}). The experiments indicate that in the photolysis of a silane-bromine mixture under irradiation by λ = 365 nm light (no excited Br atoms, σ₂ = 0) the dependence of k_{eff} on N is linear and passes through zero (Fig. 1, 1). At λ = 436 nm, the straight line intercepts the Y-axis (Fig. 1, 2), which is associated with the Br*(²P_{1/2}) reaction.

To determine k from the experimental values of k_{eff}, it is necessary to determine the light intensity I, the absorption cross-sections σ₁ and σ₂ and the heterogeneous recombination rate constant of Br atoms, k_r. Light intensity was measured calorimetrically according to the heating rate of a black copper disc with a known heat capacity. The absorption cross-sections were taken from the literature /4, 5/.

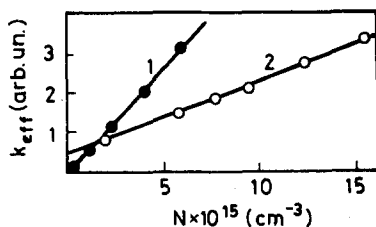


Fig. 1. Plot of k_{eff} vs. N at $T = 300$ K (1), $\lambda = 365$ nm, (2) $\lambda = 436$ nm

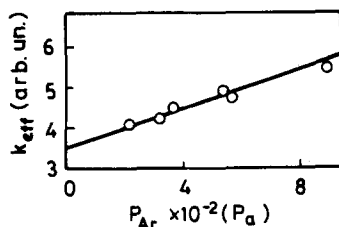


Fig. 2. Plot of k_{eff} vs. argon pressure at $T = 300$ K and $\lambda = 365$ nm

To determine k_r , we measured the SiH₄ photobromination rate at various argon pressures. Since

$$\frac{1}{k_r} = \frac{1}{k_{\text{kin}}} + \frac{1}{k_{\text{dif}}} = \frac{d}{\epsilon v} + \frac{d^2}{32D} \quad (2)$$

where k_{kin} and k_{dif} are the kinetic and diffusion recombination rate constants, d is the reactor diameter, v is the mean thermal velocity of Br atoms, ϵ is the Br recombination probability on the walls, D is the diffusion coefficient of Br in argon (inversely proportional to the argon pressure); the slope of the argon pressure vs. k_{eff} curve (Fig. 2) and the intercept are determined by the diffusion and kinetic constants, respectively. Assuming that the diameters of argon and bromine atoms are 3.48 and 3.60 Å, respectively /1/, one can determine the diffusion coefficient from the known equation /6/. The ratio of the slope to the intercept permits to calculate the Br recombination probability on the walls, $\epsilon = (1.4 \pm 0.8) \times 10^{-3}$, which is temperature independent within the range of 300–425 K and agrees fairly well with that reported in Ref. /16/. Knowing ϵ and D , the rate constant of

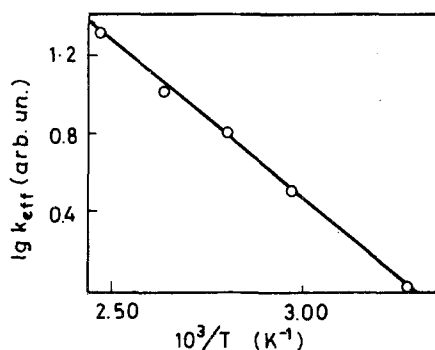


Fig. 3. Plot of $\log k_{\text{eff}}$ vs. T^{-1} at $\lambda = 365$ nm

heterogeneous Br recombination can be determined from eq. (2) at any temperature and pressure in the range studied.

Activation energy of the effective rate constant was determined by measuring the reaction rate at various temperatures. To determine the activation energy of the elementary reaction $\text{Br}^*(^2\text{P}_{3/2}) + \text{SiH}_4$, the value obtained should be correlated by two corrections associated with the temperature dependence of the Br absorption coefficient /1, 4, 5/ and with the temperature dependence of k_r . The temperature dependence of the rate constant in the Arrhenius coordinates taking into account these corrections is shown in Fig. 3. Activation energy of the elementary reaction $\text{Br}^*(^2\text{P}_{3/2}) + \text{SiH}_4$ determined from this plot in the temperature range of 300–415 K is 21.8 ± 2.5 kJ/mol. Using the values of I and σ , the rate constant for the reaction of $\text{Br}^*(^2\text{P}_{3/2})$ with SiH_4 is

$$k = 3.2 \times 10^{-11} \exp(-21.8 \pm 2.5)/RT \text{ (cm}^3/\text{s)} \quad (3)$$

Rate constant of the elementary reaction $\text{Br}^*(^2\text{P}_{1/2}) + \text{SiH}_4$ was determined from experimental data on SiH_4 photobromination under irradiation by 436 nm light (Fig. 1, 2). To determine it from eq. (1), one needs not only I and σ but also the rate constant of $\text{Br}^*(^2\text{P}_{1/2})$ relaxation on Br_2 and SiH_4 . The former is known and equal to 4.7×10^{-13} cm^3/s /7/. To estimate the relaxation rate of $\text{Br}^*(^2\text{P}_{1/2})$ on SiH_4 , k_{eff} was measured at various mixture compositions. It appeared that $\text{Br}^*(^2\text{P}_{1/2})$ relaxation on SiH_4 is slower than on Br_2 . Therefore, at the mixture composition $[\text{Br}_2] : [\text{SiH}_4] = 10$ used in our experiments (Fig. 1), $\text{Br}^*(^2\text{P}_{1/2})$ relaxation on SiH_4 can be neglected. When processed, the experimental data on

SiH₄ photobromination at $\lambda = 436$ nm afford the rate constant of the elementary reaction Br*(²P_{1/2}) + SiH₄ as $(3 \pm 1) \times 10^{-13}$ cm³/s, being temperature independent in the range of 300–415 K.

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