CHEMISTRY LETTERS, pp. 563-566, 1975. Published by the Chemical Society of Japan

# KINETICS ON THE SULFONATION REACTION OF 1-DODECENE WITH SODIUM HYDROGENSULFITE

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The kinetics on the radiation-induced addition of hydrogensulfite to 1-dodecene was investigated in the presence of a surfactant, 1-dodecanesulfonate, in an aqueous solution of t-butyl alcohol. The termination was found to be the reaction of 1-dodecanesulfonate radical with sulfite radical ion. This result was deduced to be due to the micellar effect.

When allyl alcohol was used as an olefin in the radical addition of sodium hydrogensulfite, it was found that allyl alcohol played an important role in the termination of the chain reaction.[1)] Allyl alcohol dissolves easily in water. While, 1-dodecene is almost insoluble. When this olefin and sodium hydrogensulfite were dissolved in the 1 : 1 mixture of water and t-butyl alcohol, which was an efficient co-solvent for similar reactions in photochemistry,[2)] and irradiated with Co-60 $\gamma$-rays in the absence of 1-dodecanesulfonate, no chain sulfonation practically took place until some amounts of sulfonate as a product were accumulated. While, in the presence of an appropriate amount of 1-dodecanesulfonate, the reaction was immediately observed with the start of irradiation. 1-Dodecanesulfonate has superior surface-active properties. Thus, it is interesting to elucidate the kinetics on the sulfonation of $\alpha$-olefins, insoluble in water, in the presence of a surface-active agent. This paper is concerned with the kinetics on the radiation-induced sulfonation of 1-dodecene with sodium hydrogensulfite in the presence of 1-dodecanesulfonate.

1-Dodecene was distilled in an atmosphere of nitrogen under reduced pressure. No further purification was made for sodium hydrogensulfite of GR grade. All the work to be described below was carried out in 0.11 mol/l 1-dodecanesulfonate solutions. Unreacted 1-dodecene was determined by using a gas chromatograph (Yanagimoto model G-80) equipped with a flame ionization detector and a 1.5 m glass column packed with

60-80 mesh Celite 545 coated with 30% Silicone DC 550. Sodium 1-dodecanesulfonate produced was determined by means of IR spectrum and its concentration was found to be proportional to the conversion of 1-dodecene.

The conversion of 1-dodecene was proportional to the square root of the concentration of 1-dodecene and that of sodium hydrogensulfite, respectively. Some typical plots are shown in Fig. 1.

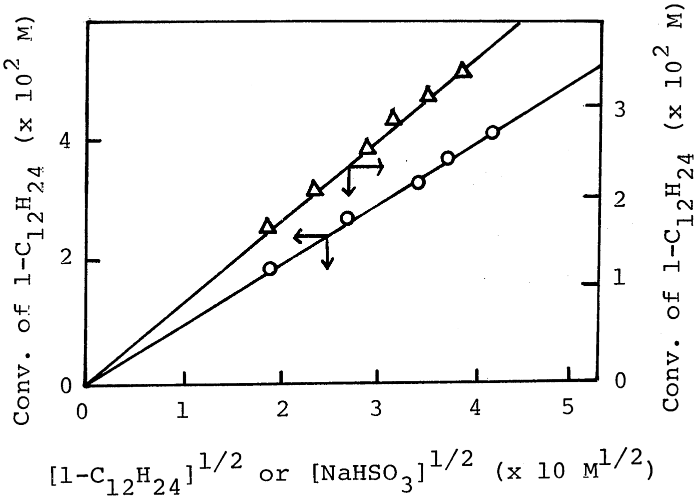

Fig. 1. Plots of the conv. of $1\text{-}C_{12}H_{24}$ vs. $[1\text{-}C_{12}H_{24}]_o^{1/2}$ or $[NaHSO_3]_o^{1/2}$.

Dose rate: $1.62 \times 10^{17}$ eV/g·min

Dose: $3.24 \times 10^{18}$ eV/g

—△— : $1\text{-}C_{12}H_{24}$ at $[NaHSO_3]_o$ 0.288 M

—○— : $NaHSO_3$ at $[1\text{-}C_{12}H_{24}]_o$ $9.01 \times 10^{-2}$ M

Some amounts of alkane disulfonate were produced in a similar reaction catalyzed by certain nitrate salts.[3] These facts suggest that the reaction of 1-dodecanesulfonate radical with sulfite radical ion would participate in the termination of this radical chain reaction. Thus, the basic reaction mechanism may be expressed as follows:

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

$$A + HSO_3^- \xrightarrow{k_2} AH + \cdot SO_3^- \tag{2}$$

$$CH_3(CH_2)_9CH{=}CH_2 + \cdot SO_3^- \xrightarrow{k_3} CH_3(CH_2)_9\dot{C}HCH_2SO_3^- \tag{3}$$

$$CH_3(CH_2)_9\dot{C}HCH_2SO_3^- + HSO_3^- \xrightarrow{k_4} CH_3(CH_2)_9CH_2CH_2SO_3^- + \cdot SO_3^- \tag{4}$$

$$CH_3(CH_2)_9\dot{C}HCH_2SO_3^- + \cdot SO_3^- \xrightarrow{k_5} CH_3(CH_2)_9CH(SO_3^-)CH_2SO_3^- \tag{5}$$

where A is the intermediate radicals participating in the initiation reaction of this addition. When the steady-state assumption is made for the concentration of A, $\cdot SO_3^-$, and $CH_3(CH_2)_9\dot{C}HCH_2SO_3^-$, the general rate Eq. (6) is

$$-\frac{d\,[RH]}{dt} = \frac{CI_o}{4}\left[1 + \left(1 + \frac{8\,k_3k_4}{k_5CI_o} \times [RH]\,[HSO_3^-]\right)^{\frac{1}{2}}\right] \tag{6}$$

derivable, where C, $I_o$, and [RH] are a number of A per absorbed dose, dose rate, and the concentration of 1-dodecene in the micellar solution, respectively. The G-value of 1-dodecene consumption was 4280 at concentrations of 0.288 mol/l sodium hydrogensulfite and 0.135 mol/l 1-dodecene. Since this is a long chain reaction, it can be safely assumed that $(8\ k_3k_4/k_5CI_o)[RH][HSO_3^-] \gg 1$, so that Eq. (6) is simplified as Eq. (7).

$$-\frac{d\ [RH]}{dt} = k\ [RH]^{\frac{1}{2}}\ [HSO_3^-]^{\frac{1}{2}} \tag{7}$$

$$k = \left(CI_o \times \frac{k_3k_4}{2\ k_5}\right)^{\frac{1}{2}} \tag{8}$$

where k denotes the overall rate constant of 1-dodecene consumption.

Equation (8) provides a way to test the validity of the assumption that the termination reaction in this addition is reaction (5). According to this equation, a plot of logarithm of k against logarithm of dose rate must be linear with a slope of 0.5. The rate constant k can be calculated as follows. Putting the initial concentrations of 1-dodecene and hydrogensulfite ion to be a and b, their unreacted concentrations at irradiation time t, a-x and b-x, respectively, and integrating Eq. (7) with the boundary condition, x = 0 at t = 0, the overall rate constant k is given by Eq. (9).

$$2\ \ln\left(\frac{(a-x)^{\frac{1}{2}} - (b-x)^{\frac{1}{2}}}{(a)^{\frac{1}{2}} - (b)^{\frac{1}{2}}}\right) = kt \tag{9}$$

Figure 2 shows a plot of $\ln[((a-x)^{1/2} - (b-x)^{1/2})/(a^{1/2} - b^{1/2})]$ against time t. Therefore, the overall rate constant k was immediately obtained to be $1.92 \times 10^{-4}\ sec^{-1}$ at the dose rate of $1.62 \times 10^{17}$ eV/g·min from the slope in Fig. 2.

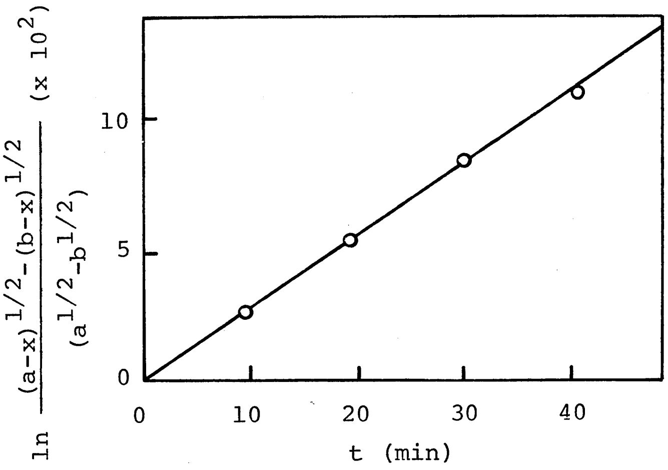

Fig. 2. Plot of $\ln[((a-x)^{1/2}-(b-x)^{1/2})/(a^{1/2}-b^{1/2})]$ vs. time t.

Dose rate: $1.62 \times 10^{17}$ eV/g·min

$NaHSO_3$: 0.288 M

$1\text{-}C_{12}H_{24}$: 0.135 M

When logarithm of k was plotted against logarithm of dose rate, a good linear correlation was obtained as shown in Fig. 3; the slope was 0.65, close to 0.5 expected by Eq. (8).

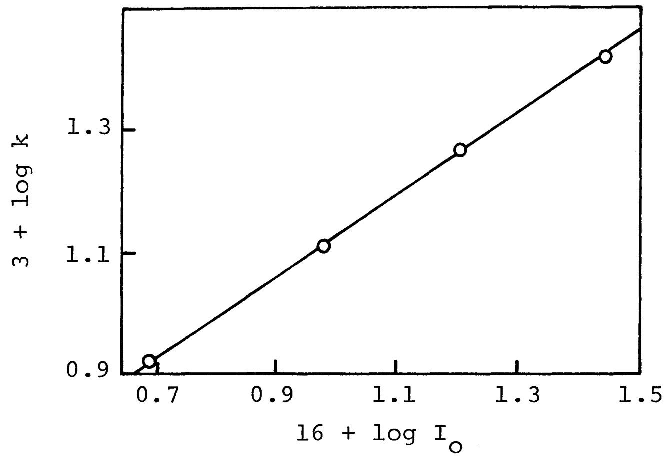

Fig. 3. Plot of log k vs. logarithm of dose rate.
$NaHSO_3$: 0.288 M
$1\text{-}C_{12}H_{24}$: 9.01 x $10^{-2}$ M
Irradiation time: 20 min

Consequently, it can be concluded that the reaction of 1-dodecanesulfonate radical with sulfite radical ion, reaction (5), is the main process for the termination in the sulfonation reaction of 1-dodecene with sodium hydrogensulfite.

This termination is different from that in the sodium hydrogensulfite addition to allyl alcohol.1) Hydrogensulfite and sulfite radical ions are in the bulk of the solution. In contrast, 1-dodecene is expected to be involved in a core formed by the hydrophobic part of 1-dodecanesulfonate as a surfactant.4) Since it is considered to be seldom to produce two or more sulfonate radicals in a micellar phase, dimerization of these radicals should be difficult. On the other hand, the odd electron produced at the 2-position of 1-dodecene by addition of sulfite radical ion should be located near the compact region known as the Stern layer.4) As a result, it is deduced that the reaction of 1-dodecanesulfonate radical with sulfite radical ion becomes to be more easily than other reactions for the termination in this reaction.

References

1) T.Miyata, A.Sakumoto, M.Washino, and T.Abe, Chem.Lett., 1975, 181.
2) C.L.Furrow and C.E.Stoops, Ind.Eng.Chem.Prod.Res.Develop., 7, 26 (1968).
3) C.J.Norton, N.F.Seppi, and M.J.Reuter, J.Org.Chem., 33, 4158 (1968).
4) E.J.Fendler and J.H.Fendler, Adv.Phys.Org.Chem., 8, 271 (1970).

(Received March 5, 1975)