Remarkable Isotope Effect on the Hydrogen-atom Reaction in the Photolysis of D_2–H_2–HI Mixtures at 4 K. A Quantum-mechanical Tunneling Effect

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Synopsis. The photolysis of D_2–H_2–HI (0.05 mol%) mixtures has been studied at 4 K by means of ESR spectroscopy. The yield of D atoms decreases sharply upon the addition of a small amount of H_2, while the yield of H atoms increases. The results of the photolysis are similar to those in the radiolysis of D_2–H_2 mixtures at 4 K. The preferential formation of H atoms in the photolysis and radiolysis of the D_2–H_2 mixtures is due to the selective H-atom-abstraction reaction from H_2 by D atoms by means of a quantum mechanical tunneling.

Basic to any theory of the chemical kinetics of elementary reactions is an understanding of the simplest atom-diatomic exchange reaction. A number of experimental and theoretical studies of the reaction of H (or D) with $H_2(D_2)$ in the gas phase have been reported previously.[1] The previous studies, however, have been undertaken above room temperature. Thus, it was difficult to discriminate between the reaction caused by a quantum mechanical tunneling effect and the reaction which proceeds by passing over a potential energy barrier. In order to clarify the tunneling effect, the present author and his colleagues have recently studied the $H_2(D_2)$+H(D) reaction at extremely low temperatures, such as 4.2 and 1.9 K.[2,3]

When solid D_2–H_2 mixtures are irradiated by γ-rays at 4 K, the yields of the trapped D atoms in the radiolysis of D_2 decrease drastically upon the addition of a small amount of H_2, while the yields of trapped H atoms increase.[2] It has been suggested that the remarkable isotope effect on the formation of the D and H atom is to be ascribed to a selective hydrogen-atom reaction caused by a quantum-mechanical tunneling.[2] Since γ-irradiation produces different active species, the selective formation of H atoms in the γ-radiolysis of the D_2–H_2 mixtures may also be explained in terms of activation transfer, such as excitation, charge, and proton transfers, from D_2 to H_2.

In order to verify the remarkable isotope effect on the hydrogen-atom reaction, the reaction of hydrogen atoms produced by the photolysis of HI has been studied here in D_2–H_2 mixtures at 4 K.

Experimental

The H_2 was more than 99.999 mol% pure. The D_2 was more than 99.5 mol% pure. An aqueous solution of HI was vaporized and passed through P_2O_5 to prepare hydrogen iodide. Then, the hydrogen iodide was subjected to trap-to-trap sublimation on a vacuum line several times. The solid sample was made by the rapid cooling of gaseous hydrogen–hydrogen iodide mixtures in a sample tube from room temperature to 4 K. UV illumination was performed at 4 K with a low-pressure mercury lamp. The trapped hydrogen atoms in the irradiated samples were measured at 4 K with a JES-3BX ESR spectrometer at a microwave power level which does not result in the saturation of the signals of the atoms. The relative yields of the H and D atoms were obtained by double integration of the signals, which was performed with a personal computer system. The details of the experimental procedure and the power saturation of the ESR signals had been described in a previous paper.[4]

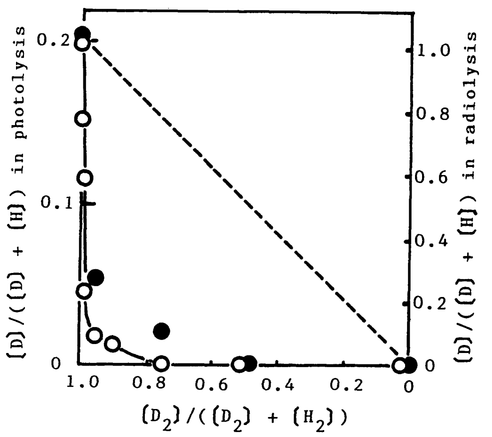

Fig. 1. Fractions of D atom yield in total hydrogen atom yield against fractions of D_2 in D_2–H_2 mixtures at 4 K: (●) D atoms in the UV photolysis of a D_2–H_2–HI(0.05 mol%) mixtures; (○) D atoms in the γ-radiolysis of the D_2–H_2 mixtures.

Results and Discussion

When pure D_2, pure H_2, and D_2–H_2 mixtures containing 0.05 mol% HI are UV-irradiated at 4 K, trapped D and/or H atoms can be observed by means of ESR spectroscopy at 4 K. Figure 1 shows the fraction of the trapped-D-atom yield in the total trapped-hydrogen-atom yield, denoted by closed circles, against a fraction of D_2 in the photolysis of the D_2–H_2–HI (0.05 mol%) mixtures at 4 K. The fraction of the trapped-D-atom yield in the radiolysis of the D_2–H_2 mixtures at 4 K is also shown by open circles. Since the total yields of the trapped D and H atoms are approximately constant over the whole range of D_2 fraction;[5] the D yields decrease sharply upon the addition of H_2, while the H yields increase complementarily. The results in the photolysis are roughly similar to those in the radiolysis. Since the ultraviolet light can be absorbed only by hydrogen iodide in the D_2–H_2–HI mixtures, the possibilities of the excitation, charge, and proton transfers from D_2 to H_2 can be discarded in the photolysis. Thus, the preferential formation of H atoms in the photolysis can be described by the following schemes of hydrogen-atom reactions:

$$HI \xrightarrow{h\nu} H^* + I \quad (1)$$

$$H^* + D_2(H_2) \longrightarrow HD(H_2) + D(H) \quad (2)$$
$$\searrow H \quad (3)$$

$$D + D_2 \longrightarrow D_2 + D \quad (4)$$

$$D + H_2 \longrightarrow HD + H \quad (5)$$

$$H + D_2 \longrightarrow HD + D \quad (6)$$

$$H + H_2 \longrightarrow H_2 + H \quad (7)$$

Hot H atoms (H*) are produced initially by the photolysis of HI. The hot atoms abstract hydrogen atoms from D_2(or H_2) to produce thermal D(or H) atoms (Reaction 2) or are thermalized to become H atoms (Reaction 3).[4] If the thermal D and H atoms do not react further at 4 K, and if the isotope effect on the hot-atom reaction (Reaction 2) is small, the fraction of the D-atom yields ([D]/([D]+[H])) may be represented by the dotted line in Fig. 1. The large isotope effect on the formation of D and H atoms in the photolysis indicates the secondary reactions of thermal D or H atoms in the D_2–H_2 mixtures at 4 K. All possible reactions of D(H) and $D_2(H_2)$ are represented in Reactions 4—7. Though these reactions have activation energies, the reaction may take place even at 4 K by means of quantum mechanical tunneling reaction.[2,3] Since Reactions 4 and 7 give the same products as the reactants, the large isotope effect is caused by the difference in rate constants between Reactions 5 and 6. Since Reaction 6 is slightly endothermic, the rate of this reaction may be very slow at 4 K.[2] D atoms produced by Reaction 2 react fast with H_2 to form H atoms, as was previously suggested by a theoretical calculation of a tunneling reaction.[3] Thus, it may be concluded that the preferential formation of H atoms in the photolysis and radiolysis of the D_2–H_2 mixtures is due to a selective H-atom-abstraction reaction from H_2 by D atoms.

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5) Though the total yields of hydrogen atoms are approximately constant in the radiolysis of the D_2–H_2 mixtures, the yields in the photolysis are affected by the experimental conditions, such as the cooling process, the sample preparation, and the UV irradiation conditions. Thus, the constancy of the total yields in the photolysis is poorer than that in the radiolysis.