H-D Isotope Effect in the Reaction of Hydrogen Radicals with Isopropyl Alcohol in 6M-H_2SO_4 in the Liquid and in the Glassy State

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Summary The kinetic isotope effect (k_H/k_D) for the hydrogen abstraction from $(CH_3)_2CHOH$ and $(CD_3)_2CDOH$ by hydrogen atoms in 6M-H_2SO_4 is 10·1 at 299°K, 18·1 at 253°K, and only 2·2 at 90°K, indicating that at 90°K the reaction is mainly diffusion controlled.

IN the radiolysis of aqueous solutions, hydrogen atoms are formed together with other reactive species, *i.e.* solvated electrons and OH radicals. In the presence of proton donors, additional hydrogen atoms are produced from solvated electrons (e^-_{solv}). The hydrogen atoms disappear either by combination or by reaction with other species present.

We have investigated the reactions of hydrogen atoms produced by the γ-irradiation of aqueous 6M-H_2SO_4 in the presence of 0·1 mole/l. isopropyl alcohol. The hydrogen α to the hydroxy-group of isopropyl alcohol is abstracted preferentially to yield H_2 (reaction 1). In the case of $(CD_3)_2CDOH$, HD should be produced *via* reaction (2).

$$H + (CH_3)_2CHOH \xrightarrow{k_H} H_2 + (CH_3)_2\dot{C}OH \qquad (1)$$

$$H + (CD_3)_2CDOH \xrightarrow{k_D} HD + (CD_3)_2\dot{C}OH \qquad (2)$$

When a mixture of $(CH_3)_2CHOH$ and $(CD_3)_2CDOH$ is used, there is competition for hydrogen atoms, and the H_2/HD ratio of the hydrogen formed can be used to determine the kinetic isotope effect (k_H/k_D) of reactions (1) and (2).

Two additional phenomena have to be considered in evaluating the kinetic isotope effect. First, there is an independent yield of H_2, the so-called "molecular hydrogen", which is not influenced by the addition of $(CD_3)_2$-CDOH. Secondly, hydrogen atoms will be abstracted from the hydroxy-group to give H_2 even in the presence of the deuteriated alcohol. Corrections for these additional H_2-yields have been made.[1]

With a temperature decrease from 299°K to 253°K, the isotope effect increases from 10·1 to 18·1. If the difference between k_H and k_D is caused by a different activation barrier for reactions (1) and (2), we can estimate this difference, ΔE, by using equation (3).

$$\Delta E = \boldsymbol{R}T \ln k_H/k_D \qquad (3)$$

Temperature dependence of the kinetic isotope (k_H/k_D) *for reactions* (1) *and* (2)

T (°K)	k_H/k_D	ΔE(kcal./mole) eqn. (3)
299	10·1 ± 0·3	1·33 ± 0·15
253	18·1 ± 1·5	1·44 ± 0·15
90	2·2 ± 0·3	(0·139)

The values in Table 1 show that, within the limits of experimental error, the difference of the activation energies remains unchanged at 299 and 253° K, whereas the ratio k_H/k_D is almost doubled. If the mechanism of reactions (1) and (2) is unchanged over the whole temperature range, a value of $k_H/k_D = 2850$ would be expected at 90°K.

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However, the experimental value at this temperature was 2·2. We have shown[2] that the reaction of hydrogen atoms is diffusion-controlled in these low-temperature glasses. It is not the activation energy of the chemical reaction, but the activation energy of diffusion of hydrogen atoms (6·5 ± 0·5 kcal./mole) that controls the kinetics. If the activation energies for reactions (1) and (2) are lower than the activation energy for the diffusion, we should expect $k_H/k_D = 1{\cdot}0$. The probabilities of the reactions (1) and (2) then become practically equal. From the experimental value at 90°K it follows that reaction (1) is still preferred to reaction (2). This means that some of the hydrogen atoms encountering $(CD_3)_2CDOH$ molecules do not react, but diffuse away. The activation energy of reaction (1) in the gas phase has been reported[3] to be about 6 kcal./mole. If the activation barrier is further raised by about 1·3 kcal./mole as a result of substitution of D for H, then reaction (2) is not necessarily a pure diffusion-controlled reaction. We assume that this is the reason why we obtain a value greater than 1·0 for k_H/k_D at 90°K.

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