DAEHAN HWAHAK HWOEJEE
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3차 아민의 4차화 반응에 관한 연구 (제 3 보). 치환 β-Phenylethyl Arenesulfonate 류와 피리딘의 반응에 관한 반응속도론적 연구

呂壽東† · 李敬兒 · 朴聖植
경북대학교 사범대학 화학과

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Studies on the Quaternization of Tertiary Amines (III). Kinetics and Mechanism for the Reaction of Substituted β-Phenylethyl Arenesulfonates with Pyridine

Soo-Dong Yoh†, Kyung-A Lee and **Sung-Sik Park**
Department of Chemistry, Teachers College, Kyungpook National University
Daegu 635, Korea

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요 약. 치환 β-phenylethyl arenesulfonate 와 피리딘의 반응에 관한 기질과 이탈기의 치환기 효과를 아세토니트릴중, 전기 전도도 법으로 50~70 °C의 범위에서 측정하였다. 기질의 치환기 효과는 기대할 정도의 큰 의미를 갖지 못했으며, 전자를 주는 치환기는 반응속도가 빨랐고 ρ값은 전 치환기를 통해 매우 적은 음(−)의 값을 가졌다. 또 Hammett 도시에서는 benzyl계 같이 현저하지는 않으나 약한 커어브를 나타내었다. 이 사실 들로서 전자주게 치환기일 경우 전이상태에서 약하게나마 결합의 깨어짐이 촉진됨을 뜻한다. 이탈기의 치환기 효과는 전자주게일 경우 반응속도는 느렸으며 전자를 끄는기에서는 그 반대였다. 또한 Hammett ρ값은 *p*-nitrobenzyl arenesulfonate 보다 아주 적어 tight 한 S_N2 반응 메카니즘으로 진행되는 것 같다. 특히 2,5-이 치환 염화물의 반응속도는 치환기 상수의 가성성에서 기대한 값보다 아주 컸으며, 이는 전이상태에서 이탈기의 음 이온이 두 강하게 끄는 치환기에 의해 안정화 되기 때문이다.

ABSTRACT. Substituent effects of substrate and leaving group for the reaction of substituted β-phenylethyl arenesulfonates with pyridine were determined conductometrically in acetonitrile at 50~70°C. The substituent effect in substrate is not so significant than expected, but still the electron donating substituent shows the slight acceleration to give a small negative ρ value and Hammett plots show slight curvature on the acting substituents, even though it is not so remarkable than that of benzyl system. These results represent a little bit the favorable bond breaking at the transition state by the electron donating substituents. The effects of leaving group in the arenesulfonates in which the rate constants are decreased by electron donating substituents, while electron withdrawing groups presented the reverse effects. Hammett ρ value is significantly smaller than that of *p*-nitrobenzyl arenesulfonates and thus, the mechanism should be closer to tight S_N2 one. Especially 2,5-dichlorobenzenesulfonate was more accelerated than expected at the additivity of substituents. This facts showed that dichlorobenzenesulfonate anion is more stabilized by the great electron withdrawing substituents at transition state.

INTRODUCTION

Menschutkin type reaction of substituted benzyl arenesulfonates with tertiary amine has been studied previously[1,2]. The goal of this study is to obtain a guide rule of the substituent effects in the substrate, leaving group and nucleophile and to see the change in mechanism, in the sense that the transition state moves from S_N1 to S_N2 mechanism. The substituted benzyl arenesulfonates are chosen for the study because the change of mechanism with the substituent is feasible. In this connection, a set of substituent effects is needed for a similar system of more firm S_N2 mechanism. Previously, we had chosen,[3] the reaction of β-phenylethyl tosylate with pyridines in acetonitrile for such a refernece system.

In the present study, we investigated the substituent effects of the substrate and that of leaving group on the substituted β-phenylethyl arenesulfonates with pyridine at the same conditions of benzyl systems.

EXPERIMENTAL

Materials

All materials used throughout were commercial products (Wako, Japan). Acetonitrile was purified by distillation after standing with anhydrous potassium carbonates for three days at room temperature. Pyridine dried over NaOH pellet was fractionated twice, b. p. 115~115.5°C and stored in brown ampoule filled nitrogen gas.

Substituted Benzenesulfonyl Chlorides

***p*-Nitrobenzenesulfonyl Chloride** was prepared by the following method[4a,b]. Sodium disulfide was obtained by the heating of sodium sulfide (30 g, 0.147 mole) and sulfur (5 g, 0.156 mole) on a steam bath at 50°C. The methanol solution of sodium disulfide was added in portions to a boiling solution of *p*-chloronitrobenzene (37.5 g, 0.239 mole) in 200 m*l* of methanol.

The mixture was heated for one hour and then cooled, the solid product, after being washed with alcohol, water and again with alcohol was recrystallized from boiling acetic acid gave *p*, *p'*-dinitrodiphenyl disulfide (25 g) in purity. This crystals were dissolved in 60 m*l* of c-HNO_3 (d:1.38) and heated for three hours at 70°C while stirring, diluted with 200m*l* of water.

After evaporated this solution at reduced pressure, the residue was neutralized with dilute aqueous ammonia and obtained ammonium *p*-nitrobenzenesulfonate (53.5 g, 0.243 mole). *p*-Nitrobenzenesulfonyl chloride was obtained by chlorosulfonation of 12g of ammonium *p*-nitrobenzenesulfonate with 16 m*l* of chlorosulfonic acid for one hour at 100 °C, after cooled, the solution poured on the ice-water. Collect the crystals by suction filteration and recrystallized from benzene-pet. ether, yield, 11g (88%). (mp 79°C, *lit*[4b]., 80°C).

***m*-Nitrobenzenesulfonyl Chloride** was obtained by chlorosulfornation of sodium *m*-nitrobenzenesulfonate with chlorosulfonic acid and recrystallized from ligroin, mp 61°C (*lit.*,[5] 61.5~62°).

Benzenesulfonyl Chloride was obtained by purification of commercial chemicals, bp 137°C /24 mmHg (*lit.*[6], bp 119~121°C/15mmHg, mp 14.5°C).

***p*-Methoxybenzenesulfonyl Chloride** was synthesized by chlorosulfonation of anisole by Morgan[7] method and recrystallized from pet. ether, m.p. 41°C (*lit.*,[7] 40~42°C).

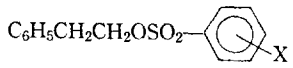
All Other Arenesulfonyl Chlorides were synthesized by chlorosulfonation of substituted benzene. Physical constants, yields and analytical data are listed in *Table* 1.

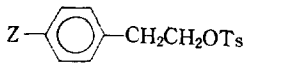
Substituted β-phenylethyl Arenesulfonates

Table 1. Physical constants, yields, and analytical data of arenesulfonyl chlorides.

Substituents	mp, °C(*lit.*)	Yields	Carbon(%)		Hydrogen(%)		Nitrogen(%)	
			Found.	Calcd.	Found.	Calcd.	Found.	Calcd.
p-NO_2	79(80)[4]	88	32.50	32.51	1.59	1.81	6.40	6.32
m-NO_2	61(61.5~62)[5]	57	32.48	32.51	1.67	1.81	6.30	6.32
p-Cl	52(53)[6]	58						
p-Br	73(74~75)[8]	70	38.05	38.33	2.14	2.14		
H	15(14~15)[8]	75						
p-CH_3O	41(41~42)[7]	60						
p-CH_3	68~69(69)[8]	62						
2,5-Cl_2	38(38)[8]	61						

Table 2. Physical constants, yields, and analytical data of substituted β-phenyelthyl arenesulfonates.





X	mp°C(*lit.*)	Yields(%)	C	H	N(%)	Z	mp°C(*lit.*)	Yields(%)
p-NO_2	100(101.5~102)[10]	72	Found 54.55 (Calcd) (54.72)	4.26 (4.13)	4.56 (4.27)	*p*-MeO	57~57.2 (57~58)[14]	49
p-Cl	50(51)[11]	62				*p*-Cl	(79~80)[15]	78.5 48
H	15~16(14~15)[12]	69						
2,5-Cl_2	75~76	66	50.87 (50.75)	3.40 (3.65)		*p*-Br	81~82 (82~83)[14]	45
p-CH_3	38~39(36~37)[13]	70						
p-CH_3O	27(26)[11]	70				*p*-NO_2	117~118	48
p-Br	57(58~59)[14]	65						

were synthesized from substituted β-phenylethyl alcohol and arenesulfonyl chlorides by the Tipson[9] procedure and purified by recrystallization from appropriate solvents. Physical constants are listed in *Table* 2.

Substituted β-Phenylethylpyridinium Tosylates.

These pyridinium salts were obtained by refluxing corresponding esters with pyridine in acetonitrile by previous method[3] and recrystallized from *i*-propyl alcohol.

β-Phenylethyl Pyridinium Tosylate, mp 133°C (*lit.*[3], 133~134°C)

Anal. Calcd. for $C_{20}H_{21}NO_3S$: C, 67.58; H, 5.59; N, 3.94. Found. C, 67.68; H, 5.62; N, 3.99.

***p*-Chloro β-Phenylethyl Pyridinium Tosylate**, mp 178.4~179°C.

Anal. Calcd. for $C_{20}H_{20}O_3SNCl$: C, 61.60; H, 5.18; N, 3.59. Found. C, 61.65; H, 5.15; N, 3.66.

Kinetic Measurements

The rates of substituted β-phenylethyl arenesulfonates with pyridines at various temperature were measured conductometrically using Conductivity-Meter LBR(Germany) by the procedure previously reported.[3] As the reaction proceeds, the electric conductance is increased because concentration of the salt formed in the reaction cell by time goes on increasing. The approximation is usually by the change in conductance in contrast with the linear function of the concentration. The temperature control was better than ±0.05°C at given temperature. The con-

Table 3. Activation parameters and kinetic data for the reaction of β-phenylethyl tosylates with pyridine in acetonitrile.

Subst. Z (Y=H), (X=CH_3)	$K_2\times10^4$(1/mol·min)			$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e. u)	$\Delta G^{\neq}$ (kcal/mol)
	50°C	60°C	70°C			
p-CH_3O	15.6	35.2	74.1	16.7	20.6	23.560
H	10.3	21.8	49.2	16.8	20.4	23.593
p-Br	8.1	15.9	40.6	14.3	28.5	23.791
p-Cl	7.9	15.5	38.1	12.8	33.1	23.822
p-NO_2	7.2	15.2	25.2	13.1	33.2	24.156

Table 4. Kinetic data for the reaction of β-phenylethyl arenesulfonates with pyridine in acetonitrile.

Subst. X (Z=H). (Y=H)	$K_2\times10^4$(1/mol·min)			$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e. u)	$\Delta G^{\neq}$ (kcal/mol)
	50°C	60°C	70°C			
2,5-Cl_2	234.1	448.7	953.8	14.8	20.5	21.627
p-NO_2	185.5	302.8	527.5	10.8	33.1	21.822
p-Cl	45.7	76.9	139.1	11.6	33.6	22.788
p-Br	39.2	66.1	138.2	13.3	29.4	22.990
H	23.2	52.3	85.1	13.6	28.2	22.991
p-CH_3	12.8	24.3	53.2	15.0	25.5	23.492
p-CH_3O	11.0	19.4	45.9	14.8	26.5	23.625

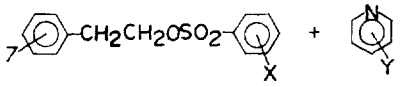
centration of substituted β-phenylethyl arenesulfonates were $7.5\times10^{-3}M$ in acetonitrile and that of pyridine used were $1.5\times10^{-1}M$.

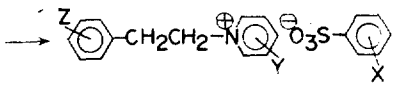
All measurements were done with pyridine in large excess over β-phenylethyl arenesulfonates.

Pseudo first-order rate constant k_{obs} was obtained from the slope of conventional plots of log $(K_\infty-K_t)$ against time. The least squares method was used for the calibration. The infinity reading was generally taken after 10 half-lives.

RESULTS AND DISCUSSION

The reactions of substituted β-phenylethyl arenesulfonates with pyridine in acetonitrile yield substituted β-phenylethylpyridinium arenesulfonates quantitatively as equation (1)





(1)

The solvolysis reactions are always negligible with respect to the nucleophilic addition. The reaction rate was measured by observing the increase of conductance of the salt formed in the reaction. The reactions, carried out in a large excess of pyridine, follow a pseudo first-order kinetics.

The rate constants, k_{obs}, are linearly correlated with the pyridine concentration, indicating that the reaction is second order overall and first order with respect to each reagent, according to the simple rate law

$$k_{obs}=k_2(\text{pyridine}) \qquad (2)$$

Second-order rate constants were calculated from the slope of the plot of k_{obs} against pyridine concentration.

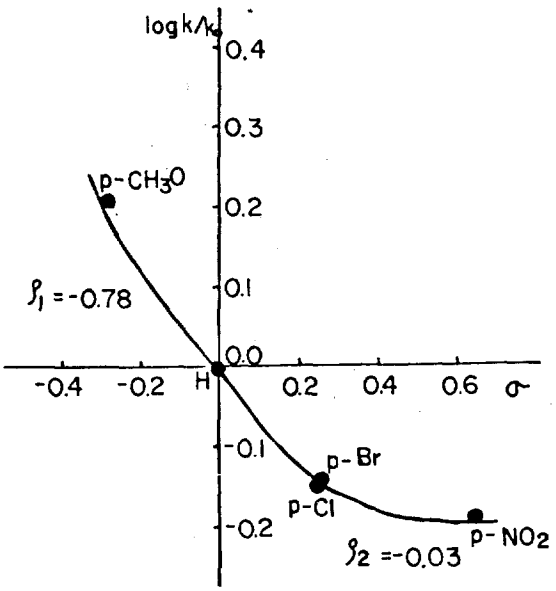


Fig. 1. Hammett plot for the reaction of β-phenylethyl tosylates with pyridine in acetonitrile at 60°C.

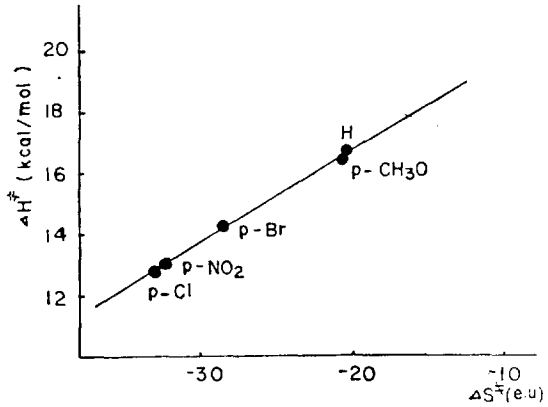


Fig. 2. The isokinetic relationship for the reaction of β-phenylethyl tosylates with pyridine in acetonitrile at 60°C.

The Substituent Effect of Substrate. The rate constants at various temperature, together with activation parameters in the substrate have been investigated for substituted β-phenylethyl tosylates (*Table* 3).

The substituent effects are not so significant than expected, but still the electron donating substituents show the slight acceleration. The substituent effects appear to be not so good correlate with linearity to give a small negative ρ value of -0.78 (p-MeO~H) (*Fig.* 1) and its small value may be one of the reason that the substituents are not so good interact with the reaction center by the insulation of additive CH_2 group. This is in clear contrast with the $\rho \cong -1.32$ for the substituted benzyl system.[1]

Further, we have shown that the corresponding substituent effect in the benzyl system can not be correlated linearly with any set of substituent constants, indicating the mechanism change from S_N2 to S_N1-like on going from electron withdrawing substituents to these electron donating substituents. The change in mechanism appears to be essential to the benzyl derivative which is capable of giving a particularly stable carbonium ion. Hammett plots show slight curvature on the acting the substituents in β-phenylethyl tosylate, even though it is not so remarkable than that of benzyl system.

These results represent a little bit the favorable bond breaking by the electron donating substituents in the β-phenylethyl tosylate. In S_N2 transition state, bond making and bond breaking are concerted, and Hammett slope value, which is variable but always negative, indicates the prevailing contribution of the bond breaking on the transition state which is looser or tighter depending on the substituents.

The isokinetic relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ was well correlated and its temperature 300°K (*Fig.* 2).

This S_N2 reaction was controlled by activation entropy.

The Substituent Effects of Leaving Groups. The second order rate constants and activation parameters for the reaction of β-phenylethyl arenesulfonate with pyridine are summarized in *Table* 4. From these results, the rate constants are decreased by the electron donating substituents.

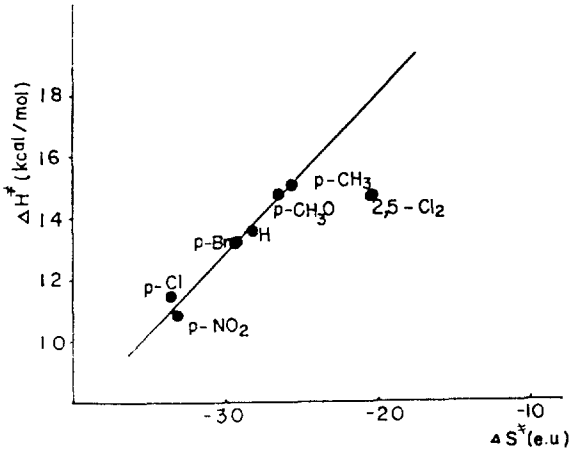


Fig. 3. The isokinetic relationship for the reaction of β-phenylethyl arenesulfonates with pyridine in acetonitrile at 60°C.

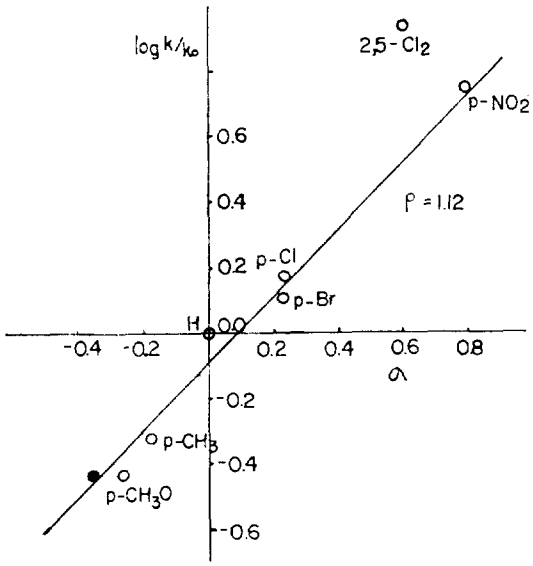


Fig. 4. Hammett plot for the reaction of β-phenylethyl arenesulfonates with pyridine in acetonitrile at 60°C.

While electron withdrawing groups were increased, in which the latter groups stabilize the sulfonate anion at the transition state by dispersing the charge. The calculated activation parameters for this reaction are about the same value of the other type of S_N2 Menschutkin reaction[16] and the rates were controlled by activation enthalpy. The isokinetic relationship between $\Delta H^{\neq}$ *vs.* $\Delta S^{\neq}$ was well correlated except for 2, 5-dichlorobenzenesulfonate and its temperature was 510°K (*Fig.* 3).

The deviation in the case of 2, 5-dichlorobenzenesulfonate is as expected for a too large activation enthalpy, which causes perhaps a change to loose S_N2 transition state contrast other substituents. *Fig.* 4 shows the Hammett plot for the reaction of β-phenylethyl arenesulfonates with pyridine in acetonitrile against ordinary σ values, where most of points fall on a line accompanying with a clearly deviating *p*-CH_3O substituent.

The apparent deviation may involve in part the deviation due to intrinsic modification of the substituent nature by the change of solvent from the reference water to acetonitrile and due in part to the possible inadequacy of ordinary constant to the leaving group effects of sulfonates, Thus, *p*-MeO value was used apparent σ value,[2] −0.35, of acetone and its results were good linearity.

As shown in *Fig.* 4, the ρ value for the reaction of β-phenylethyl esters with pyridine was 1.12 for most substituents, ommitted largely deviated 2, 5-dichloro compound.

$$\log k/k_0 = 1.12\sigma - 0.11 \quad (R = 0.991, \text{ SD} = 0.063, \text{ and } n = 6) \tag{3}$$

These are significantly smaller than 1.83 of the *p*-nitrobenzyl arenesulfonates with pyridine, that is well known S_N2 reaction mechanism in acetonitrile (*Fig.* 5).

These results indicate that the degree of C-O bond fission in β-phenylethyl system at transition state is much smaller than that of benzyl one.

The mechanism should be closer to tight S_N2 one than that of benzyl systems, in the sense of concerted mechanism that the bond-formation with nucleophile competes with the fission of leaving group at the transition state.

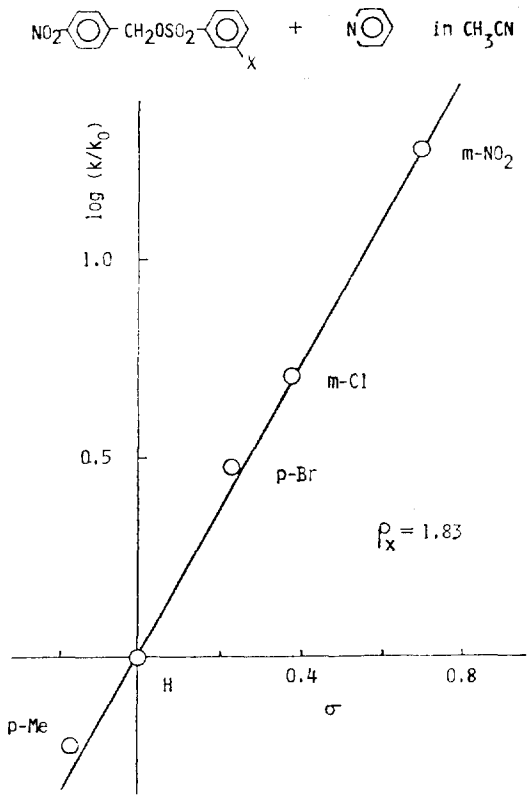


Fig. 5. Hammett plot for the reaction of *p*-nitrobenzyl arenesulfonate with pyridine in acetonitrile at 60°C

The additivity of the Hammett equation is sometimes very good, provided steric interactions are absent, the additive principle[17]

$$\text{yields: } \log k/k_0=\rho(\sigma_A+\sigma_B)=\rho\sum\sigma \qquad (4)$$

A proximity effect leading to breakdown of additivity, other than the twisting of groups, is hydrogen bonding between one substituent and a second. In this study, the reactivity of 2, 5-dichloro compound was more accelerated as expected for that of additivity of two substituents in the same benzene ring (2-Cl is usually considered as *p*-Cl).

This facts may be concerned that 2, 5-dichlorobenzene sulfonate anion is more stabilized by the electron withdrawing two substituents in one benzene ring at the transition state, as suggested above. This, as mentioned, is the reason for the deviation from isokinetic relationship and Hammett plots of 2, 5-dichloro benzenesulfonate.

For this chloro compound, we are planning to study in details for various respects.

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