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# The Mechanism for the Sulfonation of Olefins with a Sulfur Trioxide-Dioxane Complex[1)]

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The rates for the sulfonation of 1-dodecene with the sulfur trioxide-dioxane complex were measured spectrophotometrically. A bimolecular process occurred in this reaction, the rate being proportional to [1-dodecene] [$SO_3$-dioxane]. Furthermore, the stereochemistry of the initial products of the sulfonation reaction between *cis* or *trans*-2-butene and the sulfur trioxide-dioxane complex was studied. An equimolar amount of sulfur trioxide-dioxane (1: 1) was added to *cis*- or *trans*-2-butene in chloroform to give the sultone, (I) or (II); (I) 1.5(q), 4.7—5.1(m), $J_{AB}$ 7.9, $J_{BC}$ 8.0, $J_{CD}$ 6.0 Hz; (II) 1.5(q), 4.2—4.6(m), $J_{AB}$ 6.8, $J_{BC}$ 5.4, $J_{CD}$ 6.8 Hz. These results indicate that the 2,3-butanesultones were produced stereospecifically from the corresponding 2-butene isomers. Similarly, the sulfonation of *cis*- or *trans*-2-pentene with sulfur trioxide-dioxane gave the corresponding 2,3-pentanesultones.

The sulfonation reaction of olefins, in particular long chain aliphatic α-olefins, with sulfur trioxide is utilized widely, even on a commercial scale, today. The reaction mechanism for the sulfonation of aliphatics, however, is scarcely known, although that of aromatic hydrocarbons has been extensively investigated.[2)] Some reports have been published on the mechanisms for the sulfonation of aliphatic olefins, these reports suggest that a four-membered ring sultone is formed *via* a zwitter-ion intermediate.[3-5)] However, no experimental proof for such an intermediate has been described, nor has any kinetic study about the sulfonation of aliphatic compounds been done.

In this paper, we wish to report on kinetic studies of the reaction between 1-dodecene and the sulfur trioxide-dioxane complex and a stereochemical studies of the sulfonation products of *cis*- and *trans*-2-butenes and *cis*- and *trans*-2-pentenes with the sulfur trioxide-dioxane complex.

## Experimental

*Experimental Procedure.* *Kinetic Studies of the Sulfonation*: Kinetic experiments were carried out by the stopped-flow method* using a rapid scanning-type spectrophotometer (Hitachi Model RSP-2). In order to determine the rate of sulfonation, 1-dodecene and the $SO_3$-dioxane (1: 1) complex were mixed in a mixing cell (path length, 1 cm); the decay curve in the absorbance appearing on an oscilloscope at 240 nm was used.

Three different molar ratios of 1-dodecene to $SO_3$-dioxane were taken: 1.05: 1; 1: 1; 1: 1.5. A 0.2 M solution of 1-dodecene in ethylene dichloride and a 0.2 M solution of $SO_3$-dioxane in the same solvent were mixed at 25 °C, and then the absorbance was measured up to 500 ms after mixing. For the identification of the reaction products, the NMR spectra were measured.

*Stereochemical Studies of the Sulfonation*: Each of the *cis* and *trans* isomers of 2-butene and 2-pentene was allowed to react with a $SO_3$-dioxane (1: 1) complex in chloroform at 0 °C for one hr, after which the 220 MHz or 100 MHz NMR spectra of the reaction mixture were measured at −5 °C. One half of the reaction mixture was then hydrolyzed with water and neutralized wih an excess of sodium hydroxide to give white crystals. To the other half of the reaction mixture were added two equivalents of aniline, and the mixture was allowed to stand for 24 hr and then neutralized to give crystals, which were recrystallyzed from aqueous ethanol (50: 50). These crystals were subjected to NMR spectral analysis.

*Reagents.* The 1-dodecene——99.5% in purity by glc, prepared by the polymerization of ethylene——was dried over metallic sodium and distilled before use. The dioxane——a commercial product of a reagent grade——was dried over metallic sodium and distilled before use. The ethylene dichloride and chloroform——commercial materials of a reagent grade——were dried over $P_2O_5$ and distilled. The *cis*-2pentene (95.5%), *trans*-2-pentene (99.8%), *cis*-2-butene (98.3%) and *trans*-2-butene (98.0%)——all commercial materials——were used as received. The purity in parentheses were determined by glc.

## Results and Discussion

*Kinetic of the Reaction between 1-Dodecene and the $SO_3$-Dioxane Complex.* The reaction product between 1-dodecene and the $SO_3$-dioxane complex in the initial stage was identified[6)] as a β-sultone** by 100 MHz NMR analysis.

The molar extinction coefficients (ε) at 240 nm were measured for $SO_3$-dioxane, 1-dodecene and β-sultone. Lambert-Beer's law held in each case and the values of ε were found to be as follows.

| | $\varepsilon_{240\,\mathrm{nm}}$ (l/mol·cm) |
|---|---|
| $SO_3$-dioxane | 6.63 |
| 1-dodecene | 1.37 |
| $C_{12}$-β-sultone | 2.72 |
| ethylene dichloride | 0.00272 |

The $\varepsilon_{240\,\mathrm{nm}}$ value of ethylene dichloride is so much smaller than those of $SO_3$-dioxane, *etc.* that the total absorbances *versus* *x* is given by:

$$\mathrm{Abs}_{240\,\mathrm{nm}} = 6.63(a-x) - 1.37(b-x) + 2.72x$$

The reaction rate equation can be expressed as follows.

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* Immediately after the 1-dodecene and $SO_3$-dioxane complex were mixed, measurement of the UV absorbance (at 240 nm) was started *versus* time.

** β-Sultone was stable to heat (no change in the NMR spectrum in 10 min at 65 °C) but was decomposed in a short time in the presence of a relatively weak base, for example, upon addition of a small amount of $CD_3OD$.

$$dx/dt = k_{n+m}(a-x)^n(b-x)^m$$

where

$k_{n+m}$: rate constant of the $(n+m)$th-order reaction
$n,m$: integer
$a$: initial concentration of the $SO_3$-dioxane complex
$b$: initial concentration of 1-dodecene
$x$: concentration of the reacted $SO_3$-dioxane (=that of the formed $\beta$-sultone)

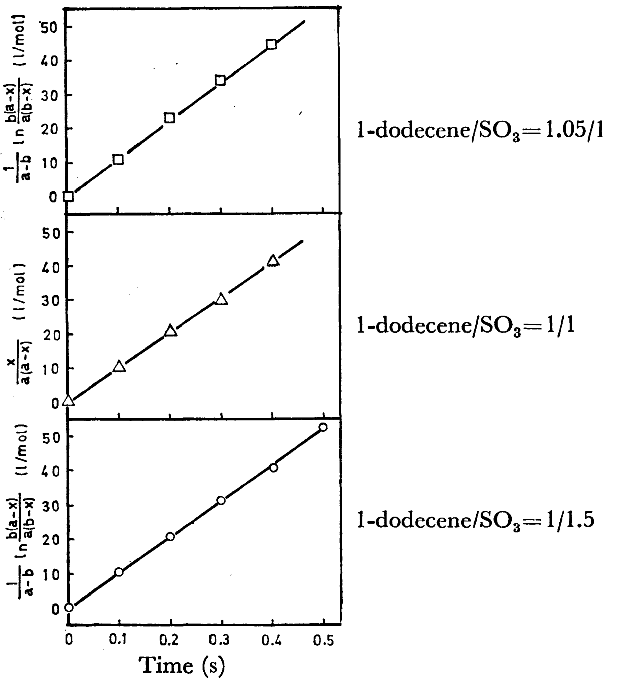


Fig. 1. The second-order type plots for different molar ratios of 1-dodecene to $SO_3$–dioxane at 25 °C.

An electrophilic addition reaction by $SO_3$ seems applicable in the first stage of this reaction; much as in the sulfonation of aromatic hydrocarbons.[7,8] The formation of sulfonic acid anhydride was not found here unlike the case of aromatic hydrocarbons; hence, the reaction is likely to become simpler thus, $m=1$. Besides, a straight line was obtained in the case of the second-order plot; $1/(a-b)\cdot\ln b(a-x)/a(b-x)$ *versus* time (Fig. 1). Therefore, in the molar ratios of 1-dodecene to the $SO_3$-dioxane complex from 1.05: 1 to 1: 1.5, the reaction is first-order with respect to both [α-olefin] and [$SO_3$] and second order as a whole. The second-order rate constant ($k_2$) was determined as follows from the figure.

$$k_2 = (1.1\pm0.1)\times10^2\ \mathrm{l\,mol^{-1}\,s^{-1}}\ (\text{at } 25°\mathrm{C})$$

This value is smaller by a factor of $10^3$ than the rate constant of the sulfonation of an α-olefin in a thin-film reactor with gaseous $SO_3$.[9]

*Stereochemical Studies.* The kinetic studies showed that (1) the reaction between an α-olefin and $SO_3$ yields a β-sultone in the initial stage, and (2) the reaction is second-order and first order with respect to α-olefin and $SO_3$ respectively. Now, to see whether $SO_3$ undergoes a step-by-step addition to the α-olefin *via* a zwitter-ion or a concerted reaction, stereochemical studies of the reaction of $SO_3$ with *cis* and *trans* isomers of 2-butene and 2-pentene were undertaken.

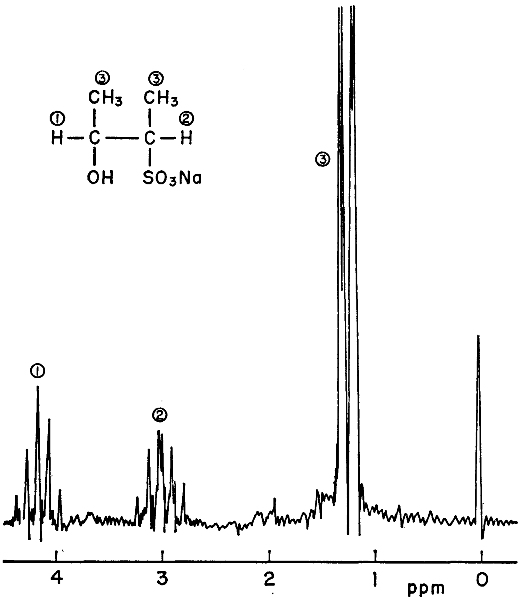


Fig. 2. The NMR spectrum of 3-hydroxybutane-2-sulfonate derived from *cis*-2-butene in $D_2O$ at 25 °C, internal standard DSS.

The NMR spectra of the hydrolyzed products from *cis*- and *trans*-2-butene were exactly the same, as is shown in Fig. 2, demonstrating them to be 3-hydroxybutane-2-sulfonate. Found: S, 18.0 (*cis*); 18.3 (*trans*)%; Calcd for $C_4H_9O_4SNa$: 18.2%. Furthermore, from either *cis*- or *trans*-2-butene, we could isolate sodium 3-anilinobutane-2-sulfonate as white crystals (Table 1). Found: S, 12.7 (*cis*); 13.0 (*trans*)%; Calcd for $C_{10}H_{14}O_3SNa$: 12.7%. Therefore, the initial sulfonation products from both *cis*- and *trans*-2-butene must be the four-membered ring 2,3-sultone and not the six-membered ring 4,5-dimethyl-1,3-dioxa-2,6-dithiacyclohexane-2,2,6,6-tetraoxide ("carbyl sulfate").[6,10]

Table 1. Chemical shifts (ppm) from the internal standard DSS and assignment of aniline derivatives of 2,3-sultones

| Assignment | | Chemical shift (ppm) *cis* | *trans* |
|---|---|---|---|
| H-C-$SO_3$Na | | 3.20 | 3.20 |
| <u>H</u>-C-NH-$C_6H_5$ | | 4.16 | 3.88 |
| $CH_3$ | | 1.25 | 1.38 |
| $C_6H_5$ | *o*-, *p*- | 6.86 | 6.86 |
| | *m*- | 7.30 | 7.30 |

It is noteworthy that the IR spectrum of the anilinobutane sulfonate obtained from *cis*-2-butene was superimposable upon that from the *trans* isomer, whereas the NMR spectra of these two samples exihibited different chemical shifts due to the <u>H</u>-C-$NHC_6H_5$ methine group, as is shown in Table 1. This difference will be discussed in some detail later in this paper.

We next studied the stereochemistry of the reaction products of *cis*- and *trans*-2-butene with the $SO_3$-dioxane complex by means of 220 MHz NMR analysis (Fig. 3). The NMR spectra of the products from the

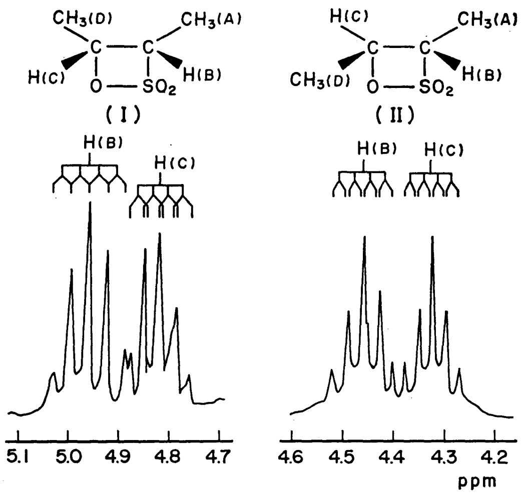


Fig. 3. The methine region of the 220 MHz NMR spectra of *cis*-butane sultone and *trans*-butane sultone derived from *cis*- and *trans*-2-butene in $CHCl_3$ at −5 °C, internal standard TMS.

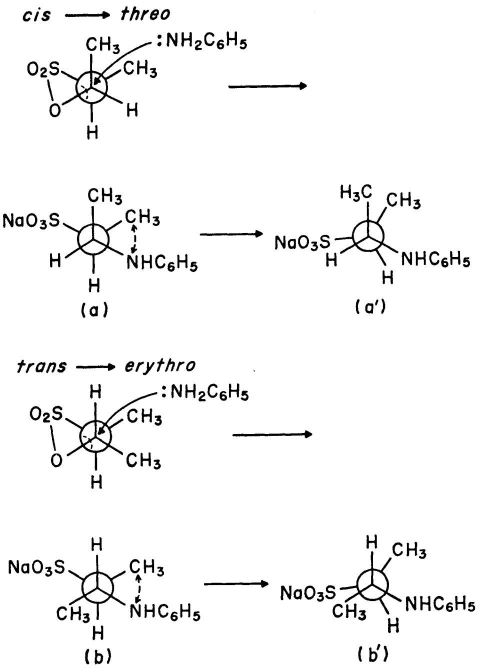
isomeric olefins both showed an ABM system with a quartet at 1.5 ppm and a multiplet at 4.7—5.1 ppm for the *cis*, while it showed a quartet at 1.5 ppm and a multiplet at 4.2—4.6 ppm for the *trans*, and no other peak was found. It follows that the 2,3-sultones were produced stereospecifically from the corresponding 2-butene isomers.

Similarly, the sulfonation of *cis*- and *trans*-2-pentene with the $SO_3$–dioxane complex gave the corresponding 2,3-sultones.

Even in a non-complex system (an equimolar amount of $SO_3$ was added to *cis*- or *trans*-2-butene in chloroform at 0 °C), the stereospecific formation of *cis*- and *trans*-2,3-butanesultone was observed and a minor amount of products as yet unidentified was obtained.

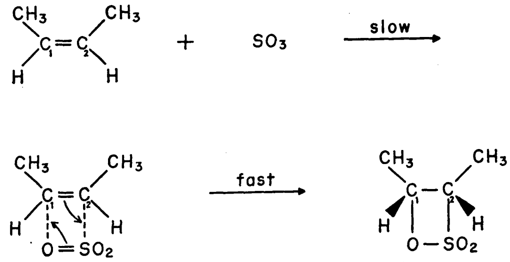
The chemical shifts for two methines of the 2,3-sultone derived from *cis*-2-butene appeared at a lower field than those of the 2,3-sultone derived from *trans*-2-butene. It is almost certain that the former sultone has a *cis* configuration, while the latter has a *trans*, because, in the *cis*-sultone, the two methine hydrogen atoms are likely to be pushed toward the O–$SO_2$ side as a result of the repulsion by two methyl groups; as a result, the resonance signal would appear at a lower field, as was indeed observed.

The above-mentioned differences between the NMR spectra of the aniline adducts can be ascribed to the *threo* and *erythro* configuration. Aniline attacks the carbon atom bonded to oxygen by the $S_N2$ mechanism, and the *threo* configuration is formed from the *cis*-sultone, whereas the *erythro* is formed from the *trans*, as is shown in Scheme 1. An examination of the molecular models indicates that the sulfonate and anilino groups are so large that the rotation about the C–C axis bearing these groups is restricted. Also, the *gauche*-disposed NH–$C_6H_5$ and $CH_3$ groups undergo mutual repulsion to take such a conformation as (a′) and (b′) and no isomerization was observed. These findings also suggest that the 2,3-sultones were produced stereospecifically.



Scheme 1.

These results contain two possible mechanisms; one is that $SO_3$ forms a ring perfectly in a concerted reaction, while the other is that a zwitter-ion is once formed. However, the sultone ring is formed much faster than the rotation of $C_1$–$C_2$, which is minimized by the dipolar attractive force (Scheme 2). In this case, dioxane merely weakens the reactivity of $SO_3$; rather, it behaves as a polar solvent to make the zwitter-ion stable. Consequently, it seems more difficult to consider a zwitter-ion intermediate in the case of the non-complex system.



Scheme 2.

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