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Hydrogen Isotope Effect on the Radical Addition of the Hydrogensulfite Ion to Allyl Alcohol in Aqueous Solutions

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A study of the radiation-induced addition of HSO_3^- to allyl alcohol was carried out in D_2O–H_2O mixtures. It was found that a linear relationship held between the apparent rate constant of $NaHSO_3$ consumption and the atom fraction of deuterium in the mixture, and that the hydrogen atom abstraction from HSO_3^- by $HOCH_2\dot{C}HCH_2SO_3^-$ was the rate-determining step. The kinetic isotope effect of this abstraction was 4.38.

In a previous paper,[1] we proposed the following mechanism for the radiation-induced addition of the hydrogensulfite ion (HSO_3^-) to allyl alcohol in aqueous solutions:

Initiation,

$$A + HSO_3^- \longrightarrow AH + \dot{S}O_3^-, \tag{1}$$

Propagation

$$\dot{S}O_3^- + CH_2{=}CHCH_2OH \longrightarrow HOCH_2\dot{C}HCH_2SO_3^-, \tag{2}$$

$$HOCH_2\dot{C}HCH_2SO_3^- + HSO_3^- \longrightarrow HOCH_2CH_2CH_2SO_3^- + \dot{S}O_3^-, \tag{3}$$

Termination

$$HOCH_2\dot{C}HCH_2SO_3^- + CH_2{=}CHCH_2OH \longrightarrow HOCH_2CH_2CH_2SO_3^- + CH_2{=}CH\dot{C}HOH, \tag{4}$$

where A represents the active species which contribute to the initiation. This addition reaction involves the hydrogen abstraction from HSO_3^- represented by Eq. 3. It follows, then, that a hydrogen isotope effect may be found if this abstraction reaction is the rate-determining step.[2]

The present study was undertaken to get direct evidence for the rate-determining step by means of the determination of the hydrogen isotope effect of the addition reaction. The reaction system employed was radiation-induced addition in D_2O–H_2O mixtures of various D_2O concentrations. The determination was made possible by finding the relationship between the atom fraction of deuterium in the mixture and the over-all rate constant of sodium hydrogensulfite consumption.

Experimental

The D_2O (Shōwa Denkō, 99.75 mol% D_2O) used was distilled twice under an atomosphere of nitrogen: first in the presence of a trace of potassium permanganate acidified with sulfuric acid and then in the absence of additives. The H_2O used was redistilled before use. The other reagents used were similar to those described previously.[1]

Solutions were prepared by dissolving 0.25 mol/l of Na_2SO_3, 0.50 mol/l of $NaHSO_3$, and 1.47 mol/l of allyl alcohol in D_2O–H_2O mixtures containing up to 100% of D_2O.

The irradiation vessel and analytical procedure used in this work were analogous to those described previously.[1] The pH measurements were carried out using a Tōa Denpa Model HM-5A pH meter with ordinary glass electrodes. The standardization of the pH meter in water solutions was made with conventional buffer solutions of an appropriate acidity. A 3450-curie Co-60 γ-source was used, and the dose rate was determined by the Fricke dosimeter in light water, taking $G(Fe^{3+})=15.6$.

Results and Discussion

Rate-determining Step. In aqueous solutions, $NaHSO_3$ dissociates into Na^+ and HSO_3^-, which is in equilibrium with the hydrogen ion, in the following two ways:

$$HSO_3^- \rightleftarrows H^+ + SO_3^{2-}, \tag{5}$$

$$HSO_3^- + H^+ \rightleftarrows H_2SO_3. \tag{6}$$

Accordingly, DSO_3^- is formed in D_2O instead of HSO_3^- being formed in H_2O. In the D_2O–H_2O mixture, a part of the HSO_3^- is assumed to be displaced with DSO_3^- in proportion to the D_2O concentration in the mixture.

The total G-value of the active species, A, produced from the radiolysis of D_2O is reported to be slightly higher than that from H_2O.[3] The concentration of DSO_3^- in D_2O can be estimated to be higher than that of HSO_3^- in H_2O since weak acids are less dissociated in D_2O than in H_2O.[4] These facts lead to the assumption that the rate of $NaHSO_3$ consumption may be greater in the D_2O–H_2O mixtures than in H_2O.

In order to evaluate the effects of D_2O on the addition reaction, the solutions were irradiated by Co-60 γ-rays at a dose rate of 8.45×10^{15} eV/cm^3 s and at room temperature. The conversion of $NaHSO_3$ decreased with the increase in the atom fraction of deuterium in the mixture, as is shown in Fig. 1. This result disagrees with the above assumption.

The addition reaction involves DSO_3^- as well as HSO_3^- in the D_2O–H_2O mixtures, as is represented in

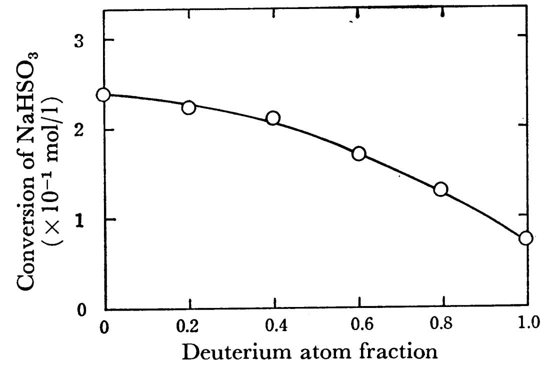


Fig. 1. Conversion of $NaHSO_3$ as a function of deuterium atom fraction in the mixture.

Eqs. 1 and 3, where the hydrogen-atom abstraction from these ions takes place. The hydrogen-atom abstraction causes an appreciable isotope effect.[2] On the basis of these findings, it is reasonable to assume that the above disagreement results from the isotope effect of these hydrogen-atom abstractions.

Reaction 1 plays a minor role in the isotope effect because most of the species formed in other reactions which involve A can initiate the addition reaction.[1] On the other hand, Reaction 3 involves $HOCH_2\dot{C}HCH_2SO_3^-$, which takes part both in the propagation shown by Reactions 2 and 3 and in the termination shown by Reaction 4. In addition, the chain length of the addition reaction is as large as 344,[1] and it is susceptible to small changes in the rate of Reaction 3 provided this reaction is the rate-determining step of the propagation. Consequently, it can be assumed that Reaction 3 is the rate-determining step of the propagation and mainly causes the isotope effect.

Total Concentration of HSO_3^- and DSO_3^- in D_2O–H_2O Mixtures. The concentration of HSO_3^- in an aqueous $NaHSO_3$ solution containing Na_2SO_3 at pH 5—7 is given by[1]

$$[HSO_3^-] = \frac{[NaHSO_3]+[Na_2SO_3]}{1+(K_5/a_H)(f_{HSO_3^-}/f_{SO_3^{2-}})}, \tag{7}$$

where $[NaHSO_3]$ and $[Na_2SO_3]$ are the initial concentrations of $NaHSO_3$ and Na_2SO_3; K_5, the dissociation constant of HSO_3^-; a_H, the activity of the hydrogen ion; and $f_{HSO_3^-}$ and $f_{SO_3^{2-}}$, the activity coefficients of HSO_3^- and SO_3^{2-}.

The dissociation constant of a weak acid in a D_2O–H_2O mixture is expressed by[5] Eq. 8:

$$K_N = K_H\frac{0.302n^3+1.37n^2(1-n)+2.04n(1-n)^2+(1-n)^3}{(1-n)+0.302(K_H/K_D)n}, \tag{8}$$

where K_N, K_H, and K_D refer to the dissociation constants of the weak acid in the D_2O–H_2O mixture, H_2O, and D_2O respectively, and where n is the atom fraction of deuterium in the mixture. In the case of HSO_3^- as the weak acid, K_H/K_D in Eq. 8 can be estimated to be 3.68 from the relationship[4] between K_H/K_D and $-\log K_H$, in which the K_H for HSO_3^- is 1.02×10^{-7}.[6] Substituting these values into Eq. 8, we obtain the K_N values shown in Table 1.

Table 1. Dissociation constants of HSO_3^-[a] in D_2O–H_2O mixtures

n[b]	0	0.2	0.4	0.6	0.8	1.0
$K_N\times10^8$	10.2	8.18	6.46	5.00	3.78	2.77

a) HSO_3^- at $n=0$, DSO_3^- at $n=1$, and the mixture of HSO_3^- and DSO_3^- at n 0.2 to 0.8. b) The atom fraction of deuterium in the mixture.

Using electrodes standardized for H_2O solutions, the pL, the generalized equivalent of pH (where L includes all the isotopically different hydrogen ions), in a mixture of the deuterium atom fraction of n is given by pL= (meter reading)$+0.40n$.[7] In addition, since the dielectric constant of D_2O is very close to that of H_2O,[8] it may be assumed that $f_{HSO_3^-}/f_{SO_3^{2-}}$ ratio is equal to that of $f_{DSO_3^{2-}}/f_{SO_3^{2-}}$ and that these ratios are independent of the atom fraction of deuterium in the mixture. Hence, the value of 1.468[1] can be used as $f_{HSO_3^-}/f_{SO_3^{2-}}$ in Eq. 7 at the concentrations of 0.25 mol/l of Na_2SO_3 and 0.50 mol/l of $NaHSO_3$ in the D_2O–H_2O mixtures. Substituting these values into Eq. 7, we obtain the total concentration of HSO_3^- and DSO_3^-, $[\mathbf{HSO_3}^-]$, in the D_2O–H_2O mixtures (Table 2). As can be seen in Table 2, the total concentration increased slightly with the increase in the atom fraction of deuterium in the mixture.

Table 2. Total concentrations of HSO_3^- and DSO_3^-, $[\mathbf{HSO_3}^-]$, in D_2O–H_2O mixtures

n[a]	pH_{obs}	pH_{corr}	$[\mathbf{HSO_3}^-]$ (mol/l)	$[\mathbf{HSO_3}^-]$[b]/$[NaHSO_3]$
0	6.48	6.48	0.516	1.03
0.2	6.40	6.48	0.550	1.10
0.4	6.41	6.57	0.555	1.11
0.6	6.40	6.64	0.568	1.14
0.8	6.46	6.78	0.562	1.12
1.0	6.50	6.90	0.567	1.13

a) The atom fraction of deuterium in the mixture.
b) The concentration ratio between $\mathbf{HSO_3}^-$ and the initial $NaHSO_3$.

Rate Constant in D_2O–H_2O Mixtures. The rate equation for the addition of HSO_3^- to allyl alcohol in an aqueous solution is expressed by[1]

$$-\frac{d[NaHSO_3]}{dt} = \frac{gIk_3[HSO_3^-]}{100k_4[\text{Allyl Alcohol}]}, \tag{9}$$

where g is the G-value of A; I, dose rate (eV/cm^3 s); k_3 and k_4, the rate constants for Reactions 3 and 4 respectively; and [Allyl Alcohol], the concentration of allyl alcohol. Equation 9 can be rewritten as

$$-\frac{d[NaHSO_3]}{dt} = \frac{gIk_3}{100k_4}\cdot\frac{[HSO_3^-][NaHSO_3]}{[NaHSO_3][\text{Ally Alcohol}]}. \tag{10}$$

Since the $[HSO_3^-]/[NaHSO_3]$ ratio is independent of the concentration of $NaHSO_3$ in H_2O,[1] the $[\mathbf{HSO_3}^-]/[NaHSO_3]$ ratio may also be assumed to be independent of the concentration of $NaHSO_3$ in the D_2O–H_2O mixtures. However, this ratio depends on the atom fraction of deuterium in the mixture, as is apparent from Table 2. The conversion of $NaHSO_3$ is equal to that of allyl alcohol.[1] Hence, the rate equation in the D_2O–H_2O mixtures is derived as:

$$\frac{dx}{dt} = \alpha k_n\cdot\frac{(a-x)}{(b-x)}, \tag{11}$$

where

$$k_n = \frac{gIk_3}{100k_4}, \tag{12}$$

$\alpha=[\mathbf{HSO_3}^-]/[NaHSO_3]$ at a concentration of D_2O given by the n of the atom fraction of deuterium, a and b are the initial concentrations of $NaHSO_3$ and allyl alcohol respectively, and x is the concentration of $NaHSO_3$ that reacts in time t. The integration of Eq. 11 yields

$$k_n = \frac{1}{\alpha t}\left\{(b-a)\ln\left(\frac{a}{a-x}\right)+x\right\}, \tag{13}$$

from which k_n can be obtained by substituting the values presented in Fig. 1 and Table 2. Table 3 presents the k_n values thus obtained.

Kinetic Hydrogen Isotope Effect. Taking the ratio

TABLE 3. OVER-ALL RATE CONSTANTS FOR THE ADDITION OF HSO^-_3 TO ALLYL ALCOHOL IN D_2O–H_2O MIXTURES

n[a)]	0	0.2	0.4	0.6	0.8	1.0
$k_n \times 10^4$ (mol/l s)	2.30	1.99	1.88	1.38	1.05	0.554

a) The atom fraction of deuterium in the mixture.

of k_n given by Eq. 12 for H_2O to that for the D_2O–H_2O mixture leads to the following equation:

$$\frac{k_H}{k_n} = \frac{g_H I_H k_{3H} k_{4n}}{g_n I_n k_{3n} k_{4H}}, \tag{14}$$

where the subscripts H and n refer to the values for H_2O and those for the D_2O–H_2O mixture respectively. Equation 14 can be simplified as

$$\frac{k_H}{k_n} = \frac{g_H k_{3H}}{g_n k_{3n}}, \tag{15}$$

since it can be assumed that I_H/I_n is nearly unity, because the electron density is nearly equal in both H_2O and D_2O, and since there are no solvent effects on Reaction 4.

The radiation-induced addition of HSO_3^- to allyl alcohol in aqueous solutions is initiated by the active species, the hydrogen atom, the hydroxyl radical, and the hydrated electron, produced from the radiolysis of water.[1)] Hence, g in Eq. 12 is assumed to be equal to the sum of the G-values of these three active species. At pH about 6, g_H is 5.20 and the g for D_2O, g_D, is 5.48,[3)] while no precise value of g_n is known. Since the formation of ions and excited molecules will occur in the same pattern in both H_2O and D_2O,[9)] it is reasonable to assume that g_n is $g_H+(g_D-g_H)n$. Using these values and the k_n values given in Table 3, we can obtain $k_n(g_H/g_n)$.

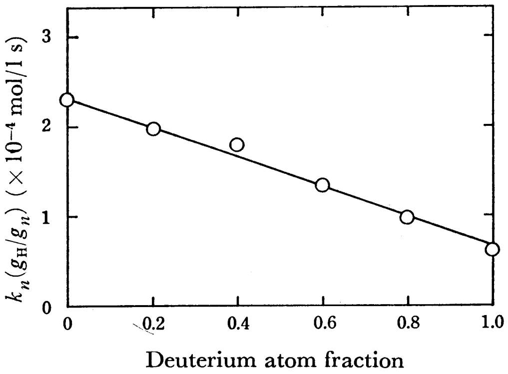
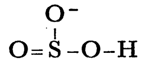


Fig. 2. k_n (g_H/g_n) as a function of deuterium atom fraction in the mixture.

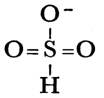
Figure 2 shows the plot of $k_n(g_H/g_n)$ against n. It is apparent from this figure that a good linear relationship holds between these terms. This means that the magnitude of the kinetic isotope effect of Reaction 3 is equal to k_{3H}/k_{3D}, which can be calculated from the k_H, k_D, g_H, and g_D values. According to Eq. 15, k_{3H}/k_{3D} is 4.38 at the dose rate of 8.45×10^{15} eV/cm^3 s since $k_H = 2.30 \times 10^{4}$ mol/l s, $k_D = 0.554 \times 10^{-4}$ mol/l s, $g_H = 5.20$, and $g_D = 5.48$. Similar values of 4.46 and 4.41 were obtained at the dose rate of 1.35×10^{16} eV/cm^3 s and 1.69×10^{16} eV/cm^3 s. Thus, the kinetic isotope effect is independent of the dose rate.

It has been reported[10)] that there are two isomeric forms of HSO_3^-, (I) and (II), in aqueous solutions:



$$\mathrm{O{=}\overset{\displaystyle O^-}{\overset{|}{S}}{-}O{-}H}$$

(I)



$$\mathrm{O{=}\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle O^-}{\overset{|}{S}}}}{=}O}$$

(II)

This means that two types of hydrogen-atom abstraction should be taken into account; one is the abstraction from the O–H bond, and the other is that from the S–H bond.

Since the stretching vibration of O–H is higher than that of S–H, it seems reasonable to predict that a greater isotope effect is found in the former case than in the latter case. In fact, a value of about 8 for the isotope effect has been reported at 30 °C in the hydrogen-atom abstraction by 2,2-diphenyl-1-picrylhydrazyl (DPPH) from the O–H bond in such phenols as 2,6-di-*t*-butyl phenol and 4-bromophenol,[11)] while the value of 5.4 has been reported for a similar abstraction by the same radical from the S–H bond in benzenethiol at 25 °C.[12)] The kinetic isotope effect found in the hydrogen-atom abstraction from HSO_3^- is closer to that for benzenethiol than for phenols.

The simplest interpretation of the kinetic isotope effects[2)] is based on the assumption that, on passing from the reactants to the transition state, the zero-point energy associated with the stretching vibration of the bond which is concerned in the abstraction is lost. It is thus predicted that

$$k_H/k_D = \exp{(\Delta E_0/RT)}, \tag{16}$$

where ΔE_0 is the difference between the zero-point energy of the bond attached to deuterium and that attached to hydrogen.

The S–H stretching vibration of $HS_2O_5^-$ in an aqueous $K_2S_2O_5$ solution is 2532 cm^{-1}, while the S–D stretching vibration of $DS_2O_5^-$ in the D_2O solution of $K_2S_2O_5$ is 1843 cm^{-1}.[10)] Hence, Eq. 16 becomes

$$k_H/k_D = \exp{(985/RT)}. \tag{17}$$

At 25 °C, according to Eq. 17, k_H/k_D is 5.3, which is comparable with the kinetic isotope effect ($k_H/k_D = 5.4$) for the hydrogen-atom abstraction from benzenethiol described above.

According to the theory of a three-center transition-state model,[13)] the magnitude of the primary isotope effect in a hydrogen-transfer reaction varies with the symmetry of the transition state, which depends on the nature of the substrate and that of the acceptor of the hydrogen. For the determination of the hydrogen-abstraction reaction in the rate-determining step, more work is clearly needed.

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