Reaction Intermediate of Organic Sulfur Compound I. Elimination Mechanism of Sulfonyl Chloride

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The reactions of alkanesulfonyl chlorides with pyridines in the presence of various solvents have been studied by means of kinetic method. Alkanesulfonyl chlorides bearing α-hydrogen with the normal attack of pyridine is found to be at the α-hydrogen with elimination to form the sulfene intermediate evidently. From the mass spectra by the reaction of ethanesulfonyl chloride with 3-picoline in the presence of methanol-d_1, it has shown that the reaction has a witness favorable to the sulfene intermediate.

Introduction

The earliest mechanistic studies of sulfonyl transfer for the reaction of sulfonly halides were believed to proceed by a direct nucleophilic substitution process.[1-5]

$$RSO_2X + Nu^- \rightarrow RSO_2Nu + X^-$$

For the reaction of benzenesulfonyl chlorides with pyridine bases, Rogne[2] concluded that the base functions as a nucleophilic catalyst, for example, sulfonyl pyridinium intermediate.

While Wedekind and Schenk[6] suggested that the reaction of tertiary amines with aliphatic sulfonyl halide may lead to a species $RR'C{=}SO_2$, which they named a "Sulfene", by analogy with ketene which had been studied. The elimination addition process going by way of an intermediate sulfene was observed from the key piece of evidence by Truce *et al.*[7] Elimination-addition is known as a usual pathway for reactions of alkanesulfonyl chlorides that have an α-hydrogen, in such as the formation of alkanesulfonate esters by reaction of the alkanesulfonyl chloride with an alcohol and a tertiary amine.[8-10]

To find reliable data for the direct displacement and the elimination-addition mechanisms, the reactions of alkanesulfonyl chlorides with water in the presence of various alkylamines were investigated by King *et al.*,[11] and the reactions were convinced strongly to proceed primarily by way of an initial vinylogous substitution reaction to form the cationic sulfene.

Neverthless the direct displacement and the elimination-addition process for sulfonyl transfer reactions have been discussed in many publications,[12] the note of doubtful authenticity associated with sulfenes remains in the reactions of alkanesulfonyl chloride with pyridines, particularly solvent-participating in the reaction. The reliable evidence for the base-induced reaction of methane- and ethanesulfonyl chlorides in protic solvent and aprotic solvent will be investigated with a point of view to observe the participation of sulfenes. This work is focussed on the non-existence of a pentacoordinate intermediate in the reactions of alkanesulfonyl chlorides with pyridines in acetonitrile and on the conformation of the sulfene intermediate. In the direct displacement reactions in the protic solvents a product of alkanesulfonyl ester should be detected.

With the reaction of alkanesulfonyl chlorides with various pyridines in the media, the intermediate and mechanism for sulfonyl transfer reaction is described by means of kinetic method.

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Experimental

Materials. Solvents, methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH) and acetonitrile (MeCN) were purified as described previously.[13] Methanesulfonyl chloride (MSC) and ethanesulfonyl chloride (ESC) were purchased from Aldrich and were dried over anhydrous magnesium sulfate (Tokyo Kasei, Certified grade) prior to evaporation. MSC and ESC were further purified by fractional distillation under reduced pressure (18 torr, b.p61-62 °C; MSC) and (2-3 torr, b.p 27-28 °C; ESC). Pyridine (Py-H), α-picoline (2-Me-py), β-picoline (3-Me-py) and γ-picoline (4-Me-py) (Aldrich) were used (99.5 + %) and methanol-d_1 (MeOD) was obtained from Sigma as the grade of 99.5 + atom% D.

Kinetic Methods. The rates were followed conductometrically as in the previous experiment[13] and the pseudo-first-order rate constants, k_{obs}, were obtined from the Guggenheim method.[14] The values of k_{obs} obeyed the simple expression,

$$k_{obs} = k_1 + k_2[\text{pyridine}]$$

with k_2, the second-order rate constants, the k_{obs} and k_2 listed in Table 1, 2 and 3 are the average of more than duplicate runs with the reproducibility of better than ± 3% in all cases.

Product Analysis. Gas chromatographic determination was carried out using an Shimadzu GC-RIA instrument with column of 8′×1/6″-10′×1/10″ Apiezon L doped with carbowax 20M-TPA on chromosorb G(70/80 mesh) and PPE OS 124 (polyphenyl ether) with Celite 545 (80/100 mesh).

GC/MS analyses were carried out using a Hewlett-Packard 5996 instrument employing column SP 2250 and OV 101 column. UV spectra were obtained by using a Shimazu, UV/vis-240 Graphicord Spectrophotometer.

Reaction of Ethanesulfonyl Chloride with β-picoline

Table 1. The Observed Pseudo-First Order Rate Constants ($k_{obs} \times 10^{-4}$sec^{-1}) for the Reaction of Methanesulfonyl Chloride with Pyridines in Protic and Aprotic Solvents

Solvents	Temp. (°C)	Py-H			2-Me-py			3-Me-py			4-Me-py		
		9.05[a]	13.0[a]	16.6[a]	16.6[a]	19.9[a]	23.0[a]	9.05[a]	13.0[a]	16.6[a]	4.74[a]	9.05[a]	13.0[a]
MeOH	30	4.79	6.52	8.11	3.71	4.31	4.88	9.19	13.4	17.0	—	—	—
	35	6.96	9.86	12.5	3.89	4.52	5.10	12.9	18.4	23.5	12.0	18.2	24.2
	40	9.90	14.3	18.3	5.73	6.63	7.49	17.7	25.8	23.2	—	—	—
EtOH	25	2.64	4.35	5.94	0.258	0.275	0.292	4.76	6.80	8.89	4.02	11.1	18.3
	35	5.18	7.49	9.45	0.444	0.500	0.531	9.25	12.9	16.2	7.13	30.6	52.6
	45	10.0	14.9	20.3	0.961	1.20	1.81	17.6	23.0	27.5	15.8	66.6	107
1-PrOH	35	5.12	7.02	9.09	1.32	1.72	1.98	8.79	11.0	12.8	13.5	46.2	66.2
MeCN	35	3.01	3.42	4.44	0.981	1.13	1.30	10.5	15.6	20.3	18.5	51.2	72.7
	35	1.135[b]	0.147[b]	0.157[b]									

[a]The order of all concentrations of pyridines are [pyridine]$\times 10^{-2}$M. [b]Rate constants for the reaction of methanesulfonyl chloride with pyridine-d_5 in acetonitrile.

Table 2. The Observed Pseudo-First Order Rate Constants ($k_{obs} \times 10^{4}$sec^{-1}) for the Reaction of Ethanesulfonyl Chloride with Pyridines in Protic and Aprotic Solvents

Sol-vents	Temp. (°C)	Py-H				2-Me-py				3-Me-py			4-Me-py		
		13.0[a]	16.6[a]	19.9[a]	23.0[a]	16.6[a]	19.9[a]	23.0[a]	25.8[a]	9.05[a]	13.0[a]	16.6[a]	13.0[a]	16.6[a]	19.9[a]
MeOH	30	4.33	5.44	6.46	7.44	0.517	0.580	0.635	0.690	5.44	8.29	10.7	—	—	—
	35	6.13	7.85	9.32	10.7	0.739	0.820	0.893	0.960	7.55	11.8	15.6	14.9	20.0	24.6
	40	8.43	10.7	12.8	14.7	0.920	1.04	1.12	1.22	10.3	14.9	18.9	—	—	—
EtOH	25	—	2.88	3.46	4.09	—	0.0726	0.0789	0.0850	2.01	3.50	4.82	10.3	15.0	19.4
	35	—	6.08	7.05	8.35	—	0.160	0.173	0.190	5.12	7.82	9.83	12.4	21.8	30.8
	45	—	11.5	13.5	15.9	—	0.416	0.438	0.458	8.30	12.7	15.6	34.4	52.6	69.7
1-PrOH	35	—	4.54	4.72	4.77	—	0.249	0.268	0.284	4.00	5.52	6.70	18.1	25.7	38.9
MeCN	35	—	0.183	0.300	0.421	—	0.033	0.0429	0.0534	0.560	0.857	1.12	4.28[b]	14.5[b]	56.0[b]
	35	—	0.109[c]	0.117[c]	0.119[c]										

[a]The order of all concentrations of pyridines are [pyridine]$\times 10^{-2}$M. [b]Rate constants for the concentration of 4.74, 9.05 and 13.0$\times 10^{-2}$M of 4-Me. [c]Rate constants for the reaction of ethanesulfonyl chloride with pyridine-d_5 in acetonitrile.

in the Presence of Methanol-*d*. Ethanesulfonyl chloride (80 m*l*, d 1.357) was dissolved in methanol-d_1 (25 m*l*) and treated with β-picoline (35 m*l*) at room temperature for 1 hr. The excess methanol-d_1 was evaporated and the residue extracted with ether and washed with 1N HCl The ether layer dried and evaporated giving methyl ethane-d_1 sulfonate, $CH_3CHDSO_3CH_3$ (97 mg, 92%), b.p 85-86 °C/10 mmHg; IR (Neat) 2890, 2876, 2220, 2191, 1409, 1350, 1285, 1265, 1186, 1167, 1146, 1049, 1026, 908, 832, 812, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.51(s), 2.45(s), 3.17(s). The mass psectral data were as follow: MS at *m/e* 93 (relative abundance 46), 29(100), 32(65), 64 (18).

Result and Discussion

The reactivities in the same solvent are in the order of 4-Me-py>3-Me-py>Py-H>2-Me-py in Table 1, 2 and 3. Especially substitutions at the 4- and 3-positions of the pyridine with electrondonating group (-CH_3) are in distinct contrast to those observed for similar reactions in an solvent environment.[15] It has been reported that the nuceophilic substitution of aromatic acid halides with substituted pyridines undergoes to form pyridinium salt easily with the order of 3-Me-py>2-Me-py≅4-Me-py[16] as the correlation with acidity of substituted pyridines except non-substituted pyridine.

The best-known and most studied reaction of a typical nucleophilic displacement of the pyridines, such as the reaction of Tschitschibabin amination,[17] gives 2-position products, and the reaction is widely applicable and has been extensively reviewed.[18]

Reference to Table 1, 2 and 3 indicates that the tendency is observed to correlate roughly with basicity[19] of the substituted pyridines except for 2-Me-py quite different from the results of the reaction path to form pyridinium salt. It has been well known that pyridinium salt formation in the nucleophilic substitution reaction of pyridines with acid halides might be induced in nonpolar media.[20]

From the tendency of the rate constants in Table 1, 2 and 3 the reaction mechanism is analogized somewhat different from that the reaction proceeds along with to make an intermediate of pyridinium salt and it is expected that the reaction proceeds through the abnormal route. The abnormal observations was reported by King *et al.*,[21] that the reaction of 1-haloalkanesulfinic acids with water, *p*-toluidine and an enamine in the presence of added base gives products expected from an intermediate sulfene. They concluded that sulfenes are formed and hence may be presumed to react, *via*

Table 3. The Second Order Rate Constants ($k_2 \times 10^3 \cdot L \cdot M^{-1}$) sec^{-1} for the Reaction of Alkanesulfonyl Chlorides with Pyridines in Protic and Aprotic Solvents at Various Temperatures

Substrates	Solvents	Temp. (°C)	Py-H	2-Me-py	3-Me-py	4-Me-py
			30	4.41	1.80	10.3
	MeOH	35	7.34	1.85	14.0	21.3
		40	11.1	2.71	20.5	—
M.S.C		25	4.37	0.0531	5.47	17.2
	EtOH	35	5.66	0.142	9.21	55.0
		45	13.6	1.320	13.1	110.0
	1-PrOH	35	5.25	1.033	5.32	64.0
	MeCN	35	1.88	0.498	13.0	65.8
		35	0.0292[a]			
		30	3.09	0.183	7.05	—
	MeOH	35	4.56	0.245	10.7	14.1
		40	6.27	0.256	12.0	—
		25	1.89	0.0203	3.84	13.2
	EtOH	35	3.54	0.0507	6.34	26.7
E.S.C		45	6.87	0.0717	9.97	51.2
E.S.C	1-PrOH	35	0.361	0.0594	3.68	27.8
	MeCN	35	0.372	0.0375	0.929	62.0
		35	[a]0.0103[a]			

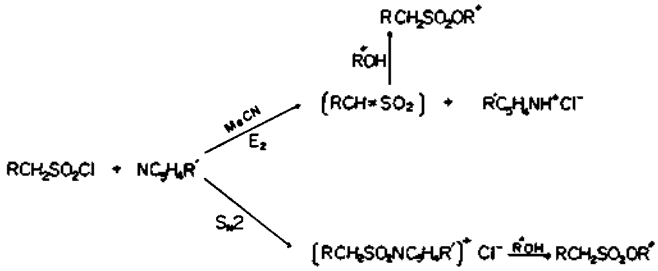
[a]Rate constants for the reaction of methane- and ethane sulfonyl chlorides with pyridine-d_5 in acetonitrile.

the abnormal route.

It is reasonable to propose such as reaction mode, at least formally, a nucleophilic attack on the carbon of the sulfene in the polar solvent[21] and the protic solvent.[21]

Our results showed the reactivity of pyridine derivatives in polar and protic solvents are higher in case of 4-Me-py and the magnitude of 3-Me-py is also shown higher than Py-H, which suggests that the reaction is influenced by the solvent basicity. These phenomena were also interpreted by Truce, Campbell,[22] and King[23] *et al.*, who noted that under a large excess of protic solvent conditions the reaction of alkanesulfonyl chloride with trialkylamine proceeds through the route to form directly from the sulfene intermediate, but under the condition of pure benzene the reaction proceeds favorably to from the sulfonylammonium salt.

Activation parameters, ΔH^*, ΔS^* and ΔG^* for the reaction of alkanesulfonyl chlorides with pyridines in MeOH and EtOH are shown in Table 4.



Scheme 1

It can be seen in this Table that ΔH^* values vary from 7.08 Kcal·mol^{-1} to 16.9 Kcal·mol^{-1} and ΔS^* values from -9.53 e.u. to -56.5 e.u. with 2-Me-py exception. The values of activation parameters approach to the values for the reaction of alkanesulfonyl chloride with bases[24] as 9.40-13.5 Kcal·mol^{-1} (ΔH^*) and -9.20~-31.8 e.u. (ΔS^*). These examples obviously show that the reaction of elimination-addition mechanism at sulfur would involve the formation of sulfene. It is reasonable to exclude any other nucleophilic substitution or addition-elimination mechanisms.[25]

The rate constants and the activation parameters of 2-Me-py deviated from other pyridines. These discrepancies could be explained[26] by the reaction which proceeds *via* base-catalyzed deprotonation from $-CH_3$, as the resulting anions are steric hinderance of the methyl group at 2-position.

The two possible routes for the reaction of alkanesulfonyl chlorides with pyridines give the different products by the solvent (Scheme 1).

If E2 mechanism is favorable, then the intermediate sulfene can be observed from the spectrum during the reaction. Figure 1 and 2 show that UV/vis spectra have been observed during the reacion of MSC and ESC with 3-Me-py in MeCN and MeOH, the absorption band of sulfene occur at 295 nm (Figure 1) and 305 nm (Figure 2) corresponding to the $-CH=SO_2$ group.

The formation of sulfonylpyridinium salt is not without precedent in Scheme 1. For example, a very rapid reaction takes place when benzenesulfonyl chloride[27] is treated with triethylamine in benzene, giving rise to a salt-like material. Hall and Hirsjarvi *et al.*[28] also observed that S_N2 attack on sulfur from the solvolytic reaction of alkanesulfonyl chlorides as well as solvolysis of arenesulfonyl chlorides and the solvolyses proceed too rapidly to be measured conveniently when

Table 4. The Thermodynamic Activation Parameters of the Reaction of Alkanesulfonyl Chlorides with Pyridines in Methanol and Ethanol at 35 °C

Solvent	Pyridines	MSC			ESC		
		ΔH^* (kcal/mol)	ΔS^* (e.u)	ΔG^* (kcal/mol)	ΔH^* (kcal/mol)	ΔS^* (e.u)	ΔG^* (kcal/mol)
	Py-H	16.8	-13.9	21.1	12.8	-27.8	21.4
MeOH	2-Me-py	7.08	-48.1	21.9	5.75	-56.5	23.3
	3-Me-py	12.4	-26.9	20.7	9.49	-36.8	20.8
	Py-H	9.99	-37.4	21.5	11.6	-32.2	21.5
EtOH	2-Me-py	11.3	-41.4	21.4	10.8	-41.3	23.5
	3-Me-py	7.63	-43.9	21.2	8.40	-41.4	21.2
	4-Me-py	16.9	-9.53	19.8	12.4	-26.2	20.3

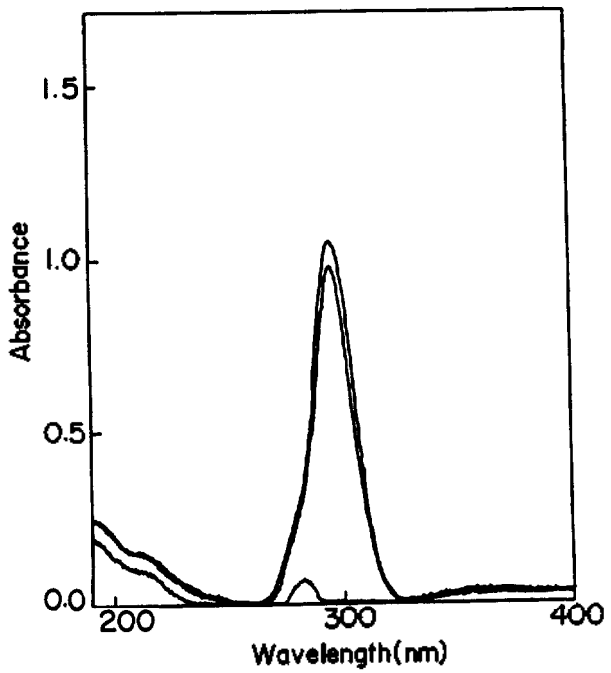


Figure 1. Spectrum recorded for the reaction of methanesulfonyl chloride with 3-Me-py in acetonitrile at 35 °C.

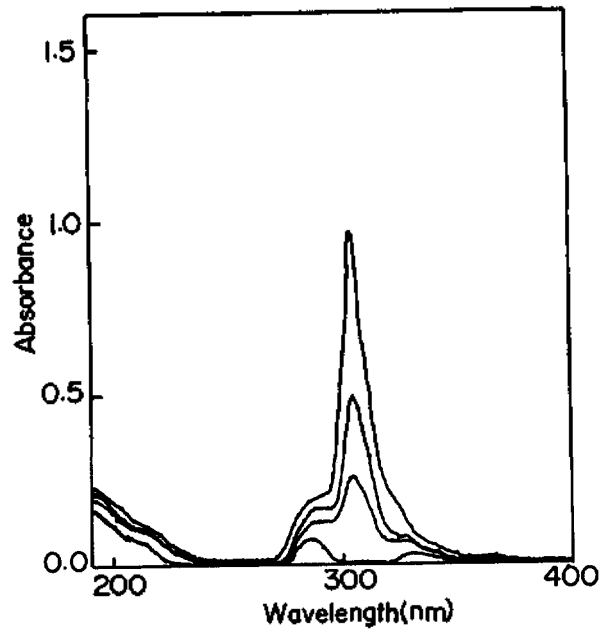
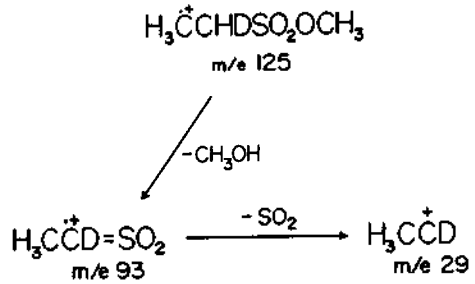


Figure 2. Spectrum recorded for the reaction of ethanesulfonyl chloride in 3-Me-py in methanol at 35 °C.

bases such as hydroxide or alkoxide are involved. This supports that hypothesis that the nucleophilic substitution on sulfur can compete with an elimination addition sequence.

In order to investigate the correct intermediate and a possibility of sulfonyl pyridinium intermediate by S_N2 mechanism the product analyses were carried out for the reaction of ESC with 3-Me-py in the presence of methanol-d_1 by GC/MS (see Experimental). If the reaction was to proceed *via* ethanesulfonyl pyridinium chloride intermediate, then the product in the presence of excess methanol-d_1 would have a



Scheme 2

non-deuterated one; that is, the product would be methyl ethanesulfonate and the peaks in the mass spectrum of the natural abundance isomer would be observed at *m/e* 92 (3%), *m/e* 46 (53%) and *m/e* 28 (100%).[29]

With an elimination-addition mechanism, on the other hand, if the sulfene ($CH_3CH=SO_2$) intermediate is favored to form, and then methanol-d_1 reacts with the sulfene, the product would be methyl ethane-d_1 sulfonate. Accurate mass spectra were recorded for the product of the reaction of ESC with 3-Me-py in the presence of methanol-d_1. Rupture of methyl ethane-d_1 sulfonate linkage is the predominant main cleavage to give fragments *m/e* 93, *m/e* 64, *m/e* 32 and *m/e* 29. The mass measurement is elucidated for *m/e* 93 arising from loss of 1 mol of methanol and is corroborated by the most abundant ion of a peak at *m/e* 29 due to loss of 1 mol of sulfurdioxide from the parent ion. The abount of deuterium incorporation as estimated from the relative intensities of the peaks at *m/e* 29 and 28 in the spectrum of the deuterated material agreed within experimental error with the values obtained from the infrared spectrum and the ^1H NMR spectrum. These fragmentation are depicted in Scheme 2.

Though the product analyses and mass spectra for methyl ethane-d_1 sulfonate are reasonably good to probe a sulfene intermediate, it cannot be excluded that the sulfene or its analogous fragment are observed from the sulfonyl pyridinium salt. We have not prepared $C_2H_5SO_2N^+$ $C_5H_5CH_3Cl^-$ and therefore cannot have the mass spectrum of this compound in the same way. If sulfonyl pyridinium salt were formed as the intermediate, the peak of *m/e*, 28 would be observed in the reaction of ESC with 3-Me-py in methanol-d_1. But a large abundance of *m/e*, 29 showed as a result from that sulfene was reacted with methanol-d_1 as following mechanism.

$$CH_3CH_2SO_2Cl + NC_5H_4CH_3$$
$$\longrightarrow [CH_3CH{=}SO_2] + [{}^+NC_5H_5CH_3]\ X^-$$
$$[CH_3CH{=}SO_2] + CH_3OD \longrightarrow CH_3CHDSO_3CH_3$$

We suggest that most likely mechanism fo the reaction of MSC and ESC with pyridines in protic and aprotic polar solvents is almost entirely *via* sulfene that has been largely by a direct elimnation.

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