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pH Effects on the Radical Addition of Hydrogensulfite Ion to Olefins

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The competitive addition of sodium hydrogensulfite to allyl and 2-methylallyl alcohols was investigated at the pH range from 3 to 5. The relative reactivity of allyl alcohol to 2-methylallyl alcohol decreased with increasing pH. Sulfite radical ion was mainly participating in the addition at pH 5, and hydrogensulfite radical at pH 3. From the kinetic analysis of the pH dependence, the ratio of reactivities of allyl alcohol and 2-methylallyl alcohol toward sulfite radical ion was 0.213, and the same ratio toward hydrogensulfite radical was 0.305. Further, the ratio of reactivities of hydrogensulfite radical and sulfite radical ion toward allyl alcohol was 1.32, and the same ratio toward 2-methylallyl alcohol was 0.927. The dissociation constant of hydrogensulfite radical was the order of 3×10^{-5} ($pK_a=4.5$).

It is well known that the addition reaction of hydrogensulfite ion on α,β-unsaturated bonds conjugated with a functional group such as carbonyl, cyano or nitro group proceeds with an ionic mechanism and produces 1-alkanesulfonates in accord with a simple Michael addition product.[1,2] In the ionic addition, the kinetics and the pH dependence have been extensively investigated.[3,4]

On the other hand, the addition reaction of hydrogensulfite ion to non-conjugated α,β-unsaturated bonds is known to proceed with a radical mechanism and to give products of the anti-Markownikoff character as a main product.[5] Since 1-alkanesulfonates have good surfactant properties and excellent biodegradability,[6] the synthetic reaction initiated by dissolved oxygen,[7] by added free radical agents[8] or by ultraviolet light[9] has been extensively studied, though the kinetics and the adding species are still insufficiently investgated.

In general, sulfite radical ion has been postulated to be the adding species as a chain carrier,[5] but the eleectrically neutral hydrogensulfite radical[10] must be taken into account as the acidity of the solution is increased.

In previous papers, we investigated the kinetics and the hydrogen isotope effect on the radiation-induced addition of sodium hydrogensulfite to allyl alcohol[11,12] and 1-dodecene,[13] in which the sulfite radical ion was postulated as an adding species, but the exact nature of the adding species was not established.

In the present work, allyl and 2-methylallyl alcohols were employed as water soluble olefins for the competitive addition of sodium hydrogensulfite by the photolysis, and the effects of pH and sodium chloride were investigated. From comparison of the ratio of the reactivities of these olefins, some information on the adding species was obtained.

Experimental

Materials. Hydroquinone, sodium hydrogensulfite, and sodium chloride were of GR grade, and no further purification was made. Allyl and 2-methylallyl alcohols of GR grade were refluxed with 2,4-dinitrophenylhydrazine for a few hours and then distilled twice under atmospheric pressure. The purification of water used was performed by distillation.[11]

Preparations of Solutions. Allyl and 2-methylallyl alcohols, and sodium hydrogensulfite were dissolved in the Sörensen solution. Concentrations of allyl and 2-methylallyl alcohols, and sodium hydrogensulfite were 0.439, 0.355, and 0.384—0.480 mol/l, respectively. The ionic strength of the solutions was 1.22 except the case of the solutions including sodium chloride.

pH Range. Figure 1 shows the distribution of ion species of sulfite–hydrogensulfite reagent, which was calculated from the dissociation constant of sulfurous acid.[14] In this work, the pH of the solutions was varied from 3 to 5. The pH value was measured with a TOA HM-18B Digital pH meter.

Irradiation. The reaction vessel was a cylindrical quartz flask fitted with a gas delivery tube which nearly reached to the bottom of the vessel, through which a fairly slow stream of oxygen was supplied during the irradiation. A 30 watt low pressure mercury lamp employed (Rikō-Kagaku UVL-30 LQ) was centered in the reaction vessel. The solution was irradiated at 25 °C for 20 min.

Identification. Allyl and 2-methylallyl alcohols remained in the solution were determined by using a gas chromatograph (Yanagimoto Model G-80) equipped with a flame ionization detector, a thermal conductivity detector, and a 2 m glass column packed with 60—80 mesh Celite 545 coated with 30% Silicone DC 550. 2-Chloroethanol was used as an internal standard.

Conversions of Olefins. The sample solution was irradiated such that from 10 to 40% of 2-methylallyl alcohol was consumed at pH 3.50. In this case, the ratio of conversions of allyl and 2-methylallyl alcohols was independent of the per cent of these olefins consumed. Thus, in this work, about 9% of allyl alcohol and 34% of 2-methylallyl alcohol were consumed.

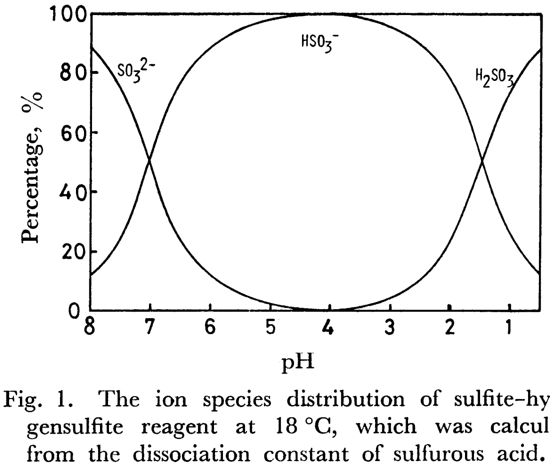


Fig. 1. The ion species distribution of sulfite–hydrogensulfite reagent at 18 °C, which was calculated from the dissociation constant of sulfurous acid.

Results

Competitive additions were performed with runs in duplicate at least. The extent of reaction, that is, the per cent of olefins consumed during a given time of irradiation was not a quite reproducible quantity. It is presumably ascribable to that the chain process by which hydrogensulfite ion adds to olefins is quite susceptible to irradiation time and to trace impurities which can serve as initiators or retardants. However, the ratio of conversions of allyl and 2-methylallyl alcohols was a reproducible quantity at any pH.

The relative reactivity of allyl alcohol (I) to 2-methylallyl alcohol(II) was calculated from the following expression:

$$\text{Relative reactivity} = \frac{(\text{moles of I consumed})/(\text{moles of I initially})}{(\text{moles of II consumed})/(\text{moles of II initially})}$$

The quantity of the relative reactivity was independent of the change from 1.2 to 2.3 in the ratio of the initial concentrations of allyl and 2-methylallyl alcohols.

A plot of the relative reactivity to pH is shown in Fig. 2. As pH was increased, the relative reactivity which remained constant up to about pH 3 decreased gradually and then reached a limiting value above pH 5. The sum of conversions of allyl and 2-methylallyl alcohols at pH 3.07 was 0.162 mol/l and that at pH 4.92 was 0.160 mol/l (Table 1).

Plots of the relative reactivity against the concentration of sodium chloride are shown in Fig. 3. No change of the relative reactivity was observed at pH 2.90. However, the relative reactivity decreased from 0.269 to 0.193 with increasing sodium chloride at pH 4.54. In this case, conversion of 2-methylallyl alcohol increased with increasing sodium chloride; on the other hand, conversion of allyl alcohol remained constant.

Table 1 shows the effect of hydroquinone on conversions of allyl and 2-methylallyl alcohols at pH's 2.90 and 4.54. The solution was added with 2.70×10^{-2} mol/l of hydroquinone and irradiated for 120 min. No consumptions of allyl and 2-methylallyl alcohols were observed in the presence of hydroquinone regardless of the change of pH. Table 1 also shows that the variation of pH in the solution is slight during the irradiation.

Discussion

There is the possibility of the reactions between allyl alcohol and the species $HOCH_2\dot{C}(CH_3)CH_2SO_3^-$ or between 2-methylallyl alcohol and the species $HOCH_2\dot{C}HCH_2SO_3^-$ in the competitive addition because the termination step in the radiation-induced addition of hydrogensulfite ion to allyl alcohol was the reaction between allyl alcohol and the radical $HOCH_2\dot{C}HCH_2SO_3^-$ which was produced by the addition of sulfite radical ion to allyl alcohol.[11)]

The kinetic chain length defined as the number of propagation steps per radical of initiator starting chains was 344 in the radiation-induced addition.[11)] Since the rate of the termination step is governed by the lability of the hydrogen atom abstracted in olefin, it is assumed that the chain length in the competitive addition is in the same order of magnitude as compared with that in the radiation-induced addition. In other words, the conversions of allyl and 2-methylallyl alcohols by the termination step may be neglected in comparison with the total conversions of these olefins.

In the competitive addition of hydrogensulfite ion to allyl and 2-methylallyl alcohols in the presence of oxygen, it is deduced from the previous paper[11)] to produce 3-hydroxypropane-1-sulfonate and 3-hydroxy-2-methylpropane-1-sulfonate with the corresponding 2-hydroxy-1-alkanesulfonates. The formation of these 2-hydroxy-1-alkanesulfonates, however, does not affect conversions of allyl and 2-mehtylallyl alcohols by the reaction of the adding species with these olefins. Therefore, conversions of allyl and 2-methylallyl alcohols in the competitive addition may be regarded as a measure of the reactivities of the corresponding olefins.

Adding Species. The optimum pH for the reaction process was reported to be near 7 by Adams *et al.*[15)] or 5—7 by Norton *et al.*[4)] This was partly due to a good proportion of hydrogensufite and sulfite ions involved in the propagation during the initial state of the reaction and partly due to decrease in the acidity of the solution causes the undesired side reaction such as the two-electron oxidation of hydrogensulfite ion to hydrogensulfate ion.[4)] In this work, the pH range of 3 to 5 was used where nearly 100% of sodium hydrogensulfite dissociated to hydrogensulfite ion.

It is assumed that the species such as SO_2^-, SO_4^- or SO_5^-, produced by the flash photolysis or the pulse radiolysis of sulfite–hydrogensulfite–disulfite ion system,[16)] may add to various olefins. Such species, however, should be excluded from the adding species as chain carriers because it is difficult to imagine they can sustain the chain reaction.

Sulfite radical ion, which is proposed as an adding species in the radical addition of hydrogensulfite ion to olefins,[17)] possibly exists in equilibrium with hydrogensulfite radical as follows:

$$HSO_3\cdot \rightleftharpoons \cdot SO_3^- + H^+$$

Hydrogensulfite radical, an acidic form of sulfite radical ion, may add to allyl and 2-methylallyl alcohols. Furthermore, this radical in addition to sulfite radical ion had been postulated as one of chain carriers in the autoxidation of sulfite and hydrogensulfite ions, which is one of the most well konwn chain reaction in solution.[18)] Therefore, the hydrogensulfite radical is deduced to be one of the adding species in the addition reaction of hydrogensulfite ion.

Addition of hydroquinone suppressed the addition reaction of hydrogensulfite ion as shown in Table 1. Since hydroquinone is an efficient radical scavenger, this observation suggests that the addition reaction proceeds with a radical mechanism over the whole pH range studied.

The effect of hydrogen ion on the relative reactivity was studied. It is well known that when reactions

Table 1. Effect of hydroquinone on conversions of allyl and 2-methylallyl alcohols, and the pH change during the irradiation

Initial concentrations of allyl and 2-methylallyl alcohols are 0.439 and 0.355 mol/l, respectively.

Run	[NaCl][c]	pH		Concentration[d]	
		Initial	Final	Allyl alcohol	2-Methylallyl alcohol
1[a]	0.835	4.41		0.434	0.350
2[a]	0.835	2.90		0.436	0.351
3[a]	0	2.95		0.435	0.351
4[b]	0	3.07	3.02	0.395	0.237
5[b]	0	4.92	4.84	0.403	0.231

a) [Hydroquinone] = 2.70×10^{-2} mol/l; irradiation time, 120 min. b) Irradiation time, 20 min. c) mol/l. d) mol/l, after irradiation.

between dipolar molecules or between ions and dipolar molecules occur in solution, there are dipole-dipole interactions between such molecules which promote chemical changes. These interactions are modified by the solvent through its dielectric constant and polar properties.[19] However, the effects of the solvent on such reactions are very small in comparison with the effects on the reactions between ions,[19] as shown in the solvent effects on diazo-coupling reactions.[20,21] Since both allyl and 2-methylallyl alcohols are neutral molecules, the effect of the solvent through the pH change appears to be small. In addition, the extent of the solvent effect tends to cancel in the ratio of the rate constants. Then, if sulfite adical ion is the adding species over the whole pH range studied, the relative reactivity in the competitive addition should be fairly constant, despite change in pH.

The relative reactivity decreased with pH as shown in Fig. 2. Taking account of the equilibrium of sulfite radical ion, it is deduced that hydrogensulfite radical mainly participates in the addition reaction at pH 3 and sulfite radical ion at pH 5. The electronegativity of hydrogensulfite radical is assumed to be different from that of sulfite radical ion. Therefore, decrease of the relative reactivity may be explained by the difference in reactivities of hydrogensulfite radical and sulfite radical ion toward allyl alcohol, and toward 2-methylallyl alcohol.

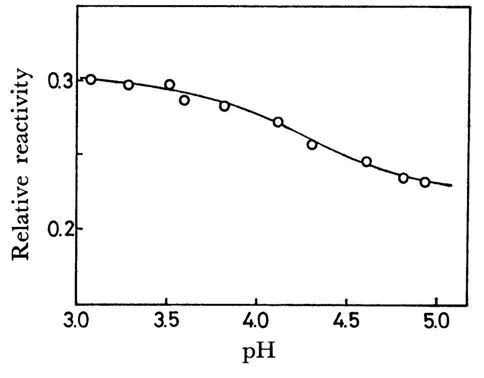


Fig. 2. Variation of the relative reactivity of allyl alcohol to 2-methylallyl alcohol as a function of pH.

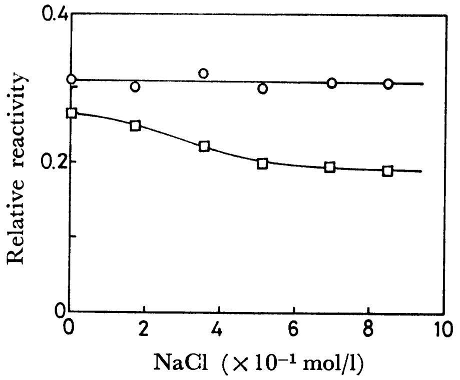
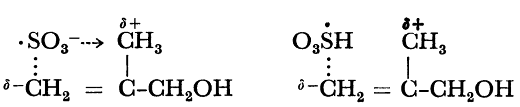


Fig. 3. Effect of sodium chloride on the relative reactivity.
—○— : pH 2.90, —□— : pH 4.54.

In reactions involving neutral molecules or ions and neutral molecules, the influence of the ionic strength on the rate constants is small.[22] The influence of the ionic strength on the relative reactivity in the competitive addition was observed. Namely, the relative reactivity at pH 4.54 decreased with increasing sodium chloride as shown in Fig. 3. In this case, conversion of allyl alcohol remained constant regardless of sodium chloride, while conversion of 2-methylallyl alcohol increased. This observation can also be explained by postulating hydrogensulfite radical and sulfite radical ion as adding species. Hydrogensulfite radical was deduced to be the main adding species at pH 2.90 and sulfite radical ion at pH 4.54. Hence, it is evident that there is the influence of the ionic strength in the reaction between sulfite radical ion and 2-mehtylallyl alcohol.

The methyl group on β-position of 2-methylallyl alcohol is deficient in the electron density because of a electron-donating group. On this basis it is considered that there is the interaction between the negative charge on sulfite radical ion and the methyl group in 2-methylallyl alcohol. Therefore, the influence of the ionic strength is attributable to the difference in the interactions of sulfite radical ion and hydrogensulfite radical toward the methyl group in 2-methylallyl alcohol as follows:



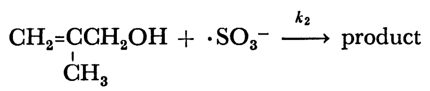
$$\begin{array}{ll} \cdot SO_3^- \dashrightarrow & \overset{\delta+}{CH_3} \\ \ \vdots & \ | \\ {}^{\delta-}CH_2 = & C\text{-}CH_2OH \end{array} \qquad \begin{array}{ll} O_3\overset{\bullet}{S}H & \overset{\delta+}{CH_3} \\ \ \vdots & \ | \\ {}^{\delta-}CH_2 = & C\text{-}CH_2OH \end{array}$$

At present, however, no explanation is available to explain the influence of the ionic strength on increase in conversion of 2-methylallyl alcohol.

Dissociation Constant of Hydrogensulfite Radical. The dissociation constant of hydrogensulfite radical, K, was evaluated from the relative reactivity.

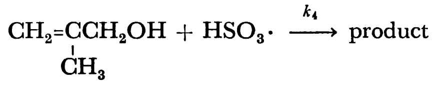
Rate constants of reactions between two olefins, allyl and 2-methylallyl alcohols, and the adding species, hydrogensulfite radical and sulfite radical ion, were defined as follows:

$$CH_2{=}CHCH_2OH + \cdot SO_3^- \xrightarrow{k_1} \text{product} \qquad (1)$$



$$\mathrm{CH_2{=}C(CH_3)CH_2OH} + \cdot\mathrm{SO_3^-} \xrightarrow{k_2} \text{product} \tag{2}$$

$$\mathrm{CH_2{=}CHCH_2OH} + \mathrm{HSO_3}\cdot \xrightarrow{k_3} \text{product} \tag{3}$$



$$\mathrm{CH_2{=}C(CH_3)CH_2OH} + \mathrm{HSO_3}\cdot \xrightarrow{k_4} \text{product} \tag{4}$$

The ratio of conversion of allyl alcohol, x, to that of 2-methylallyl alcohol, y, at the initial stage of the reaction is expressed by the following equation:

$$\frac{x}{y}=\frac{x_0(k_1[\cdot\mathrm{SO_3^-}]+k_3[\mathrm{HSO_3}\cdot])}{y_0(k_2[\cdot\mathrm{SO_3^-}]+k_4[\mathrm{HSO_3}\cdot])} \tag{5}$$

where $[\mathrm{HSO_3}\cdot]$ and $[\cdot\mathrm{SO_3^-}]$ are concentrations of hydrogensulfite radical and sulfite radical ion, and x_0 and y_0 are initial concentrations of allyl and 2-methylallyl alcohols, respectively.

The K is expressed by the following equation:

$$K=\frac{[\cdot\mathrm{SO_3^-}][\mathrm{H^+}]}{[\mathrm{HSO_3}\cdot]}\times\frac{f(\cdot\mathrm{SO_3^-})f(\mathrm{H^+})}{f(\mathrm{HSO_3}\cdot)} \tag{6}$$

where $[\mathrm{H^+}]$ is the concentration of hydrogen ion, and $f(\mathrm{HSO_3}\cdot)$, $f(\cdot\mathrm{SO_3^-})$, and $f(\mathrm{H^+})$ are activity coefficients of hydrogensulfite radical, sulfite radical ion, and hydrogen ion, respectively.

Substituting Eq. 6 to Eq. 5, the equation required to calculate the K was obtained as follows:

$$\frac{f(\cdot\mathrm{SO_3^-})}{f(\mathrm{HSO_3}\cdot)}\times\frac{k_4}{k_2}\times\frac{1}{K}\times[\mathrm{H^+}]\times f(\mathrm{H^+})=\frac{\alpha-a}{b-\alpha} \tag{7}$$

where α, a, and b are $(x/y)(y_0/x_0)$, k_1/k_2, and k_3/k_4, respectively.

According to this equation, the term $(\alpha-a)/(b-\alpha)$ should be proportional to the activity of hydrogen ion $[\mathrm{H^+}]\times f(\mathrm{H^+})$, because the term $f(\cdot\mathrm{SO_3^-})/f(\mathrm{HSO_3}\cdot)\times k_4/k_2\times 1/K$ is constant with a fixed ionic strength. Therefore, the a and b to give this linear relation could be obtained by trial and error. The fitted values of a and b were 0.213 and 0.305, respectively. The solide line in Fig. 4 was drawn by substituting these values into Eq. 7, and the slope was 2.26×10^4.

The term $f(\cdot\mathrm{SO_3^-})/f(\mathrm{HSO_3}\cdot)\times k_4/k_2\times 1/K$ in Eq. 7 is equivalent to the slope of the straight line in Fig. 4. Hence, the K can be evaluated by using $f(\mathrm{SO_3^-})$, $f(\mathrm{HSO_3}\cdot)$, and k_4/k_2.

The $f(\mathrm{HSO_3}\cdot)$ is assumed to be unity because hydrogensulfite radical is a non-charged species.[23] The value of $f(\mathrm{HSO_3^-})$ may be employed to $f(\cdot\mathrm{SO_3^-})$ because the effective diameter of hydrated sulfite radical ion is deduced to be close to that of hydrated hydrogensulfite ion.[24] Now, using the relation between the activity coefficient of ion and the ionic strength in water,[24] the $f(\mathrm{HSO_3^-})$, and hence $f(\cdot\mathrm{SO_3^-})$, was estimated to be 0.70 at the ionic strength 1.2.

The k_4/k_2 was estimated as follows. As shown in Fig. 1, the concentration of hydrogensulfite ion at pH 3.07 is almost equal to that at pH 4.92. Moreover, the pH of the solution hardly changed during the irradiation. Therefore, the sum of rates of hydrogensulfite radical and sulfite radical ion formed by the photolysis at pH 3.07 appears to be equal to that at pH 4.92. In addition, the sum of conversions of allyl and 2-methylallyl alcohols at pH 3.07 was almost equal to that at pH 4.92. In these cases, the irradiation time was fixed for 20 min. On the basis of these results, it is permissible to neglect the difference in the sum of rates of hydrogensulfite radical toward two olefins, allyl and 2-methylallyl alcohols, and sulfite radical ion toward same olefins. Therefore, it may be regarded that allyl and 2-methylallyl alcohols are converted by sulfite radical ion at pH 4.92 and by hydrogensulfite radical at pH 3.07.

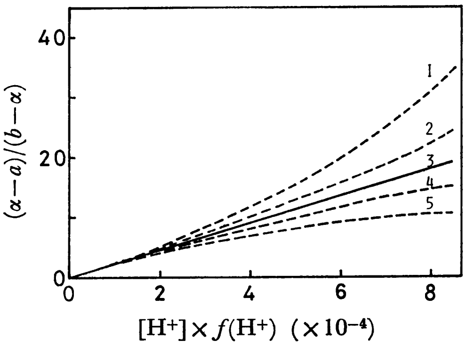


Fig. 4. Variation of $(\alpha-a)/(b-\alpha)$ as a function of the activity of hydrogen ion $[\mathrm{H^+}]\times f(\mathrm{H^+})$.
(1) For $a=0.213$ and $b=0.303$, (2) for $a=0.214$ and $b=0.303$, (3) for $a=0.213$ and $b=0.305$, (4) for $a=0.217$ and $b=0.306$, (5) for $a=0.220$ and $b=0.308$.

Now, the ratio of the total amount of allyl and 2-methylallyl alcohols consumed at pH 4.92, S_1, and that at pH 3.07, S_2, at the initial stage of the reaction may be expressed by the following equation.

$$\frac{S_1}{S_2}=\frac{k_2}{k_4}\times\frac{(ax_0+y_0)}{(bx_0+y_0)}\times\frac{[\cdot\mathrm{SO_3^-}]}{[\mathrm{HSO_3}\cdot]} \tag{8}$$

Taking into account that the rate of the formation of sulfite radical ion at pH 4.92 is deduced to be equal to that of hydrogensulfite radical at pH 3.07 and that the sum of conversions of allyl and 2-methylallyl alcohols at pH 4.92 was almost equal to that at pH 3.07, it may be permitted to postulate $[\cdot\mathrm{SO_3^-}]/[\mathrm{HSO_3}\cdot]=1$. Now, substituting known values of $a=0.213$, $b=0.305$, $S_1=0.160$, $S_2=0.162$, $x_0=0.439$, and $y_0=0.355$ into Eq. 8, the k_4/k_2 was estimated to be 0.927.

Using the values of k_4/k_2, $f(\mathrm{HSO_3}\cdot)$, and $f(\cdot\mathrm{SO_3^-})$, the dissociation constant K was evaluated to be the order of 3×10^{-5} ($\mathrm{p}K_\mathrm{a}=4.5$). This value is similar to that of $\mathrm{HO_2}\cdot$ ($\mathrm{p}K_\mathrm{a}=4.8$)[25] or simple organic free radical such as $\dot{\mathrm{C}}\mathrm{H(OH)CONH_2}$ ($\mathrm{p}K_\mathrm{a}=5.5$)[26] or $\mathrm{CH_3\dot{C}(OH)COOH}$ ($\mathrm{p}K_\mathrm{a}=5.3$).[27]

Apparent Dissociation Constant Obtained Graphically. Since conversion of 2-methylallyl alcohol is more remarkable than that of allyl alcohol, and there is little difference in reactivities of hydrogensulfite redical and sulfite radical ion toward 2-methylally alcohol ($k_4/k_2=0.927$), the relative reactivity-pH curve in Fig. 2 appears to be similar to the dissociation curve of hydrogensulfite radical.

The pH value for the inflection point in Fig. 2 was obtained graphically to be 4.3. Thus, from this pH value, an apparent dissociation constant of hydrogensulfite radical was calculated to be the order of

5×10^{-5} which is compared to the corrected value of 3×10^{-5}.

Reactivities of Olefins and Adding Species. Replacement of one hydrogen atom on β-position of allyl alcohol by a methyl group should donate a negative charge on the terminal methylene carbon. Hence, the electron density on the terminal carbon in 2-methylallyl alcohol is deduced to be higher than that in allyl alcohol.

As already described, k_1/k_2, the ratio of rates in the reactions of allyl and 2-methylallyl alcohols toward sulfite radical ion, was 0.213 and k_3/k_4, the same ratio toward hydrogensulfite radical, was 0.305. These results mean that the reactivity of 2-methylallyl alcohol is larger than that of allyl alcohol regardless of the adding species. This difference in the reactivities is attributed to the difference in the electron densities on the terminal methylene carbon in allyl and 2-methylallyl alcohols.

The k_4/k_2 and k_3/k_1 were used for comparison with the reactivities of hydrogensulfite radical and sulfite radical ion. Since k_4/k_2 was 0.927 as mentioned above, k_3/k_1 was estimated to be 1.32. The former is the ratio of rates in the reactions of hydrogensulfite radical and sulfite radical ion toward 2-methylallyl alcohol, and the latter is the same ratio toward allyl alcohol. Apparently, the reactivity of hydrogensulfite radical toward allyl alcohol is large as compared with that of sulfite radical ion toward same olefin, while the reactivity of hydrogensulfite radical toward 2-methylallyl alcohol is smaller than that of sulfite radical ion toward same olefin. This difference in the trend of reactivities of hydrogensulfite radical and sulfite radical ion is considered, as already described, to be due to the difference in the interactions of hydrogensulfite radical and sulfite radical ion toward the methyl group in 2-methylallyl alcohol.

The addition reaction in this work proceeded with a radical mechanism. Moreover, this addtion was governed by the electronic effect of the methyl group in 2-methylallyl alcohol. This is considered to be due to some degree of electrophilic character of hydrogensulfite radical or sulfite radical ion. No individual rate constant k was determined in this work. Further investigations with different approaches will be necessary.

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