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KINETIC STUDY ON THE RADICAL ADDITION OF SODIUM HYDROGENSULFITE TO ALLYL ALCOHOL

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The kinetics of the radical chain reaction of sodium hydrogensulfite with allyl alcohol in aqueous solutions was investigated. The apparent rate constant was found to be 4.69×10^{-4} $M \cdot sec^{-1}$ at the dose rate of 1.35×10^{16} $eV \cdot g^{-1} \cdot sec^{-1}$. The kinetic chain length was estimated to be 345.

Although ionic additions of sodium hydrogensulfite to olefins conjugated with an electron-accepting group such as carbonyl, cyano or nitro group have been studied extensively,$^{1-3)}$ little is known about the kinetics of the radical addition to non-conjugated olefins. The object of our study is to elucidate the reaction mechanism and the kinetics of the radiation-induced addition of sodium hydrogensulfite to allyl alcohol.

Irradiation was carried out with Co-60 γ-rays at ordinary temperature. Sodium hydrogensulfite of GR grade was used without further purification. Allyl alcohol was purified by distillation with 2,4-dinitrophenylhydrazine. The concentration of hydrogensulfite ion was calculated from the observed pH values and the activity coefficient ratio $f_{SO_3^{2-}}/f_{HSO_3^-} = 0.681^{4)}$ by using its dissociation constant ($pK_2 = 6.991$)$^{5)}$. Unreacted sodium hydrogensulfite was determined gravimetrically as precipitate of barium sulfite. The determination of allyl alcohol unreacted was performed using a gas chromatograph equipped with a thermal conductivity detector and a 2 m stainless-steel column packed with 60-80 mesh Celite 545 coated with 30% Silicone DC 550.

The disappearance of sodium hydrogensulfite was proportional to hydrogensulfite ion concentration (Fig.1) and the reciprocal concentration of allyl alcohol (Fig.2).

Therefore, the radiation-induced radical addition of sodium hydrogensulfite

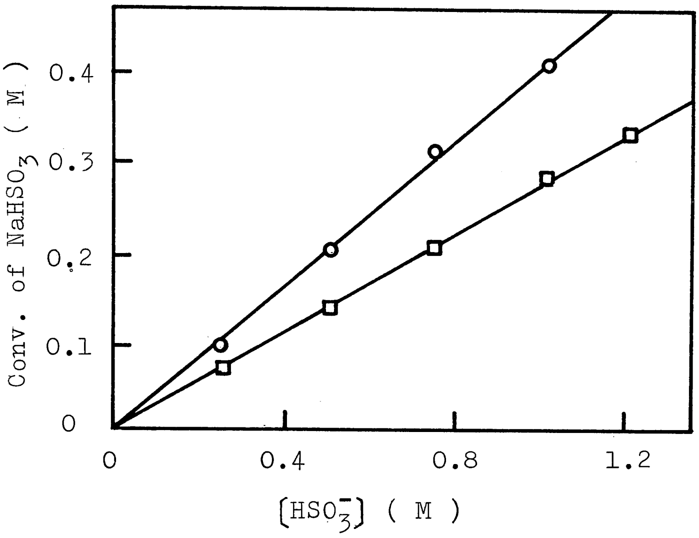

Fig.1. Plots of conversion of NaHSO$_3$ vs. [HSO$_3^-$].

—○— : allyl alcohol 1.11 M

—□— : " 1.47 M

Na_2SO_3: 0.25 M

Dose: 2.43 X 10^{19} eV$\cdot$g^{-1}

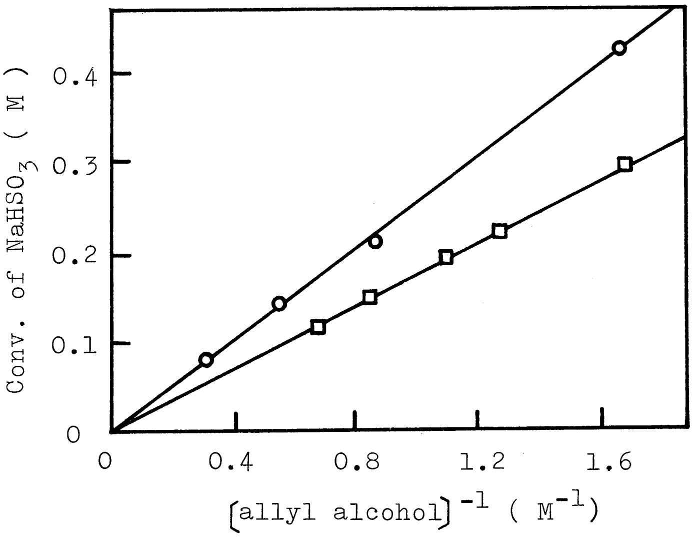

Fig.2. Plots of conversion of NaHSO$_3$ vs. [allyl alcohol] $^{-1}$.

Dose: —□— 1.52 X 10^{19} eV$\cdot$g^{-1}

—○— 2.43 X 10^{19} eV$\cdot$g^{-1}

$NaHSO_3$: 0.50 M, Na_2SO_3: 0.25 M

to allyl alcohol is considered to proceed as follows:

$$H_2O \rightsquigarrow e^-_{aq}, \cdot H, \cdot OH, H_2, H_2O_2 \qquad (1)$$

$$A + HSO_3^- \longrightarrow AH + \cdot SO_3^- \qquad (2)$$

$$\cdot SO_3^- + CH_2{=}CHCH_2OH \longrightarrow HOCH_2\dot{C}HCH_2SO_3^- \qquad (3)$$

$$HOCH_2\dot{C}HCH_2SO_3^- + HSO_3^- \longrightarrow HOCH_2CH_2CH_2SO_3^- + \cdot SO_3^- \qquad (4)$$

$$HOCH_2\dot{C}HCH_2SO_3^- + CH_2{=}CHCH_2OH \longrightarrow HOCH_2CH_2CH_2SO_3^- + CH_2{=}CH\dot{C}HOH \qquad (5)$$

where A denotes the intermediate radicals concerned in the initiation of the addition reaction.

Application of the steady-state approximation to the concentrations of A, $\cdot SO_3^-$ and $HOCH_2\dot{C}HCH_2SO_3^-$ leads to the following rate equation.

$$\frac{d[NaHSO_3]}{dt} = gI_o + gI_o \frac{k_4[HSO_3^-]}{k_5[RH]} \qquad (6)$$

where g, I_o and [RH] denote G-value of A, dose rate and the concentration of allyl alcohol, respectively. The concentration of hydrogensulfite ion is caluculated to be 1.03 times that of sodium hydrogensulfite in the presence of 0.25 M of sodium sulfite for pH adjustment. The gI_o is negligibly small as compared with $gI_o k_4 [HSO_3^-]/k_5[RH]$ because of $k_4 \gg k_5$. Therefore, Eq.(6) may be simplified as follows:

$$\frac{dx}{dt} = 1.03\ k \frac{(a - x)}{(b - x)} \qquad (7)$$

$$k = gI_o \frac{k_4}{k_5} \qquad (8)$$

where a and b are the initial concentrations of sodium hydrogensulfite and allyl alcohol respectively, and x denotes the disappearance of sodium hydrogensulfite at irradiation time t.

Integrating Eq.(7) with the boundary condition, x = 0 at t = 0, the apparent rate constant of sodium hydrogensulfite is expressed by

$$k = \frac{1}{1.03\ t} \ (a - b)\ \ln \frac{(a - x)}{a} + x \qquad (9)$$

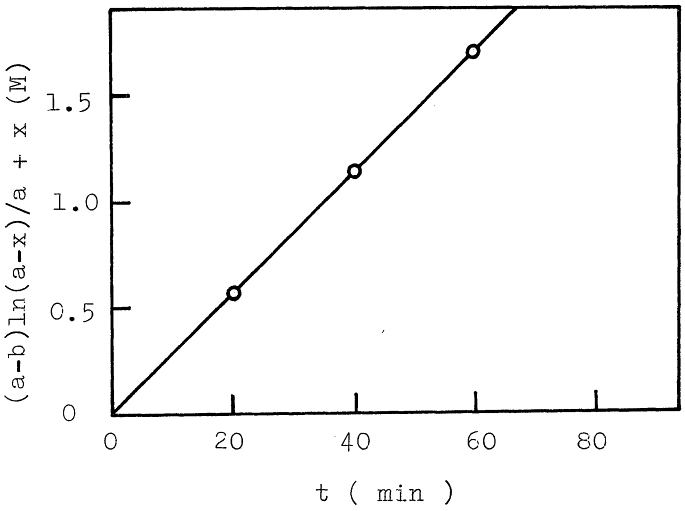

Fig.3. Plot of [(a - b) ln (a - x)/a + x] vs. irradiation time t. $NaHSO_3$: 0.50 M, Na_2SO_3: 0.25 M, allyl alcohol: 1.47 M. Dose rate: 1.35 X 10^{16} $eV \cdot g^{-1} \cdot sec^{-1}$

As is shown in Fig.3, a good linear relationship has been obtained by plotting [(a - b) ln (a - x)/a + x] in Eq.(9) against t.

This fact indicates that the experimental findings are well explained by the mechanism given in Eqs.(2)-(5). The apparent rate constant of sodium hydrogensulfite $k = 4.69 \times 10^{-4}$ M·sec^{-1} at the dose rate of 1.35×10^{16} eV·g^{-1}·sec^{-1} was obtained from the slope in Fig.3.

When log k was plotted against logarithm of dose rate, a straight line was obtained. A typical plot is shown in Fig.4. This shows that the apparent rate constant k is proportional to dose rate. Then, the kinetic chain length defined as the numbers of propagation steps per radical of initiator starting chains is obtained from Eq.(8) to be 345, when g is assumed to be 6.05$^{6)}$ as the total yields of the active species, e^-_{aq}, ·H and ·OH, produced in γ-radiolysis of water.

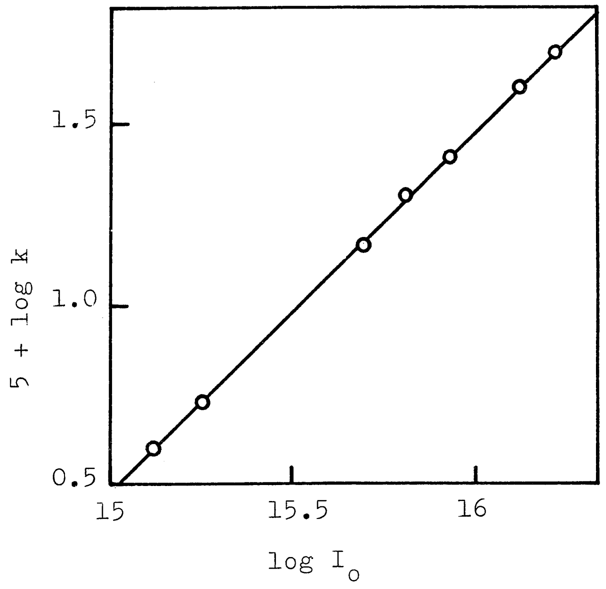

Fig.4. Plot of log k vs. log I_0.

References

1) R. T. E. Schenk and I. Daniskefsky, J. Org. Chem., 16, 1683 (1951).

2) M. Morton and H. Landfield, J. Amer. Chem. Soc., 74, 3523 (1952).

3) H. D. Finch, J. org. Chem., 27, 649 (1962).

4) The **dissociation** constant is expressed by $pK_2 = pH - \log(f_{SO_3^{2-}} / f_{HSO_3^-}) - \log[SO_3^-]/[HSO_3^-]$. When a plot of $\log[SO_3^-]/[HSO_3^-]$ vs. pH value gave a straight line of the slope of one by inserting an appropriate value into $[HSO_3^-]$, $f_{SO_3^{2-}}/ f_{HSO_3^-} = 0.681$ was calculated from the intercept of $- (pK_2 + \log(f_{SO_3^{2-}} / f_{HSO_3^-}))$ by using $pK_2 = 6.991$.

5) Landolt-Börnstein, " Zahlenwerte und Funktionen ", p 842, IIB., 7 teil, Springer (1960).

6) B. H. J. Bielski and A. O. Allen, Int. J. Phys. Chem., 1, 153 (1969).

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