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The Kinetics and Mechanism of the Radical Addition of Hydrogensulfite Ions to 1-Dodecene in a Micellar Solution of Sodium 1-Dodecanesulfonate

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The addition reaction induced by Co-60 gamma-rays proceeded without any detectable induction period under homogeneous conditions in the presence of sodium 1-dodecanesulfonate. The consumption rate of 1-dodecene was equal to that of sodium hydrogensulfite and proportional to the square roots of the hydrogensulfite-ion and 1-dodecene concentrations. The *g*-value of 1-dodecene consumption was 860 at the concentrations of 0.260 mol/l of sodium hydrogensulfite, 0.0966 mol/l of 1-dodecene, and 0.11 mol/l of sodium 1-dodecanesulfonate at the dose rate of 2.70×10^{15} eV/g·s and the dose of 1.62×10^{18} eV/g. The apparent rate constant was 2.6×10^{-4} s^{-1} under these reaction conditions. The reaction of $CH_3(CH_2)_9\dot{C}HCH_2SO_3^-$ with the sulfite radical ion was proposed as the termination step of the reaction.

It is well known that the addition of hydrogensulfite ions to olefins initiated by oxidizing agents,[1–4] by ultraviolet light[5] or gamma irradiation[6] proceeds by a radical process, but the reaction is still not sufficiently understood. Investigations in this area have recently been stimulated by the interest in converting 1-alkenes with 8 to 18 carbon atoms into 1-alkanesulfonates, but to date no kinetic study has been made, probably because of the low solubilities of these olefins in water.

1-Alkanesulfonates with 8 to 18 carbon atoms have good surfactant properties.[7] Surfactants have been utilized extensively for the enhancement and the inhibition of industrially and biologically important radical processes.[8] Emulsion polymerization[9] is perhaps the prime example of this application of surfactants. Similarly, micellar amphiphiles affect the rate of the oxidation of dispersed or emulsified hydrocarbons,[10] aldehydes,[11] and unsaturated esters.[12] In the present study, some preliminary experiments showed that the addition reaction started at a significant rate and without any detectable induction period in the presence of sodium 1-dodecanesulfonate, though hardly no reaction occurred in its absence.

The present study was undertaken in order to throw some light on the kinetics and mechanism of the radiation-induced addition of hydrogensulfite ions to 1-dodecene in micellar solutions of sodium 1-dodecanesulfonate. In this study an aqueous *t*-butyl alcohol solution, which has been reported to be the most appropriate solvent for the similar photo-reaction,[5] was used as the solvent, and the reaction was carried out under homogeneous conditions.

Experimental

Materials. The sodium hydrogensulfite was of a guaranteed grade and was used without further purification. The 1-dodecene (97.8%) was distilled under a reduced pressure of nitrogen. The water and *t*-butyl alcohol were distilled. The sodium 1-dodecanesulfonate was prepared from sodium hydrogensulfite and 1-dodecene as follows. Sodium hydrogensulfite (0.25 mol/l), 1-dodecene (0.25 mol/l), water (200 ml), and *t*-butyl alcohol (200 ml) were added to a flask (1000 ml) fitted with a stirrer. The rapidly stirred mixture was irradiated with Co-60 gamma-rays (3.47×10^{15} eV/g·s) for about 2 h at room temperature and then neutralized with dilute hydrochloric acid. After the neutralization, the mixture was irradiated again for 1 h to complete the reaction. The irradiated mixture was then dried under reduced pressure overnight to give a white powder as the product. Neither sodium hydrogensulfite nor 1-dodecene was observed in the product.

Procedure and Irradiation. A reaction mixture was prepared by dissolving sodium hydrogensulfite, 1-dodecene, and sodium 1-dodecanesulfonate (0.11 mol/l) in a *t*-butyl alcohol-water (50 vol%) mixture. In order to keep the starting reaction mixture a single liquid phase, it is necessary that the initial concentrations of sodium hydrogensulfite and 1-dodecene be in the ranges of 0.04—0.30 mol/l and 0.03—0.20 mol/l respectively. The reaction mixture was placed in a glass tube (50 ml) and irradiated with Co-60 gamma-rays at room temperature after the tube had been deaerated under reduced pressure. The dose rate was determined by means of a Fricke dosimeter, taking $G(Fe^{3+}) = 15.6$. No correction was introduced (<1%) for the electronic density difference between the dosimetric solutions and those studied. The pH of the reaction mixture was measured before and after irradiation using a Tōa Denpa HM-5A pH meter; no significant differences in the pH values (about 4.1) were found.

Analytical Procedure. The determination of unreacted 1-dodecene was made on a gas chromatograph (Yanagimoto model G-80) equipped with a flame-ionization detector and a 1.5 m stainless steel column packed with 60—80 mesh Celite 545 and coated with 30% Silicone DC 550, where aqueous samples were directly injected into the gas chromatograph without pretreatment.

Unreacted sodium hydrogensulfite was determined by titration: after the oxidations of sulfite and hydrogensulfite ions into the sulfate ion with hydrogen peroxide, the sulfate ion was titrated with barium perchlorate using 4,5-dihydroxy-3,6-[(2-sulfo-4-methylphenyl)azo]-2,7-naphthalenedisulfonic acid, Na_2 salt (*m,m'*-dimethyl sulfonazo III[13]) as the indicator.

The product was identified as sodium 1-dodecanesulfonate by a comparison of its infrared spectrum [721, 798 (νC–S), 1063 (νS–O), 1175, 2855, 2924 cm^{-1} (νC–H)] with the spectra of the alkanesulfonates in the literature.[14] The spectrum was obtained by the use of an infrared spectrophotometer, Hitachi EPI-S_2, using a potassium bromide disk method.

Results and Discussion

Hydrogensulfite-ion Concentration. The hydrogensulfite-ion concentration in an aqueous solution is given by[15]

$$[HSO_3^-] = \left\{1+\left(\frac{[a_{H^+}]}{K_1}\right)\left(\frac{f_{HSO_3^-}}{f_{H_2SO_3}}\right)+\left(\frac{K_2}{[a_{H^+}]}\right)\left(\frac{f_{HSO_3^-}}{f_{SO_3^{2-}}}\right)\right\}^{-1} \cdot [NaHSO_3], \tag{1}$$

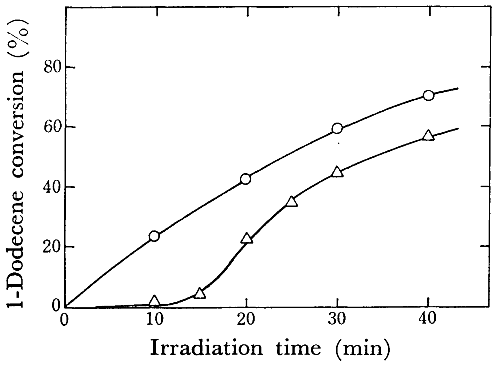

Fig. 1. The conversion of 1-dodecene as a function of irradiation time.
○—$NaHSO_3$: 0.260 mol/l, 1-dodecene: 0.0966 mol/l, $1\text{-}C_{12}H_{25}SO_3Na$: 0.11 mol/l, dose rate: 2.70×10^{15} eV/g·s. △—$NaHSO_3$: 0.46 mol/l, 1-dodecene: 0.47 mol/l, dose rate: 1.11×10^{16} eV/g·s.

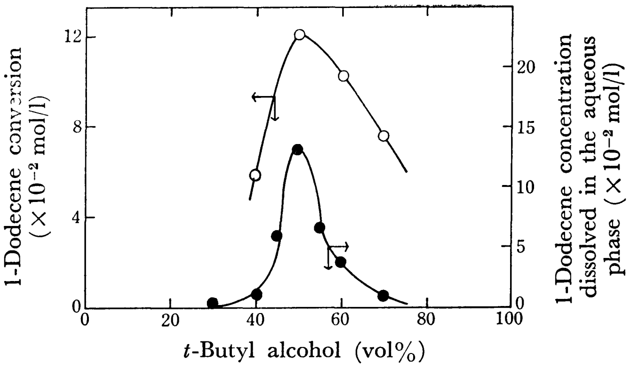

Fig. 2. The conversion of 1-dodecene and the concentration of 1-dodecene dissolved in the aqueous phase as a function of the content of *t*-butyl alcohol.
○—$NaHSO_3$: 0.458 mol/l, 1-dodecene: 0.214 mol/l, dose: 1.42×10^{17} eV/g at the dose rate of 2.37×10^{15} eV/g·s. ●—$NaHSO_3$: 0.229 mol/l, 1-dodecene: 0.225 mol/l, $1\text{-}C_{12}H_{25}SO_3Na$: 0.055 mol/l.

where K_1 and K_2 are the dissociation constants of H_2SO_3 and HSO_3^- respectively; $f_{H_2SO_3}$, $f_{HSO_3^-}$, and $f_{SO_3^{2-}}$, the activity coefficients of H_2SO_3, HSO_3^-, and SO_3^{2-} respectively; $[a_{H^+}]$, the activity of the hydrogen ion, and $[NaHSO_3]$, the concentration of the sodium hydrogensulfite initially dissolved in the solution.

The pH values of sodium hydrogensulfite solutions in water and in a *t*-butyl alcohol–water (50 vol%) mixture were roughly independent of the sodium hydrogensulfite concentration. The pH value observed in the *t*-butyl alcohol–water mixture was only about 0.2 pH-units higher[16] than that (about 3.9) in water. Therefore, the pa_{H^+}, $-\log[a_{H^+}]$, value in the mixture was roughly estimated to be equal to the pH value in water, by analogy with the pa_{H^+}-determination of succinate buffer solutions in alcohol–water mixtures.[17] Accordingly, $[a_{H^+}]$ in Eq. 1 is 1.3×10^{-4} mol/l. Since K_1 and K_2 are 1.54×10^{-2} and 1.02×10^{-7} [18] respectively at 18 °C, and since the activity coefficient ratios of $f_{HSO_3^-}/f_{H_2SO_3}$ and $f_{HSO_3^-}/f_{SO_3^{2-}}$ do not differ greatly from unity,[15,19] the substitution of these values into Eq. 1 gives,

$$[HSO_3^-] \approx [NaHSO_3].$$

Reaction in Micellar Solution. Alkanesulfonates with a straight-chain alkyl group of from 8 to 18 carbon atoms are usually capable of forming micelles and solubilizing olefins in aqueous solutions above their critical micelle concentrations.[20] The critical micelle concentration of sodium 1-dodecanesulfonate in an aqueous solution is 9.8×10^{-3} mol/l at 31 °C[21], and the addition of alcohols except methyl alcohol to the solution causes a decrease in the critical micelle concentration.[22–25] In the present work, 0.11 mol/l of sodium 1-dodecanesulfonate was added to the reaction solution so that the reaction might be carried out under homogeneous conditions. It follows, then, that the micelles must be formed in this solution. Accordingly, it may be noted that the solution, though it is seemingly a single liquid phase under the homogeneous conditions, comprises both a micellar phase and a bulk phase in the presence of the surfactant. In such a solution, it is necessary to consider that the rate of the addition reaction is subject to the influence of the solubilization of 1-dodecene by the micelles, since this olefin is hardly soluble in water.

Figure 1 shows two typical plots of the 1-dodecene conversion against the absorbed dose. The reaction began without any detectable induction period in the presence of the surfactant, while hardly no reaction occurred for up to 10 min in its absence. In this case, at the beginning of the reaction, the reaction solution was apparently homogeneous in the former case, while it comprised both an organic (olefin) phase and an aqueous (hydrogensulfite ion) phase in the latter case. The 1-dodecene concentration in the aqueous phase was only 0.014 mol/l, less than that in the former solution by a factor of about 10. Figure 2 shows the plots of the 1-dodecene conversion and of the 1-dodecene concentration in the aqueous phase as functions of the vol% of *t*-butyl alcohol under such heterogeneous conditions that this solution comprises both the organic and aqueous phases in the presence of 0.055 mol/l of sodium 1-dodecanesulfonate. The 1-dodecene concentration in the aqueous phase decreased with the decrease in the *t*-butyl alcohol content below 50 vol% of *t*-butyl alcohol. It follows, then, that the 1-dodecene concentration in the organic phase must increase with the decrease in the *t*-butyl alcohol content below 50 vol% of *t*-butyl alcohol. In addition, the organic-phase portion of the solution increased with the decrease in the *t*-butyl alcohol content. If the reaction takes place predominantly in the organic phase, the 1-dodecene conversion will increase with the decrease in the *t*-butyl alcohol content below 50 vol% of *t*-butyl alcohol. On the contrary, if the reaction takes place predominantly in the aqueous phase, the rate of 1-dodecene consumption will depend on the 1-dodecene concentration in the aqueous phase. As is evident from Fig. 2, the 1-dodecene conversion did not increase with the decrease in the *t*-butyl alcohol content below 50 vol% of *t*-butyl alcohol; rather a nearly close correlation was found between the 1-dodecene conversion and the 1-dodecene concentration in the aqueous phase. From the facts described above, it appears more likely that

Table 1. Conversions of 1-dodecene under various reaction conditions

[NaHSO$_3$] (×10^{-2} mol/l)	[1-Dedecene] (×10^{-2} mol/l)	[1-C$_{12}$H$_{25}$SO$_3$Na] (×10^{-2} mol/l)	1-Dodecene conv. (×10^{-2} mol/l)
9.61	6.75	1.8	2.01
9.61	6.75	3.7	2.03
9.61	6.75	7.3	2.08
9.61	6.75	11.0	1.97
14.4	6.75	1.8	2.46
14.4	6.75	3.7	2.59
14.4	6.75	7.3	2.54
14.4	4.50	11.0	1.86
26.0	9.66	11.0	4.10

Dose: 3.24×10^{18} eV/g at the dose rate of 2.70×10^{15} eV/g·s.

the reaction takes place predominantly in the aqueous phase in the presence of the surfactant.

1-Dodecene was hardly soluble in the aqueous phase in the absence of the surfactant. As can be seen in Fig. 2, however, the 1-dodecene concentration in the aqueous phase was 0.255 mol/l at 50 vol% of *t*-butyl alcohol in the presence of 0.055 mol/l of sodium 1-dodecanesulfonate. Since this surfactant can solubilize 1-dodecene in aqueous solutions above its critical micelle concentration, most of this olefin dissolved in the aqueous phase can be considered to be solubilized by the surfactant. Table 1 shows the 1-dodecene conversion at various surfactant concentrations under the homogeneous conditions. This conversion was independent of the surfactant concentration in the range studied. It can, therefore, be considered that most of the olefin is solubilized by the surfactant under the homogeneous conditions, because the distribution of the olefin between the micellar and the bulk phases, which is responsible for the alteration of the reaction rate, will vary with the surfactant concentration if the olefin is present in these two phases. From this result and from the experimental findings described above, it can be concluded that solubilized 1-dodecene predominantly takes part in the addition reaction in the presence of the surfactant.

Reaction Mechanism. The addition of the hydrogensulfite ion to 1-dodecene is known to proceed by a radical chain process involving the chain-carrying steps given by[1)]

$$\dot{S}O_3^- + CH_3(CH_2)_9CH{=}CH_2 \rightarrow CH_3(CH_2)_9\dot{C}HCH_2SO_3^-, \qquad (2)$$

$$CH_3(CH_2)_9\dot{C}HCH_2SO_3^- + HSO_3^- \rightarrow CH_3(CH_2)_9CH_2CH_2SO_3^- + \dot{S}O_3^-. \qquad (3)$$

In general, the action of ionization radiation upon dilute solutions results in the degradation of the solvent.[26)]

The degradation of water by radiation is expressed as[27)]

$$H_2O \rightsquigarrow \cdot OH,\ \cdot H,\ e_{aq}^-,\ H_2,\ H_2O_2$$

and the radiolysis of *t*-butyl alcohol gives such species as ·H, $\dot{C}H_2(CH_3)_2COH$, and e_{sol}^-.[28)] Of these species, ·H, ·OH, and e_{aq}^- or e_{sol}^- react with the hydrogensulfite ion to give the sulfite radical ion.[29,30)]

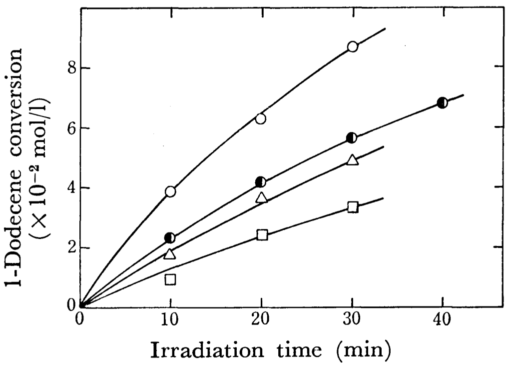

Fig. 3. The conversion of 1-dodecene as a function of irradiation time with various dose rates and concentrations.

○, △, □—NaSHO$_3$: 0.252 mol/l, 1-dodecene: 0.144 mol/l, 1-C$_{12}$H$_{25}$SO$_3$Na: 0.11 mol/l, dose rate (eV/g·s): 4.75×10^{15} for ○, 1.68×10^{15} for △, 8.19×10^{14} for □. ◐—NaSHO$_3$: 0.260 mol/l, 1-dodecene: 0.0966 mol/l, 1-C$_{12}$H$_{25}$SO$_3$Na: 0.11 mol/l, dose rate: 2.70×10^{15} eV/g·s.

Table 2. The conversion ratio of 1-dodecene to NaHSO$_3$ in the addition of HSO$_3^-$ to 1-dodecene

Dose rate ×10^{-15} (eV/g·s)	Dose ×10^{-18} (eV/g)	Conversion(mol/l) 1-Dodecene	Conversion(mol/l) NaHSO$_3$	Conv. ratio $\left(\frac{\text{1-Dodecene}}{\text{NaHSO}_3}\right)$
0.81	2.43	0.048	0.044	1.09
1.68	2.02	0.040	0.043	0.93
1.68	2.43	0.035	0.032	1.09
2.70	3.24	0.053	0.053	1.00
2.70	3.53	0.058	0.057	1.02
2.70	4.86	0.069	0.070	0.99
4.57	5.48	0.061	0.063	0.97

Figure 3 shows the plots of the 1-dodecene conversion as a function of the irradiation time at various dose rates and at various concentrations of the hydrogensulfite ion and of 1-dodecene. The reaction began without any detectable induction period under these reaction conditions. Table 2 shows that a 1 : 1 product is formed independently of the dose and the dose rate. Most of the product obtained was identified as sodium 1-dodecansulfonate.

The termination of the addition reaction may result mostly from processes such as the dimerization of the chain-carrying radicals given in Eqs. 2 and 3 or a coupling reaction of these radicals. If the dimerization of the sulfite radical ion takes place as the termination, the rate of 1-dodecene disappearance should be proportional to the 1-dodecene concentration, by analogy with kinetic analysis in general.[31)] Similarly, if the dimerization of the alkanesulfonate radical takes place, the rate should be proportional to the hydrogensulfite ion concentration. On the other hand, if the alkanesulfonate radical couples with the sulfite radical ion to terminate the addition reaction, the rate should be proportional to the square roots of both the 1-dodecene

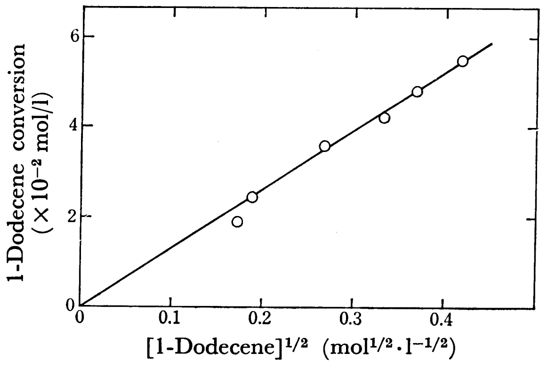

Fig. 4. The conversion of 1-dodecene as a function of the square root of the initial concentration of 1-dodecene.

$NaHSO_3$: 0.260 mol/l, $1\text{-}C_{12}H_{25}SO_3Na$: 0.11 mol/l, dose: 2.43×10^{18} eV/g at the dose rate of 2.70×10^{15} cV/g·s.

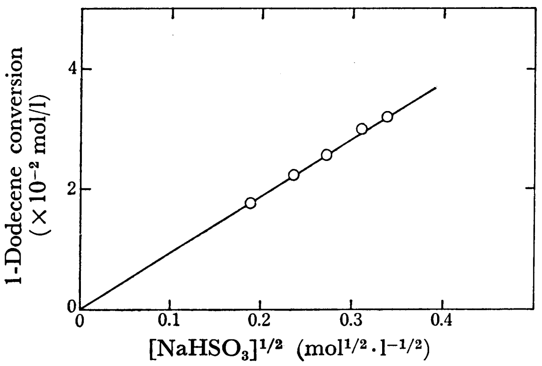

Fig. 5. The conversion of 1-dodecene as a function of the square root of the initial concentration of sodium hydrogensulfite.

1-Dodecene: 0.0902 mol/l, $1\text{-}C_{12}H_{25}SO_3Na$: 0.11 mol/l, dose: 4.05×10^{18} eV/g at the dose rate of 2.70×10^{15} eV/g·s.

and hydrogensulfite ion concentrations. The conversion was independent of the surfactant concentration in the range studied, as can be seen in Table 1. Figures 4 and 5 show the plot of the 1-dodecene conversion against the square root of the initial 1-dodecene concentration, and that against the square root of the initial hydrogensulfite ion concentration, respectively. These results indicate that the rate of 1-dodecene disappearance is proportional to the square roots of both the 1-dodecene and hydrogensulfite ion concentrations. Consequently, the termination can be deduced to be the coupling reaction of the alkanesulfonate radical with the sulfite radical ion to give dodecanedisulfonate. In fact, substantial amounts of dodecanedisulfonate were identified in a similar radical-addition initiated by nitrate salts.[1]

On the basis of the above experimental findings and the chain-carrying steps cited above, the basic reaction mechanism of the addition reaction may be deduced to be as follows:

$$\text{Solvent} \rightsquigarrow \text{A}, \tag{4}$$

$$\text{A} + HSO_3^- \longrightarrow \text{AH} + \dot{S}O_3^-, \tag{5}$$

$$\dot{S}O_3^- + CH_3(CH_2)_9CH{=}CH_2 \longrightarrow CH_3(CH_2)_9\dot{C}HCH_2SO_3^-, \tag{6}$$

$$CH_3(CH_2)_9\dot{C}HCH_2SO_3^- + HSO_3^- \longrightarrow CH_3(CH_2)_9CH_2CH_2SO_3^- + \dot{S}O_3^-, \tag{7}$$

$$CH_3(CH_2)_9\dot{C}HCH_2SO_3^- + \dot{S}O_3^- \longrightarrow CH_3(CH_2)_9CH(SO_3^-)CH_2SO_3^-, \tag{8}$$

where A represents the above-mentioned radiolytic species which participate in the initiation of the addition reaction.

Rate Equation. According to Eqs. 4 to 8, and assuming the usual steady-state approximation for each radical we obtain the over-all rate equation of the 1-dodecene consumption in the micellar solution as follows:

$$-\frac{d[RCH{=}CH_2]}{dt} = \frac{g_0 I_0}{4}\left\{1+\left(1+\frac{8k_6k_7}{g_0I_0k_8}[RCH{=}CH_2][HSO_3^-]\right)^{1/2}\right\}, \tag{9}$$

where g_0 is the number of A per absorbed dose of one eV; I_0, the dose rate (eV/g·s); k_6, k_7, and k_8, the rate constants of Eqs. 6, 7, and 8 in the micellar solution respectively, and $[RCH{=}CH_2]$, the 1-dodecene concentration.

From Fig. 1, the g-value (the number of molecules reacted per 100 eV of radiation energy absorbed) of 1-dodecene consumption was calculated to be 860 at the absorbed dose of 1.62×10^{18} eV/g (in irradiation time of 10 min) and at the concentrations of 0.0966 mol/l of 1-dodecene, 0.260 mol/l of sodium hydrogensulfite, and 0.11 mol/l of sodium 1-dodecanesulfonate. This g-value is very large compared to the primary yields of the active species produced from the radiolysis of water and organic compounds,[32,33] so it may be assumed that, in Eq. 9, $8k_6k_7[RCH{=}CH_2][HSO_3^-]/g_0I_0k_8 \gg 1$. Consequently, Eq. 9 can be simplified to

$$-\frac{d[RCH{=}CH_2]}{dt} = k[RCH{=}CH_2]^{1/2}[HSO_3^-]^{1/2}, \tag{10}$$

where,

$$k = \left(\frac{g_0I_0k_6k_7}{2k_8}\right)^{1/2}. \tag{11}$$

The expression of Eq. 10 agrees well with the experimental findings shown in Figs. 4 and 5.

Since the conversion of 1-dodecene was equal to that of sodium hydrogensulfite, Eq. 10 becomes

$$\frac{dx}{dt} = k(a-x)^{1/2}(b-x)^{1/2}, \tag{12}$$

where x is a variable representing the decrease in the concentrations of the reactants in the given time and where a and b are the initial concentrations of 1-dodecene and the hydrogensulfite ion respectively. On integrating Eq. 12 with the boundary condition, $x=0$ at $t=0$, the apparent rate constant of the 1-dodecene consumption can be derived as

$$k = \frac{2}{t}\ln\left\{\frac{(a-x)^{1/2}-(b-x)^{1/2}}{a^{1/2}-b^{1/2}}\right\}. \tag{13}$$

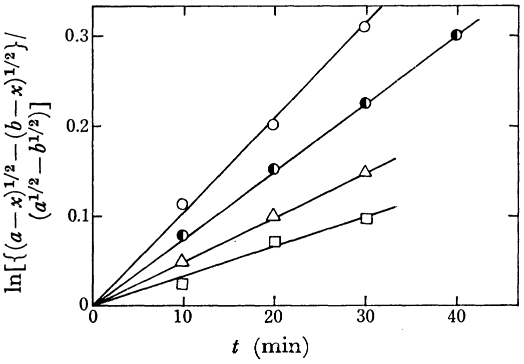

Fig. 6. Plots of $\ln[\{(a-x)^{1/2}-(b-x)^{1/2}\}/(a^{1/2}-b^{1/2})]$ against t.
○, ◐, △, □: See Fig. 4.

Table 3. THE APPARENT RATE CONSTANTS FOR THE ADDITION OF HSO_3^- TO 1-DODECENE UNDER VARIOUS REACTION CONDITIONS IN MICELLAR SOLUTIONS AT ROOM TEMPERATURE

$[NaHSO_3]$ $\times 10^2$ (mol/l)		[1-Dodecene] $\times 10^2$ (mol/l)	$[1\text{-}C_{12}H_{25}SO_3Na]$ $\times 10^2$ (mol/l)	Dose rate $\times 10^{-15}$ (eV/g·s)	k $\times 10^4$ (s^{-1})
9.61		6.75	1.8	2.70	2.4
9.61		6.75	3.7	2.70	2.4
9.61		6.75	7.3	2.70	2.5
9.61		6.75	11.0	2.70	2.4
14.4	Table 1	6.75	1.8	2.70	2.4
14.4		6.75	3.7	2.70	2.6
14.4		6.75	7.3	2.70	2.5
14.4		4.50	11.0	2.70	2.3
26.0		9.66	11.0	2.70	2.6
25.2		14.4	11.0	4.57	3.6
25.2	Fig. 6	14.4	11.0	1.68	1.7
25.2		14.4	11.0	0.819	1.0

Apparent Rate Constant. According to Eq. 13, a plot of $\ln[\{(a-x)^{1/2}-(b-x)^{1/2}\}/(a^{1/2}-b^{1/2})]$ against the time, t, should be a straight line, passing through the point of origin, with a slope equal to $k/2$. As is shown in Fig. 6, a good straight line was obtained for each dose rate by using the same data as those given in Fig. 3. The apparent rate constants can be calculated from the slopes of these straight lines; they are summarized in Table 3, together with those calculated from the values given in Table 1.

Dose-rate Dependence of the Apparent Rate Constant. According to Eq. 11, a plot of the logarithm of k against the logarithm of I_0 should be a straight line with a slope of 0.5. The plot of the experimental data gave a straight line with a slope of 0.73, as is shown in Fig. 7. This value is somewhat different from 0.5. This difference may be attributable to the termination steps other than Eq. 8, a part of which is presumably the reactions of the alkanesulfonate radical with radicals from the irradiated solvent.

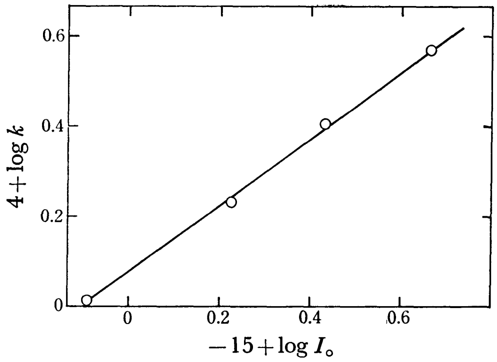

Fig. 7. Plot of log k against log I_0.

Surfactant Effects. Although the coupling reaction of the alkanesulfonate radical with the sulfite radical ion was proposed as the termination of the addition reaction, it is possible to postulate another coupling reaction, the dimerization of the alkanesulfonate radical, by analogy with radical reactions in general. According to the accepted model[34] for ionic micelles, the hydrophobic part of the aggregated surfactants forms the core of the micelles, which is liquid-paraffin-like in character, while the polar-head groups are located at the micelle-water interface in contact with, and hydrated by, a number of water molecules. The unpaired electron of the alkanesulfonate radical is assumed, on this basis, to be located at the micelle-water interface. On the contrary, the charged species, such as the sulfite, hydrogensulfite or sulfite radical ions, are generally in the bulk phase.[20] However, water molecules very probably penetrate beyond the polar-head groups at the micellar exterior.[35] Accordingly, it is assumed that solutes in the bulk phase may interact with the alkanesulfonate radical solubilized in the micelle, without penetrating into the nonpolar micellar core. Since there are a great number of micelles in the reaction solution, two or more alkanesulfonate radicals are scarcely ever produced in the micelle at the same time. Therefore, the rate of the dimerization of this radical may be very slow because there is electrostatic repulsion between the micelles. Consequently, the coupling reaction of the alkanesulfonate radical with the sulfite radical ion may be more predominant than the dimerization of the alkanesulfonate radical as the termination of the addition reaction.

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