

H-D Isotope Effect in the Reaction of Hydrogen Radicals with Isopropyl Alcohol in 6M-H₂SO₄ in the Liquid and in the Glassy State

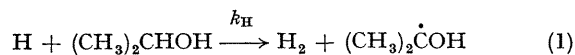
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Summary The kinetic isotope effect (k_H/k_D) for the hydrogen abstraction from (CH₃)₂CHOH and (CD₃)₂CDOH by hydrogen atoms in 6M-H₂SO₄ is 10.1 at 299°K, 18.1 at 253°K, and only 2.2 at 90°K, indicating that at 90°K the reaction is mainly diffusion controlled.

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-H₂SO₄ 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 H₂ (reaction 1). In the case of (CD₃)₂CDOH, HD should be produced *via* reaction (2).



When a mixture of (CH₃)₂CHOH and (CD₃)₂CDOH is used, there is competition for hydrogen atoms, and the H₂/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 H₂, the so-called "molecular hydrogen", which is not influenced by the addition of (CD₃)₂CDOH. Secondly, hydrogen atoms will be abstracted from the hydroxy-group to give H₂ even in the presence of the deuteriated alcohol. Corrections for these additional H₂-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).

$$\Delta E = RT \ln k_H/k_D \quad (3)$$

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 shown² 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 $k_H/k_D = 1.0$. 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 reported³ 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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¹ K. Vacek and C. von Sonntag, to be published.

² K. Vacek and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1968, **72**, 2686.

³ K. T. Organesyan and A. B. Nalbandyan, *Trudy Akad. Nauk Armyan. S.S.R., Khim. Nauki*, 1965, **18**, 237.