CHEMISTRY LETTERS, pp. 367-370, 1975. Published by the Chemical Society of Japan

HYDROGEN ISOTOPE EFFECT ON RADICAL ADDITION REACTION OF SODIUM HYDROGENSULFITE TO ALLYL ALCOHOL

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The radical addition reaction of sodium hydrogensulfite to allyl alcohol in D_2O solution was investigated. The hydrogen isotope effect was found to be 4.11. This effect is attributed to the hydrogen atom abstraction of $HOCH_2\dot{C}HCH_2SO_3^-$ radical ion from hydrogensulfite ion.

In a previous paper,[1)] the reaction mechanism on the radiation-induced addition reaction of sodium hydrogensulfite to allyl alcohol in aqueous solution was proposed as follows:

$$A + HSO_3^- \longrightarrow AH + \cdot SO_3^- \qquad (1)$$

$$\cdot SO_3^- + CH_2{=}CHCH_2OH \longrightarrow HOCH_2\dot{C}HCH_2SO_3^- \qquad (2)$$

$$HOCH_2\dot{C}HCH_2SO_3^- + HSO_3^- \xrightarrow{k_3} HOCH_2CH_2CH_2SO_3^- + \cdot SO_3^- \qquad (3)$$

$$HOCH_2\dot{C}HCH_2SO_3^- + CH_2{=}CHCH_2OH \xrightarrow{k_4} HOCH_2CH_2CH_2SO_3^- + CH_2{=}CH\dot{C}HOH \qquad (4)$$

and the apparent rate constant of sodium hydrogensulfite conversion was expressed by

$$k = gI_o \ X \ \frac{k_3}{k_4} \qquad (5)$$

where A, g, and I_o represent the intermediate radicals participating in the initiation of the addition reaction, G-value of A, and dose rate, respectively.

The mechanism involves the abstraction of a hydrogen atom from hydrogensulfite ion. Replacement of the hydrogen atom of hydrogensulfite ion by a deuterium atom should result in the decrease of the rate of hydrogen abstraction. Therefore, it is reasonable to expect that the hydrogen isotope effect for hydrogensulfite ion, HSO_3^- or DSO_3^-, would be observed in the addition reaction. When sodium hydrogensulfite is dissolved in D_2O, deuterohydrogensulfite ion DSO_3^- is formed instead of HSO_3^- in H_2O. Therefore, the hydrogen isotope effect can be determined by using D_2O as solvent.

On the other hand, the concentration of DSO_3^- ion in D_2O may be larger than that of HSO_3^- ion in H_2O because the dissociation constant of DSO_3^- ion in D_2O would be smaller than that of HSO_3^- ion in H_2O.$^{2)}$ As a result, it might be assumed that the conversion of sodium hydrogensulfite in D_2O is larger than that in H_2O.

The aim of this work is to investigate the extent of the hydrogen isotope effect and to elucidate the reaction step responsible for this effect.

In the present study, sodium hydrogensulfite was dissolved in both D_2O and H_2O-D_2O mixture. After irradiation with Co-60 γ-rays the unreacted sodium hydrogensulfite was determined gravimetrically as barium sulfite. The conversion of sodium hydrogensulfite decreased with increasing deuterium atom fraction. A plot of the conversion of sodium hydrogensulfite against deuterium atom fraction is shown in Fig. 1. It is considered that there is little solvent isotope effect in the addition reaction. Accordingly, the hydrogen isotope effect observed is suggested to be due to the abstraction of a hydrogen atom from hydrogensulfite ion in reaction (1) and/or (3).

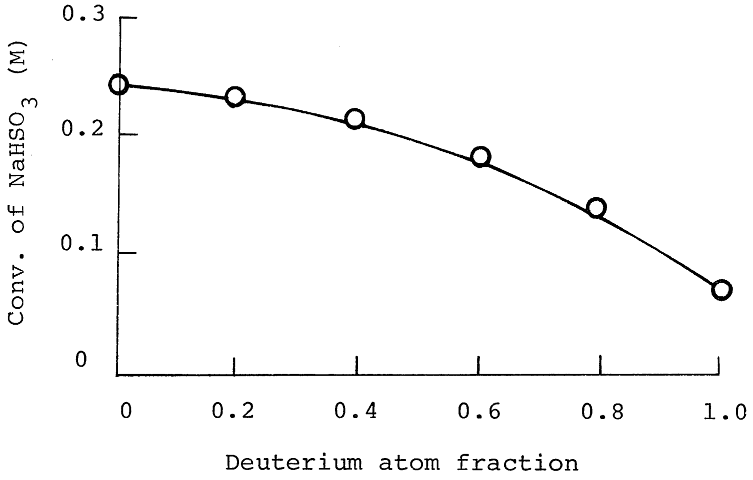

Fig.1. Plot of conv. of $NaHSO_3$ vs. deuterium atom fraction.

$NaHSO_3$: 0.50 M, Na_2SO_3: 0.25 M

Allyl alcohol: 1.47 M

Dose rate: 5.06 X 10^{17} eV/g·min

Dose: 3.04 X 10^{19} eV/g

The ·OH radical produced in the radiolysis of water, the most probable active species in reaction (1), adds predominantly to the carbon-carbon double bond of allyl alcohol.$^{3)}$ Since the rate constant of reaction (3) is much higher than that of reaction (4),$^{1)}$ the intermediate radical resulted from the addition of ·OH radical to the double bond of allyl alcohol is expected to abstract a hydrogen atom much more rapidly from hydrogensulfite ion than from allyl alcohol. Consequently, it is reasonable to presume that the extent of the hydrogen isotope effect observed is essentially that of the isotope effect in reaction (3).

From Eq. (5), the ratio of the apparent rate constant of sodium hydrogensulfite in H_2O to that in D_2O is expressed as follows:

$$\frac{k_{H_2O}}{k_{D_2O}} = \frac{g_{H_2O}\ I_o}{g_{D_2O}\ I_o} \times \frac{k_{3\ H_2O}}{k_{3\ D_2O}} \times \frac{k_{4\ D_2O}}{k_{4\ H_2O}} \qquad (6)$$

The ratio $k_{4\ D_2O}/k_{4\ H_2O}$ takes a value very close to 1 because of little solvent isotope effect in reaction (4). The ratio g_{H_2O}/g_{D_2O} is calculated to be 0.93 since it is reasonable to deduce that the ratio of the concentration of A_{H_2O} to that of A_{D_2O} is practically equal to the ratio of the total yield of active species produced in the radiolysis of H_2O to that of D_2O.[4] Therefore, Eq. (6) may be expressed in terms of the rate constant ratio of reaction (3) between in H_2O and D_2O.

$$\frac{k_{H_2O}}{k_{D_2O}} = 0.93 \times \frac{k_{3\ H_2O}}{k_{3\ D_2O}} \qquad (7)$$

The apparent rate constant of sodium hydrogensulfite, k_{D_2O}, in D_2O can be obtained, similar to k_{H_2O},[1] by using the concentration of deuterohydrogensulfite ion, which is calculated from its dissociation constant K estimated from the application of the theory on the dissociation constant of weak acid in H_2O-D_2O mixture[5] and the activity coefficient ratio, $f_{SO_3^{2-}}/f_{HSO_3^-} = 0.681$, obtained in H_2O.[1] The values used for the calculation of the apparent rate constant are listed in Table 1.

Table 1. Comparison of the apparent rate constant, k_{H_2O} and k_{D_2O}

Solvent	pH_o	pH	K	$[HSO_3^-]$	k, $M\cdot sec^{-1}$
D_2O	6.50	6.90	0.277×10^{-7}	0.519	0.605×10^{-4}
H_2O	6.36	6.36	1.020 "	0.515	2.31 "

where pH_o is the reading of the pH meter, pH, the corrected value of the " pH meter reading" with the 0.40 pH unit in D_2O solution,[6] and $[HSO_3^-]$, the concentration of hydrogensulfite ion. Therefore, the extent of the hydrogen isotope effect in reaction (3) was calculated to be 4.11 instead of the experimental value of 3.77 obtained from Fig. 1. The hydrogen isotope effect was independent of dose rate under our experimental conditions as is summarized in Table 2. This is close to the value of the isotope effect in the C - H bond scission by some radicals.[7]

The details of the isotope effect at various concentrations of deuterohydrogensulfite ion will be described elsewhere.

Table 2. Hydrogen isotope effect at various dose rates

Dose rate, eV/g·min	k_{H_2O}, $M\cdot sec^{-1}$	k_{D_2O}, $M\cdot sec^{-1}$	$k_{3\ H_2O}/k_{3\ D_2O}$
5.06×10^{17}	2.31×10^{-4}	0.605×10^{-4}	4.11
8.10 "	4.74 "	1.22 "	4.18
1.00×10^{18}	6.23 "	1.62 "	4.14

Irradiation time: 60 min

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(Received February 4, 1975)