Bull. Chem. Soc. Jpn., ***68***, *211—218(1995)*

Model Reaction of Self-Condensation of Sulfenic Acids. Kinetic Investigation for the Reaction of Methyl Benzenesulfenate with *trans*-Decalin-9-sulfenic Acid# and 2-Methyl-2-propanesulfenic Acid

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(Received May 20, 1994)

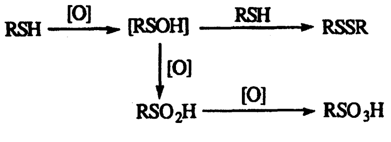
Reaction of 2-methyl-2-propanesulfenic acid (**1**) with methyl arenesulfenates (**2**) gave *S*-aryl 2-methyl-2-propanethiosulfinates quantitatively, and kinetic investigation was carried out. Second-order rate dependence (first-order in methyl benzenesulfenate (**2a**) and first-order in the sulfenic acid (**1**)) was observed, and a small activation enthalpy ($\Delta H^{\ddagger}=28\ \mathrm{kJ\,mol^{-1}}$) and a large negative activation entropy ($\Delta S^{\ddagger}=-130\ \mathrm{J\,K^{-1}\,mol^{-1}}$) were obtained. Kinetics for the reaction of *trans*-decalin-9-sulfenic acid (**3**) with the sulfenates **2** under acidic conditions in methanol–water gave the observation of the second-order dependence, a small activation enthalpy ($\Delta H^{\ddagger}=30.5\ \mathrm{kJ\,mol^{-1}}$), a large negative activation entropy ($\Delta S^{\ddagger}=-140\ \mathrm{J\,K^{-1}\,mol^{-1}}$), a large negative Hammett ρ-value ($\rho=-1.39$) and no solvent isotope effect ($k_{\mathrm{MeOH}}/k_{\mathrm{MeOD}}=1.10$—$1.14$ in the range of 15.64—29.98 °C). Kinetics for acidic hydrolysis of the sulfenate **2** under the same conditions afforded the similar activation parameters ($\Delta H^{\ddagger}=40.7\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ddagger}=-200\ \mathrm{J\,K^{-1}\,mol^{-1}}$ at $[\mathrm{H_2O}]=0.80\times10^{-3}\ \mathrm{mol\,dm^{-3}}$) and a larger negative Hammett ρ-value ($\rho=-2.22$) than that for the reaction of the sulfenic acid **3** with the sulfenate **2**. From these results, structures of the transition state for both the self-condensation of sulfenic acid and the hydrolysis of the sulfenate ester **2** were discussed. The reaction of sulfenate esters **2** with stable sulfenic acids is a good model for studying the self-condensation of sulfenic acids.

Sulfenic acids (RSOH) have been considered as transient intermediates in the oxidation process of thiols (RSH) in organic and living systems forming the corresponding disulfides (RSSR), sulfinic acids (RSO_2H), sulfonic acids (RSO_3H), etc. as shown in Scheme 1.

Further, formation of protein sulfenic acids in certain enzymes are known in oxidation of the cysteine residues in proteins.[1] The oxidation products undergo no further oxidation and reduction by mild reducing agents back to the corresponding thiols, i.e., the active enzymes.[1] It is also known that some acylsulfenic acids[2] are generated in the process converting carboxyl groups to thio acids by bacterium.[3]

Although existence of sulfenic acids is well recognized and an importance of their chemistry has been shown, most of the sulfenic acids are seldom isolated or even detected. Only a few special examples are known, and the reasons for their high reactivity still remain unclear. Main cause of their instability is facile self-condensation to form the corresponding thiosulfinates (RS(O)SR), and thus mechanistic investigation for the chemistry of sulfenic acids have been difficult. Only ten sulfenic acids[4—11] have been isolated at room temperature to date. Recently we briefly reported an isolation of *trans*-decalin-9-sulfenic acid (**3**)[11] as crystals at room temperature. One of the most effective way to stabilize sulfenic acids may be a steric inhibition of the decomposition. 2-Methyl-2-propanesulfenic acid (**1**)[12] is an example of a sterically hindered aliphatic sulfenic acid, although it is observed only in solution. 9-Triptycenesulfenic acid[9] and **3**[11] are the examples of highly bulky sulfenic acids isolated.

Shelton and Davis[12] examined kinetically the self-condensation of the sulfenic acid **1** to give *S*-*t*-butyl 2-methyl-2-propanethiosulfinate (**4**) in benzene by ^{1}H NMR. They reported that the self-condensation is catalyzed by both acid and base. In spite of expectation of bimolecular reaction in the self-condensation of sulfenic acids, they observed a first-order kinetics. The



Scheme 1.

The common name decalin is used in this paper instead of bicyclo[4.4.0]decane.

kinetic behavior may reveal that the starting state is already a dimer by intermolecular hydrogen bonding.

Many workers[12—20] have suggested that the reason why sulfenic acids form thiosulfinates so easily is that the intermolecular hydrogen bonding leads to a five-membered ring transition state lowering the potential energy and entropy (Scheme 2). The exceptional stability of anthraquinone-1-sulfenic acid[4] has been proposed to be attributed to intramolecular hydrogen bonding[20] with adjacent functional group that inhibits from the intermolecular hydrogen bonding.

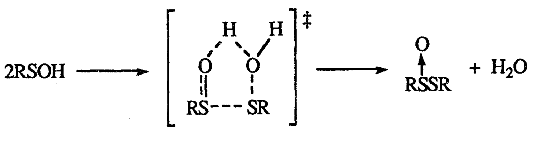
However Okuyama et al. and we[21] recently reported that the sulfenic acid **1** readily undergoes self-condensation even in aqueous acetonitrile which inhibits from the intermolecular hydrogen bonding between two sulfenic acid molecules by predominant hydrogen bonding with water. From the observation of second-order kinetic behavior, it was suggested that the mechanism involves the nucleophilic attack of free sulfenic acid at the backside of the S–O bond of the protonated sulfenic acid.

In order to investigate further reactivity of sulfenic acid, it is necessary to prepare more stable sulfenic acids, i.e., more bulky sulfenic acids. However, the more bulky sulfenic acids may lead us the more difficulty to investigate the mechanism of the self-condensation. As one of the best ways to surmount such difficulty, a condensation of the bulky sulfenic acids with esters of some reactive sulfenic acids will promise us to give a good model of self-condensation of sulfenic acids.

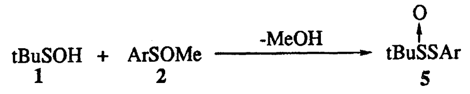
In this paper, we will describe kinetic investigations for the reactions of 2-methyl-2-propanesulfenic acid (**1**) and *trans*-decalin-9-sulfenic acid (**3**) with methyl benzenesulfenate (**2a**)[22] under acidic conditions to give *S*-phenyl 2-methyl-2-propanethiosulfinate (**5**) and *S*-phenyl *trans*-decalin-9-thiosulfinate (**6**), respectively, together with the hydrolysis of methyl benzenesulfenate under the same conditions as a related reaction.

Results and Discussion

Reaction of 2-Methyl-2-propanesulfenic Acid with Methyl Arenesulfenate. When the sulfenic acid **1**[12,21] was mixed with methyl *p*-chlorobenzenesulfenate[22] in aqueous methanol in NMR tube, the reaction was completed immediately to give *S*-*p*-chlorophenyl 2-methyl-2-propanethiosulfinate quantitatively under neutral and acidic conditions (Scheme 3). Since the present system is convenient for kinetic experiment, the reaction will become a good model for investigation of the self-condensation of sulfenic acids.



Scheme 2.


$$\underset{\mathbf{1}}{\text{tBuSOH}} + \underset{\mathbf{2}}{\text{ArSOMe}} \xrightarrow{\text{-MeOH}} \underset{\mathbf{5}}{\text{tBu}\overset{\text{O}}{\overset{\uparrow}{\text{S}}}\text{SAr}}$$

Scheme 3.

Kinetics for the condensation of the sulfenic acid **1** with methyl benzenesulfenate (**2a**) was carried out in acidic aqueous solution (H_2O/CH_3CN 1/1, $[HClO_4]=5.0\times10^{-5}$ mol dm^{-3}) at 10.94—39.12 °C. The reaction was followed by monitoring the increasing UV absorbance at 260 nm of *S*-phenyl 2-methyl-2-propanethiosulfinate (**5**). The reaction of the sulfenate **2a** with excess sulfenic acid **1** was found nicely to correlate to pseudo-first-order kinetic law, and isosbestic point was observed at 292 nm. The pseudo-first-order rate constants k_1 obtained are compiled in Table 1, and the k_1 values were plotted against the concentration of the sulfenic acid **1** as shown in Fig. 1. From the Fig. 1, it was found that the k_1 values are approximately proportional to the concentration of the sulfenic acid **1** suggesting the second-order kinetics involving the first-order in the concentration of both **1** and **2a**. Some scatter shown in Fig. 1 is due mainly to inaccuracy of the initial concentration of the sulfenic acid **1** because of its decomposition during preparation of the stock solution containing high concentration of **1**. The second-order kinetic observation is consistent with the previous results[21] for the self-condensation of sulfenic acid **1**.

The self-condensation of sulfenic acid **1** was too slow to measure under the same conditions. Conversion of the self-condensation during the 10-fold period of the half-life of the reaction with the sulfenate **2a** was estimated as only 0.006% at 34.60 °C in H_2O/CH_3CN 80/20 from the data of the self-condensation previously reported[21] by extrapolation to pH 4.3. Assuming that the solvent effect is small, the self-condensation at 20.40 °C is negligible during the reaction with the sulfenate **2a**.

Okuyama et al.[23] reported kinetics for the acidic hydrolysis of ethyl benzenesulfenate in aqueous solution.

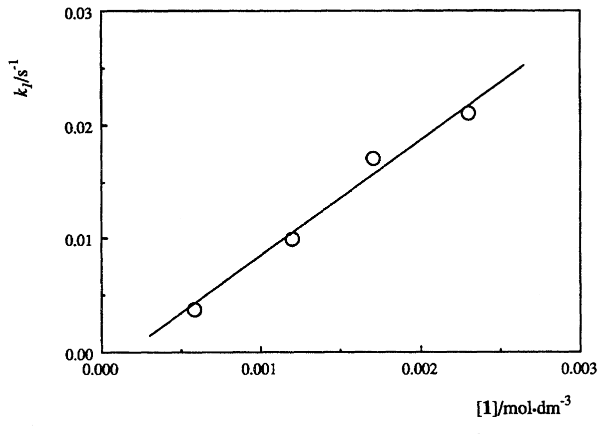


Fig. 1. Dependence of the rate constants for the reaction of 2-methyl-2-propanesulfenic acid (**1**) with methyl benzenesulfenate (**2a**) on the concentration of the sulfenic acid **1**.

Table 1. Kinetic Data for the Reaction of 2-Methyl-2-propanesulfenic Acid (**1**) with Methyl Benzenesulfenate (**2a**) in H_2O/CH_3CN 1/1 in the Presence of $HClO_4$ (5.0×10^{-5} $mol\,dm^{-3}$)

Temp	$[\mathbf{1}]\times10^4$	$[\mathbf{2a}]_0\times10^5$	$k_1\times10^3$	k_2
°C	$mol\,dm^{-3}$	$mol\,dm^{-3}$	s^{-1}	$mol^{-1}\,dm^3\,s^{-1}$
20.40	5.8	3.29	3.7	6.4
20.40	12	3.29	9.9	
20.40	17	3.29	17	
20.40	23	3.29	21	
10.94	5.8	3.29	2.4	4.1
29.98	5.8	3.29	5.2	9.0
39.12	5.8	3.29	7.7	13.3
20.40[a)]	0.0	23.4	0.00282±0.00001	

a) Hydrolysis rate of PhSOMe under the same conditions.

In order to examine the contamination of the hydrolysis in the present reaction, the rate of hydrolysis of methyl benzenesulfenate (**2a**) was measured under the same reaction conditions. As a result the hydrolysis of the sulfenate **2a** was found to be more than ca. 1300 times slower than the reaction with **1**.

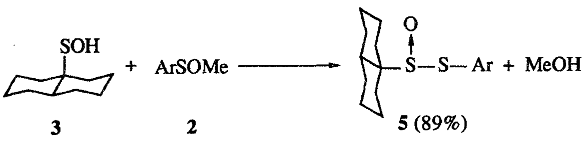
Arrhenius plot of the second-order rate constants (k_2) and k_1 gave a small activation enthalpy (28 $kJ\,mol^{-1}$) and large negative activation entropies (-130 $J\,K^{-1}\,mol^{-1}$ per $mol\,dm^{-3}$, and -200 $J\,K^{-1}\,mol^{-1}$ at present concentration of the sulfenic acid). The small value of the activation enthalpy reflects the high reactivity of the sulfenic acids, and the magnitude of the activation entropy is consistent with a bimolecular reaction mechanism. The second-order kinetics does not fit the S_N1 type mechanism involving an initial formation of a sulfenium cation, nor the radical mechanism via a rate-determining homolytic cleavage of the S–O bond of the ester. The present data are also inconsistent to the idea of substantial formation of the complex between the sulfenic acid and the ester, unlike the results of Shelton and Davis[12)] in which a hydrogen bonded dimer of the sulfenic acid **1** in organic solvent and first-order kinetic behavior of the self-condensation in benzene were observed. From these results the reaction of the sulfenic acid **1** with the sulfenate **2a** is considered to proceed via a nucleophilic substitution by the free sulfenic acid on the sulfur atom of the protonated sulfenate ester.

Therefore, the present system is a good model reaction which is faster than both the self-condensation of the sulfenic acid **1** and the hydrolysis of the sulfenate **2a**.

Reaction of *trans*-Decalin-9-sulfenic Acid (3) with Methyl Arenesulfenates (2). Unlike the sulfenic acid **1**, *trans*-decalin-9-sulfenic acid (**3**) can be obtained as a pure crystal form, and thus it is an excellent substance for kinetics. Further, it is interesting to examine if such highly bulky sulfenic acids as **3** react with other sulfenic acids. Therefore, the reaction of the sulfenic acid **3** with methyl benzenesulfenate (**2a**) was carried out in $CDCl_3$ in NMR tube. The reaction was completed in an hour to give *S*-phenyl *trans*-decalin-9-thiosulfinate (**6**) quantitatively (Scheme 4). This reaction also proceeded in methanol to afford the corresponding thiosulfinate in 89% yields as an oil, though the thiosulfinate **6** is not very stable and decomposes to diphenyl disulfide and some unidentified compounds at room temperature in one week.

Kinetics for the condensation of the sulfenic acid **3** and the sulfenates **2** was carried out in acidic aqueous methanol solution ($[HClO_4]=0$—8.43×10^{-3} $mol\,dm^{-3}$) at 15.64—29.98 °C. The reaction was followed by monitoring the increasing UV absorbance at 280 nm of the thiosulfinate **6**. The reaction of the sulfenate **2a** with excess sulfenic acid **3** was found nicely to correlate to pseudo-first-order kinetic equation, and an isosbestic point was observed (Ar=Ph, at 305 nm). The UV spectra of the final stage of the kinetic run displayed the shape of the thiosulfinate **6** and the pseudo-first-order rate constants k_3 obtained are compiled in Table 2. The rate of self-condensation of the sulfenic acid **3** is too slow to be estimated unlike that of the sulfenic acid **1** under acidic conditions, and thus negligible in the present system.

It is necessary to take into account the contamination from the hydrolysis of the sulfenate in the present reactions. The rate of hydrolysis of the sulfenate **2a** was measured under two conditions ($[H_2O]=0.80\times10^{-3}$ $mol\,dm^{-3}$, $[H^+]=2.41\times10^{-3}$ $mol\,dm^{-3}$ in MeOH, at 34.60 °C and $[H_2O]=4.4\times10^{-3}$ $mol\,dm^{-3}$, $[H^+]=4.22\times10^{-3}$ $mol\,dm^{-3}$ in MeOH, at 25.20 °C), and the pseudo-first-order rate constants obtained were compiled in Table 2. The hydrolysis of the sulfenate **2a** was found to be about 85 or 12 times slower under each condition than the reaction with the sulfenic acid **3**. Therefore, the hydrolysis of the sulfenate **2a** is



Scheme 4.

Table 2. Kinetic Data for the Reaction of *trans*-Decalin-9-sulfenic Acid (**3**) with Methyl Arenesulfenate (XC_6H_4SOMe (**2**)) in Aqueous Methanol Solution

X	Temp	[**3**] × 10^3	[**2**]$_0$ × 10^3	[H^+] × 10^3	[H_2O] × 10^3	$k_3 \times 10^3$	k_4
	°C	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	mol dm^{-3}	s^{-1}	mol^{-1} dm^3 s^{-1}
H	34.60	3.35	0.234	2.41	0.80	3.29 ±0.01	
H	34.60	6.70	0.234	2.41	0.80	5.64 ±0.09	0.842±0.001
H	34.60	10.05	0.234	2.41	0.80	8.46 ±0.06	
H	34.60	13.40	0.234	2.41	0.80	11.7 ±0.1	
H[a)]	25.20			0.00	4.4		1.56 ±0.07
H[a)]	25.20			0.0430	4.4		1.62 ±0.09
H[a)]	25.20			0.853	4.4		0.269±0.013
H[a)]	25.20			2.16	4.4		0.365±0.012
H[a)]	25.20			4.22	4.4		0.578±0.068
H[a)]	25.20			8.43	4.4		1.01 ±0.14
H	15.64	3.42	0.213	4.32	4.4	1.86 ±0.01	0.546±0.002
H	20.40	3.42	0.213	4.32	4.4	2.33 ±0.01	0.682±0.001
H	25.20	3.42	0.213	4.32	4.4	2.88 ±0.01	0.843±0.002
H	29.98	3.42	0.213	4.32	4.4	3.58 ±0.01	1.05 ±0.01
H[b)]	15.64	3.42	0.205	4.32	4.4	1.70 ±0.01	0.498±0.002
H[b)]	20.40	3.42	0.205	4.32	4.4	2.10 ±0.01	0.614±0.002
H[b)]	25.20	3.42	0.205	4.32	4.4	2.53 ±0.01	0.741±0.001
H[b)]	29.98	3.42	0.205	4.32	4.4	3.15 ±0.01	0.920±0.001
m-Cl	34.60	6.70	0.234	2.41	0.80	2.43 ±0.01	0.362±0.001
p-Cl	34.60	6.70	0.234	2.41	0.80	3.98 ±0.01	0.594±0.001
p-Me	34.60	6.70	0.234	2.41	0.80	13.9 ±0.1	2.08 ±0.01
p-MeO	34.60	6.70	0.234	2.41	0.80	19.9 ±0.1	2.96 ±0.01
H[c)]	34.60	0.00	0.234	2.41	0.80	0.0708±0.0003	
H[c)]	25.20	0.00	0.331	4.22	4.4	0.319 ±0.01	

a) [**3**] = 5.60×10^{-3}—8.43×10^{-3} mol dm^{-3}, [**2**]$_0$ = 1.59×10^{-4}—7.87×10^{-4} mol dm^{-3}. b) The solvent is MeOD. c) The rate constants of hydrolysis of PhSOMe.

neglected under all these kinetic conditions.

Plot of the k_3 values against the concentration of the sulfenic acid **3** gave the straight line as shown in Fig. 2, suggesting that the reaction is of the second-order, the first-order in the concentration of both the sulfenic acid **3** and the sulfenate **2a**. The second-order rate constants k_4 were plotted against the concentration of perchloric acid as depicted in Fig. 3 and were found to have a first-order dependence on the concentration of perchloric acid in the acidic region.

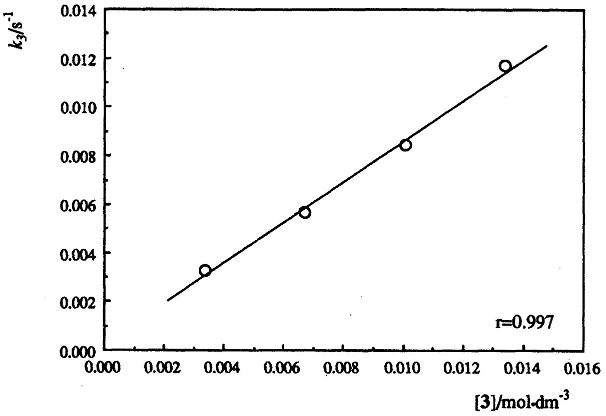


Fig. 2. Plot of the rate constants for the reaction of *trans*-decalin-9-sulfenic acid (**3**) with methyl benzenesulfenate (**2a**) against the concentration of **3**.

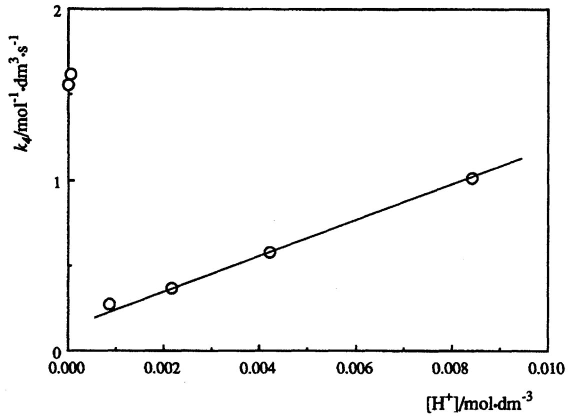
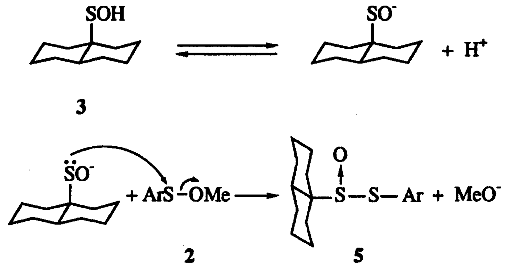


Fig. 3. Dependence of the second-order rate constants for the reaction of *trans*-decalin-9-sulfenic acid (**3**) with methyl benzenesulfenate (**2a**) on the concentration of perchloric acid.

The unusual acceleration in the reaction without perchloric acid may be a participation of the reaction with dissociated sulfenic acid as shown in Scheme 5. We previously reported that pK_a of 2-methyl-2-propanesulfenic acid (**1**) is estimated as 10.47 and it's self-condensation under alkaline conditions is much faster than under acidic conditions.[21)] Even a very slight dissocia-

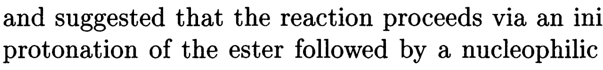


Scheme 5.

tion of the sulfenic acid **3** may cause the acceleration of both the reaction with the sulfenate **2a** and the self-condensation of the sulfenic acid **3**. The product of the reaction of the sulfenic acid **3** with the sulfenate **2a** in methanol under neutral conditions was the thiosulfinate **6** without contamination of the self-condensation product, though the concentration was much higher than the kinetic conditions. The product under the kinetic conditions also considered to be the thiosulfinate **6**, because the UV spectra of the final stage of the kinetic run under the neutral conditions displayed the shape of the thiosulfinate **6** like that under the acidic conditions.

Arrhenius plot of the second-order rate constants (k_4) and k_3 for the reaction in MeOH gave a small activation enthalpy (30.5 kJ mol^{-1}) and large negative activation entropies (-140 J K^{-1} mol^{-1} per mol dm^{-3}, -190 J K^{-1} mol^{-1} ([**3**]$=3.42\times10^{-3}$ mol dm^{-3})) in the range of 15.64—29.98 °C. Magnitude of these parameters is very similar to that obtained for the reaction of the sulfenic acid **1** with the sulfenate **2a**, and thus the mechanism for the reaction of the sulfenic acid **3** with the sulfenate **2a** is considered to be bimolecular reaction involving a nucleophilic substitution of the free sulfenic acid on the sulfur atom of the protonated sulfenate.

Then in order to examine a possibility of the rate-determining protonation of the oxygen atom of the sulfenate or a possibility to proceed via a five-membered cyclic transition state involving a proton transfer, the rate of the reaction was measured in MeOD. Arrhenius plot of the second-order rate constants (k_4) and k_3 for the reaction in MeOD gave similar activation parameters ($\Delta H^{\ddagger}=28.4$ kJ mol^{-1}, $\Delta S^{\ddagger}=-150$ J K^{-1} mol^{-1} per mol dm^{-3}, $\Delta S^{\ddagger}=-200$ J K^{-1} mol^{-1} ([**3**]$=3.42\times10^{-3}$ mol dm^{-3})). The rate constants of the reaction k_{MeOD} in MeOD were found to be almost the same as k_{MeOH} ($k_{\mathrm{MeOH}}/k_{\mathrm{MeOD}}=1.10$—$1.14$) in the range of 15.64—29.98 °C suggesting that the protonation step of the sulfenate **2a** cannot be rate-determining and the five-membered cyclic mechanism involving the concerted proton transfer shown in Scheme 2 is also unlikely. Since the acid catalyst is actually not H_3O^+ but MeO^+H_2 in this system, the solvent deuterium isotope effect for the equilibrium protonation is estimated as K_H/K_D 0.69 from the isotopic fractionation factors.[24] Therefore the observed isotope effect is considered to be the result of cancellation by the effect for other step k_H/k_D ca. 1.6. The small kinetic isotope effect k_H/k_D 1.6 may be attributed to rather secondary isotope effect than primary one.

 (1)

$$\mathrm{PhSOMe}+\mathrm{Me}\overset{+}{\mathrm{O}}\mathrm{H_2}\rightleftarrows\mathrm{PhS}\underset{\mathrm{H}}{\overset{+}{\mathrm{O}}}\mathrm{Me}+\mathrm{MeOH}\quad K_H/K_D=0.69 \qquad (1)$$

Substituent effect on the phenyl group for the reaction of the sulfenate ester **2a** was studied in MeOH ([H_2O]$=8.0\times10^{-3}$ mol dm^{-3}, [$HClO_4$]$=2.41\times10^{-3}$ mol dm^{-3}) at 34.60 °C. As is apparent from the Hammett plot shown in Fig. 4, $\log_{10} k_4$ nicely correlates to the σ-values to give a negative ρ-value ($\rho=-1.39$). This is the first example of Hammett ρ-value for the reaction related to the self-condensation of sulfenic acids. The negative trend reveals importance of pre-equilibrium protonation of the sulfenate ester **2**. From these results, the reaction is considered to proceed via an initial protonation of the sulfenate ester **2** followed by a rate determining attack of the sulfenic acid **3** as shown in the following Scheme 6. The observed negative Hammett ρ-value may be a result of cancellation of a positive one expected for the second step attack of sulfenic acid by the more negative one for the pre-equilibrium protonation. The result of the negative ρ-value also reveals that sulfenic acids bearing the more electron-withdrawing group will be the more stable under acidic conditions since sulfenic acids bearing the more electron-donating group are the more active as both electrophile and nucleophile in the self-condensation reaction.

Acidic hydrolysis of the sulfenate **2a** has been considered to proceed by a similar mechanism. Okuyama et al.[23] reported a mechanistic investigation for the acidic hydrolysis of ethyl benzenesulfenate in aqueous $HClO_4$ and suggested that the reaction proceeds via an initial protonation of the ester followed by a nucleophilic attack of water to form a sulfurane intermediate and that the rate-determining step is changeable depending on the pH. Apart from the formation of the sulfurane in-

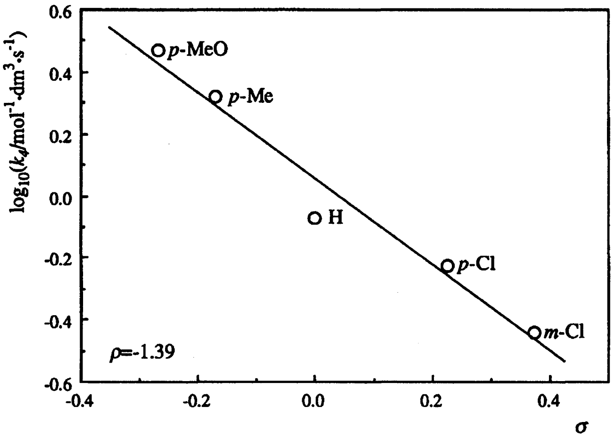
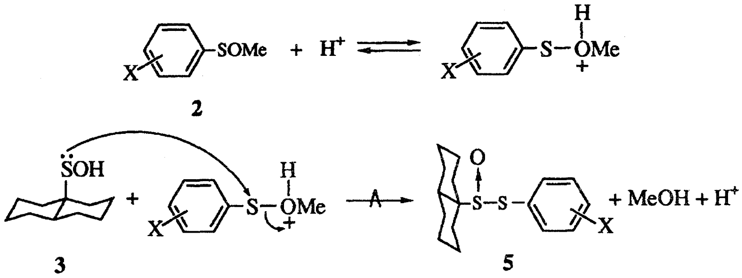


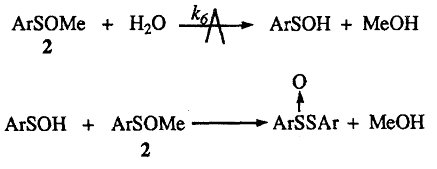
Fig. 4. Hammett plot for the rates of the reaction of *trans*-decalin-9-sulfenic acid (**3**) with methyl arenesulfenates (**2**).



Scheme 6.

Table 3. The Kinetic Data for The Hydrolysis of Methyl Arenesulfenate (XC_6H_4SOMe (**2**)) in Aqueous Methanol Solution

X	Temp	$[\mathbf{2}]_0\times10^4$	$[H^+]\times10^3$	$[H_2O]\times10^3$	$k_5\times10^5$	$k_6\times10^5$
	°C	$mol\,dm^{-3}$	$mol\,dm^{-3}$	$mol\,dm^{-3}$	s^{-1}	s^{-1}
H	25.20	2.34	2.41	0.80	4.23±0.02	2.12 ±0.01
H	34.60	2.34	2.41	0.80	7.08±0.03	3.54 ±0.01
H	43.90	2.34	2.41	0.80	11.83±0.10	5.92 ±0.05
m-Cl	34.60	2.34	2.41	0.80	1.08±0.01	0.539±0.003
p-Cl	34.60	2.34	2.41	0.80	2.92±0.03	1.46 ±0.01
p-Me	34.60	2.36	2.41	0.80	16.1 ±0.1	8.07 ±0.03
p-MeO	34.60	2.35	2.41	0.80	35.5 ±0.2	17.8 ±0.1

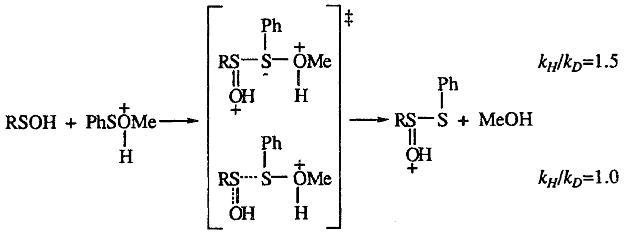


Scheme 7.

termediate, both of the S–O bond lengths of leaving side and attacking side are considered to be balanced in the transition state of the hydrolysis. Since the initial protonation process of the sulfenate ester is common for both the hydrolysis and the reaction with sulfenic acids, comparison of the ρ-values of both reactions will give us some information for the transition state of the self-condensation of sulfenic acids. Therefore the substituent effect for the acidic hydrolysis of methyl arenesulfenates (**2**) was examined under the same conditions ($[H_2O]=0.80\times10^{-3}$ $mol\,dm^{-3}$, $[H^+]=2.41\times10^{-3}$ $mol\,dm^{-3}$ in MeOH at 34.60 °C). The hydrolysis product, unstable arenesulfenic acid is expected to undergo rapid reaction with the sulfenates **2** to give *S*-aryl arenethiosulfinate (Scheme 7). Therefore, actual hydrolysis rate constants (k_6) are considered to be a half of the observed rate constants (k_5).

Hydrolysis of the sulfenate **2** with excess H_2O also correlated to the pseudo-first-order kinetic equation, and isosbestic point was observed (Ar=Ph, at 254 nm). The pseudo-first-order rate constants k_6 obtained were compiled in Table 3.

Arrhenius plot of the pseudo-first-order rate constants (k_6) for the hydrolysis of the sulfenate in the range of 25.20—43.90 °C gave a small activation enthalpy (40.7 $kJ\,mol^{-1}$) and a large negative activation entropy (-200 $J\,K^{-1}\,mol^{-1}$ at $[H_2O]=0.80\times10^{-3}$ $mol\,dm^{-3}$).



Scheme 8.

The magnitude of these activation parameters is similar to the values obtained by the reaction of the sulfenic acid **1** and **3** with the sulfenate **2a**, suggesting the analogous reaction mechanisms. Hammett plot for the hydrolysis gave a larger negative ρ-value ($\rho=-2.22$) than that for the reaction with the sulfenic acid **3**. Namely, the ρ-value for the pre-equilibrium protonation can be estimated as larger negative than -2.22. The very large ρ-value for the basic cite separated by the sulfur atom from the phenyl group is attributable to that in organic solvent. In comparison of the electronic structure of the transition states in the second step nucleophilic attack of the sulfenic acid and water, electron density on the sulfur atom of the sulfenate ester is higher in the former than in the latter. In other words, in the transition state of the hydrolysis S–O bond formation and S–O bond cleavage is considered to be balanced, however, in the reaction with sulfenic acid the S–S bond formation is expected to be more advanced relative to the S–O bond cleavage.

Supposing that the partial solvent isotope effect k_H/k_D 1.6 is attributed to that for the second step rate-determining attack of the sulfenic acid **3**, the kinetic isotope effect varies from 1.0 to 1.5 depending on the bond order index in the transition state. In an extreme case the transition state structure is sulfurane-like shown in the Scheme 8 and the kinetic isotope effect is estimated as k_H/k_D 1.5 and thus the total solvent isotope effect k_{MeOH}/k_{MeOD} 1.0. The observed solvent isotope effect is near that for the extreme case suggesting the development of the S–S bond formation, although the present isotope effect data are not enough to discuss about the structure of the transition state without comparison with those for the hydrolysis of the ester **2a**.

In conclusion, reaction of stable sulfenic acids with the sulfenate **2a** is a good model to elucidate the mechanism of the typical self-condensation reaction of sulfenic acids. From the comparison of ρ-values for the reaction of the sulfenic acid **3** and the sulfenate **2a** with its hydrolysis, nucleophilic attack of the sulfenic acid is found to be more progressed than that of water in the transition state.

Experimental

General. The IR spectra were taken on a JASCO IR-810 spectrometer. The ^{1}H NMR spectra were recorded with a Hitachi R-1200 spectrometer (60 MHz) in $CDCl_3$ or H_2O using TMS or DSS as an internal standard. The mass spectra were recorded with a JEOL-JMS-D 300 mass spectrometer. The UV spectra were recorded with a Hitachi U-3000 spectrometer. The temperature in the UV cell was maintained within ±0.02 °C by means of a Hitachi thermoelectric cell holder 131-0040. All the reactions were monitored by TLC using Merck Kieselgel 60 GF, and the substrates were separated by column chromatography using Merck Kieselgel 60. The substrates obtained were identified by IR, ^{1}H NMR, MS, and elemental analyses. The computations were performed on the NEC 9801VX computer. All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co., Ltd., and Aldrich Chemical Co. The reagents and solvents used were further purified by general methods.

2-Methyl-2-propanesulfenic Acid (1):[21] Di-*t*-butyl sulfoxide, (200 mg) was placed in the chamber of the FVP apparatus. The sample chamber was heated in a water bath maintained at 30—50 °C. The sample gas inlet tube was preheated with nichrome wire at a temperature approximately 60 °C above the melting point of the sulfoxide. The pyrolysis chamber was set at a temperature 250 °C, and the gas generated was condensed in a vacuum trap which was precondensed with water and cooled to −196 °C under high vacuum. After complete sublimation of the sulfoxide the vacuum was disengaged and the system was vented. To a condenser was added water and the solution obtained was analyzed by ^{1}H NMR.

***trans*-Decalin-9-sulfenic Acid (3):**[11] To a stirred solution of *trans*-decalin-9-yl methoxymethyl sulfoxide in methanol was added dropwise aqueous 15% perchloric acid solution (15 ml) at room temperature over 10 min. After addition, the solution was kept for 10 min. The mixture was poured into water, extracted with dichloromethane, and dried over anhydrous sodium sulfate in a refrigerator. Then, the solvent was evaporated, the residue was separated by column chromatography on silica gel using hexane/ether 10/1 as an eluent, and *trans*-decalin-9-sulfenic acid (**3**) separated was recrystallized from methanol–water. Mp 52—54 °C.

Methyl Arenesulfenates (2):[22] To a stirred solution of methanol (4.53 g) and triethylamine (14.3 g) in ether (100 ml) was added dropwise arenesulfenyl chlorides[25] (Ar=Ph, 20.2 g) at 0 °C for 30 min under nitrogen atmosphere. The mixture was filtered, the filtrate was concentrated in vacuo, and the residue was distilled. Ar=Ph, 13% yield, bp 61 °C/25 mmHg,## ^{1}H NMR ($CDCl_3$) δ=3.72 (3H, s, SOMe) and 7.2—7.5 (5H, m, Ph), IR (neat) 985 cm^{-1} (ν_{SO}); Ar=*p*-Cl-C_6H_4, 19% yield, bp 83—84 °C/5 mmHg, ^{1}H NMR ($CDCl_3$) δ=3.62 (3H, s, SOMe) and 7.0—7.4 (4H, m, aromatic-H), IR (neat) 986 cm^{-1} (ν_{SO}); Ar=*m*-Cl-C_6H_4, 11% yield, bp 118 °C/22 mmHg, ^{1}H NMR ($CDCl_3$) δ=3.75 (3H, s, SOMe) and 7.0—7.4 (4H, m, aromatic-H), IR (neat) 986 cm^{-1} (ν_{SO}); Ar=*p*-Me-C_6H_4, 9.1% yield, bp 43 °C/5 mmHg, ^{1}H NMR ($CDCl_3$) δ=2.29 (3H, s, Me) and 3.56 (3H, s, SOMe) and 7.0—7.3 (4H, m, aromatic-H), IR (neat) 990 cm^{-1} (ν_{SO}); Ar=*p*-MeO-C_6H_4, 17% yield, bp 92—93 °C/3 mmHg, ^{1}H NMR ($CDCl_3$) δ=3.59 (3H, s, SOMe) and 3.83 (3H, s, OMe) and 6.95 (2H, d, J=9 Hz, aromatic-H) and 7.54 (2H, d, J=9 Hz, aromatic-H), IR (neat) 992 cm^{-1} (ν_{SO}).

***S*-*p*-Chlorophenyl 2-Methyl-2-propanethiosulfinate:** 2-Methyl-2-propanesulfenic acid (**1**) (ca. 0.5 mmol) obtained by FVP was mixed with methyl *p*-chlorobenzenesulfenate (0.10 g, 0.57 mmol) in aqueous methanol solution at −196 °C. This reaction mixture was allowed to warm to room temperature, and poured into 100 ml of water, and the mixture was extracted twice with 50 ml portions of dichloromethane. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was then removed under reduced pressure to afford the corresponding thiosulfinate. It was purified by column chromatography on silica gel using hexane/ether 8/1 as an eluent, and by recrystallization from methanol–water, 60% yield, mp 53.6 °C. ^{1}H NMR ($CDCl_3$) δ=1.43 (9H, s, *t*Bu) and 7.32 (2H, d, J=9 Hz, aromatic-H) and 7.57 (2H, d, J=9 Hz, aromatic-H), IR (KBr) 1075 cm^{-1} (ν_{SO}). Found: C, 48.27; H, 5.31%. Calcd for $C_{10}H_{13}ClOS_2$: C, 48.27; H, 5.27%.

***S*-Phenyl *trans*-Decalin-9-thiosulfinate (6):** *trans*-Decalin-9-sulfenic acid (**3**) (0.409 g, 2.20 mmol) was dissolved in 50 ml of methanol. Then to this was added methyl benzenesulfenate (0.308 g, 2.20 mmol) in methanol (50 ml). The reaction mixture was stirred for 30 min at room temperature and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using hexane/ether 10/1 as an eluent to give oily *S*-phenyl *trans*-decalin-9-thiosulfinate (**6**) in 90% yield. ^{1}H NMR ($CDCl_3$) δ=0.6—2.6 (17H, m, decalyl) and 7.2—7.8 (5H, m, aromatic-H), IR (neat) 1075 cm^{-1} (ν_{SO}).

Kinetic Measurements. A typical kinetic run for all reactions is as follows. A quartz cuvette containing 3.0 ml solution of required concentration of the sulfenic acid **1** or **3** and perchloric acid in aqueous acetonitrile or methanol was preincubated at a set temperature (±0.02 °C) for 30 min. The reaction was started by introducing an appropriate amount of stock solution of methyl arenesulfenate **2** in acetonitrile or methanol with micro syringe. At an appropriate time interval UV intensities were measured by scanning and an isosbestic point was observed at 305 nm (in the reaction of **2a** with **3**). The pseudo-first-order rate constants

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1 mmHg=133.3 Pa.

were determined by a least-squares method using the 10—20 points at 280 nm (in the reaction of **2a** with **3**) accumulated during the first 75% completion of the reaction and initial and final absorbances at more than 7th half-life. Some reactions showed no isosbestic point and inaccurate absorbance at infinite time, and the kinetic plots $\ln[1/(1-x)]$ vs. time (where x is the conversion at reaction time t) did not show straight lines. In those cases the value at infinite was estimated by Guggenheim plot.[26)]

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