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## Mechanistic Change-Over in Nucleophilic Solvent Assisted Reactions

Dae Dong Sung\*, Yang Hee Kim, Yoo-Mee Park, Zoon Ha Ryu<sup>†</sup>, and Ickchoon Lee<sup>‡</sup>

*Department of Chemistry, Dong-A University, Pusan 604-714*

<sup>†</sup>*Department of Chemistry, Dong-Eui University, Pusan 614-010*

<sup>‡</sup>*Department of Chemistry, Inha University, Incheon 402-751. Received March 20, 1992*

Rate constants of methanolyse of *para-Z*-substituted benzenesulfonyl chlorides have been determined in various iso-dielectric solvent mixtures. A third-order kinetic behavior has been observed in the methanolysis of *p*-nitrobenzenesulfonyl chloride in methanol-nitromethane mixture from the correlation figure of logarithms of rate constants were plotted against *Y*-values based on solvolyses of 1-adamantyl tosylate.  $S_N1$ - $S_N2$  mixing mechanisms are favored by neutral or weak electron-donating and weak electron-withdrawing substituents of *p-Z*-substituted benzenesulfonyl chlorides in methanol-nitrobenzene mixture. While the methanolyse of *para-Z*-substituted benzenesulfonyl chlorides in methanol-ethylene glycol solvent mixture are appropriate for  $S_N2$  mechanism from the mechanistic criterion by means of *m*-values.

### Introduction

Factors influencing nucleophilicity of anions and transition state involved in the nucleophilic substitution reactions have long held the interest of mechanistic chemists. The solvolytic reactions in which a solvent molecule attacks to the electrophilic center as a nucleophile have been investigated widely. The solvolytic reaction mechanism, were studied for various organic reactions based on the model substrates such as *tert*-butyl chloride and 2-adamantyl tosylate.<sup>1</sup> The conclusions derived from the detailed solvent effects on the rates of nucleophilic substitution reactions were applied to a large number of solvent-assisted reactions.<sup>2</sup> While a correlation of these kinetic results with thermodynamic properties of nucleophile has generally been unsatisfactory.

A different mechanistic view is raised a question in argument for the sulfonyl transfer reaction<sup>3</sup> involved solvent assistance when the kinetic results have been applied to the mechanistic criterion based on the correlation of kinetic results and thermodynamic properties.

A much discussed question<sup>3</sup> arising in the direct displace-

ment process for sulfonyl transfer concerns the timing of bond formation and cleavage, that is, whether the structure of seven-coordinate including sulfur atom corresponds to a transition state or penta-coordinate intermediate.

A good case of a two-step process proceeding *via* a pentacoordinate intermediate has been suggested by Kice<sup>3b</sup> and supported by the isolation of hypervalent analogues by Perkins and Martin.<sup>4</sup> Even though those proposals are well recognized in that case of sulfonyl transfer reaction such as alkyl sulfonyl halide solvolyses, while a very different mechanistic aspect is shown in the particular case of nucleophilic substitution reaction of arenesulfonic ester with hydroxide as shown their evidence is in better agreement with a one-step mechanism.<sup>5</sup>

On the other hand, the solvolytic reactions of arenesulfonyl chlorides were proposed to occur through very different mechanisms extend from dissociative  $S_N2$  to  $S_N$ .<sup>6</sup> In sulfonyl transfer reactions, each mechanism could show variable transition state structures, *e.g.*, from dissociative  $S_N2$  to  $S_N$  with increasing nucleophilic assistance by influence of solvent. Recently isodielectric binary solvent mixtures such as aceto-

**Table 1.** Rate Constants ( $k_{\text{obs}} \times 10^4 \text{ s}^{-1}$ ) for Solvolyses of *p*-Substituted Benzenesulfonyl Chlorides in MeOH-MeNO<sub>2</sub> at 45°C

Solvents*	Substituents					
	<i>p</i> -OCH <sub>3</sub>	<i>p</i> -CH <sub>3</sub>	<i>p</i> -H	<i>p</i> -F	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>
95	7.81	5.75	5.17	5.00	4.72	7.31
90	7.95	5.86	5.31	5.13	4.85	7.76
85	7.81	6.15	5.37	5.20	4.93	8.65
80	7.64	6.26	5.43	5.31	5.01	9.61
70	6.36	5.63	4.84	5.10	4.85	10.4
50	4.62	4.53	4.37	4.26	4.46	12.2
40	3.47	3.51	3.59	3.72	3.94	13.6
30	2.92	3.04	3.24	3.31	3.77	15.7

\*MeOH Composition (v/v%).

**Table 2.** Rate Constants ( $k_{\text{obs}} \times 10^4 \text{ s}^{-1}$ ) for Solvolyses of *p*-Substituted Benzenesulfonyl Chlorides in MeOH-PhNO<sub>2</sub> at 45°C

Solvents*	Substituents					
	<i>p</i> -OCH <sub>3</sub>	<i>p</i> -CH <sub>3</sub>	<i>p</i> -H	<i>p</i> -F	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>
95	6.75	5.07	4.65	4.71	5.15	7.18
90	6.28	4.79	4.38	4.54	4.85	6.89
85	5.83	4.46	4.04	4.25	4.61	6.62
80	5.40	4.23	3.84	3.96	4.40	6.39
70	4.46	3.72	3.43	3.74	3.83	5.77
50	2.79	2.23	2.22	2.25	2.26	4.63
40	1.88	1.53	1.41	1.67	1.71	3.99
30	1.30	1.06	1.04	1.04	1.05	3.31

\*MeOH Composition (v/v%).

nitrile-methanol solvent system are reported<sup>7</sup> that the mechanistic variation is analyzed clearly even though a vague mixing mechanism exists in very complicated nucleophilic substitution reaction.

A clear cut of mechanistic change-over in the sulfonyl transfer reactions would be expected if the reactions proceed in the isodielectric binary solvent mixtures. Especially a mechanistic change-over which would be shown widely from dissociative S<sub>N</sub>2 through concerted S<sub>N</sub>2 to associative S<sub>N</sub>2 seems to be observed kinetically as to be selected an appropriate substrate and solvent system. For this purpose the methanolyses of arenesulfonyl chlorides in isodielectric binary solvent mixtures have been chosen.

We report here a qualitative mechanistic change-over for the solvolyses of various *para*-Z-substituted benzenesulfonyl chlorides in isodielectric binary solvent mixtures which would be involved nucleophilic solvent participation in transition state

## Experimental

**Materials.** Arenesulfonyl chlorides (ZC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl) were commercially available (Aldrich). The reagents (Z-C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl) used after distillation or recrystallization according to the literature.<sup>8</sup> Methanol (MeOH), nitromethane (MeNO<sub>2</sub>) and nitrobenzene (PhNO<sub>2</sub>) were purified as described previously.<sup>9</sup>

**Table 3.** Rate Constants ( $k_{\text{obs}} \times 10^4 \text{ s}^{-1}$ ) for Solvolyses of *p*-Substituted Benzenesulfonyl Chlorides in MeOH-EG at 45°C

Solvents*	Substituents					
	<i>p</i> -OCH <sub>3</sub>	<i>p</i> -CH <sub>3</sub>	<i>p</i> -H	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>	
95	7.83	6.01	5.61	4.73	7.60	
90	8.43	6.40	6.12	5.15	7.83	
85	8.50	6.95	6.30	5.35	8.32	
80	9.50	7.41	6.46	5.49	8.54	
70	10.8	8.25	7.16	6.23	9.33	
50	12.2	9.34	8.56	7.36	10.8	
40	13.4	10.5	9.03	8.70	11.6	
30	14.8	11.0	9.64	8.02	12.5	

\*MeOH Composition (v/v%).

Ethylene glycol (EG) was purified according to Koizumi and Hanai's method<sup>10</sup> as drying over with dehydrated sodium sulfate and then running three successive fractional distillations at 8 torr pressure, retaining only the middle fractions. Then it was fractionally crystallized twice at -13°C. Solvent mixtures were prepared in volume percentage (v/v).

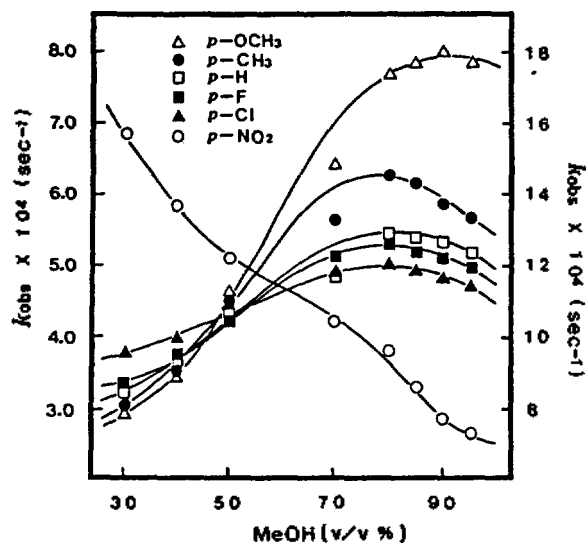
**Kinetic Methods.** The rates were followed conductrimetrically as conducting as pseudo-first order reactions and the solvolytic rate constants,  $k_{\text{obs}}$  were obtained by the Guggenheim method.<sup>11</sup> The values listed in Tables 1, 2 and 3 are the averages of several runs with a reproducibility of  $> \pm 3\%$  in all reactions.

## Results and Discussion

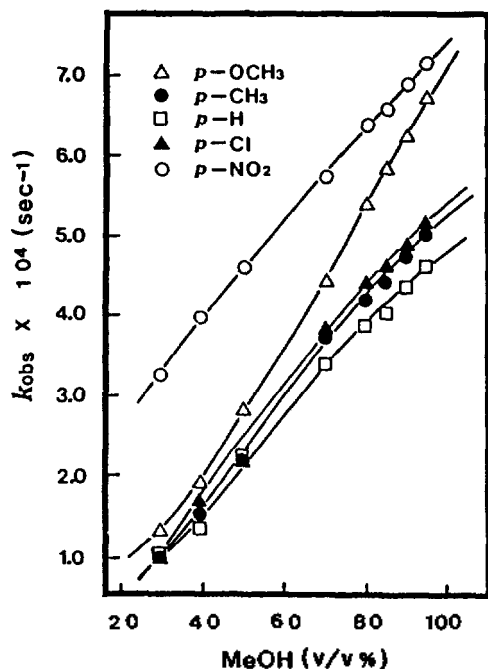
Pseudo-first-order rate constants,  $k_{\text{obs}}$ , for the solvolyses of *para*-Z-substituted benzenesulfonyl chlorides are shown to be changed as the order of magnitude as, *p*-Cl < *p*-F < *p*-H < *p*-CH<sub>3</sub> < *p*-OCH<sub>3</sub> in MeOH-MeNO<sub>2</sub>, *p*-H < *p*-F < *p*-CH<sub>3</sub> < *p*-Cl < *p*-OCH<sub>3</sub> in MeOH-PhNO<sub>2</sub>, and *p*-Cl < *p*-H < *p*-CH<sub>3</sub> < *p*-OCH<sub>3</sub> in MeOH-EG, at high volume percentage region of MeOH in various binary solvent mixtures as shown in Tables 1, 2 and 3 except *p*-NO<sub>2</sub>. Especially *p*-OCH<sub>3</sub> is shown a higher value of rate constant at any solvent mixtures except *p*-NO<sub>2</sub>. This seems that the solvolytic reaction of *p*-OCH<sub>3</sub> is involved the generation of positive charge in a position of reaction center by a direct resonance interaction with electron-donating substituent of methoxy group. The solvolysis of *p*-OCH<sub>3</sub> almost certainly involves the generation of a sulfonyllium cation intermediate ( $-\text{S}_2\text{O}^+$ ). Therefore the reaction of *p*-OCH<sub>3</sub> seems to be proceeded by S<sub>N</sub>1-like mechanism at a high volume percentage region of MeOH. The relative magnitude of the rate constants for neutral, or weak electron-donating and weak electron-withdrawing substituents in Tables 1, 2 and 3 are of interest as shown the order of magnitude of rate constants as stated previously. It appears that these solvolytic reactions are affected only a little by nucleophilic solvent assistant (NAS) ability compared with the strong electron-withdrawing substituent (*p*-NO<sub>2</sub>) and strong electron-donating substituent (*p*-OCH<sub>3</sub>).

The rate profiles with MeOH content for solvolyses of *p*-substituted benzenesulfonyl chlorides in various isodielectric binary solvent mixtures are presented in Figures 1-3.

There are very different trends in rate behaviour for these



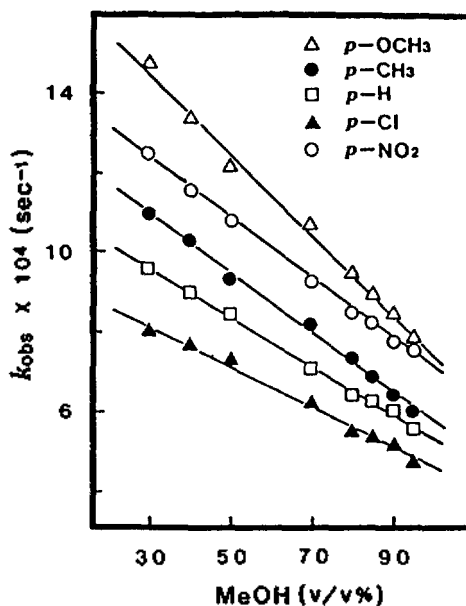
**Figure 1.** Correlation of methanol content vs.  $k_{obs} \times 10^4$  for the solvolyses of *p*-substituted benzenesulfonyl chlorides in MeOH-MeNO<sub>2</sub> solvent mixtures at 45°C. The scale of vertical line of right side indicates for *p*-NO<sub>2</sub> and the left side scale indicates for *p*-OCH<sub>3</sub>, *p*-CH<sub>3</sub>, *p*-H and *p*-Cl.



**Figure 2.** Correlation of methanol content vs.  $k_{obs} \times 10^4$  for the solvolyses of *p*-substituted benzenesulfonyl chlorides in MeOH-PhNO<sub>2</sub> solvent mixtures at 45°C.

three solvent mixtures. Figure 1 shows an evidence for a mechanistic change over a wide range.

The rate profile for *p*-nitro benzenesulfonyl chloride (*p*-NO<sub>2</sub>) in MeOH-MeNO<sub>2</sub> (Figure 1) is not consistent with the other *p*-substituted benzenesulfonyl chlorides from a mechanistic point of view. *p*-Methoxy benzenesulfonyl chloride (*p*-OCH<sub>3</sub>), *p*-toluenesulfonyl chloride (*p*-CH<sub>3</sub>), benzenesulfonyl chloride (*p*-H), *p*-fluorobenzenesulfonyl chloride (*p*-F) and *p*-chloro benzenesulfonyl chloride (*p*-Cl) show the rate maxima



**Figure 3.** Correlation of methanol content vs.  $k_{obs} \times 10^4$  for the solvolyses of *p*-substituted benzenesulfonyl chlorides in MeOH-EG solvent mixtures at 45°C.

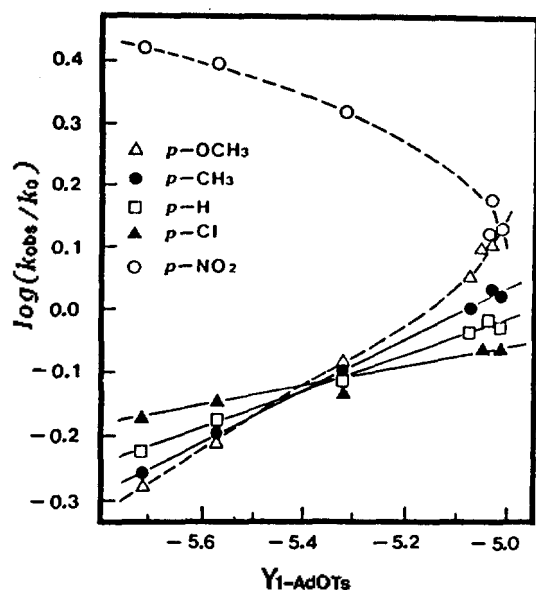
at 80-90% MeOH-MeNO<sub>2</sub> binary mixtures. The isodielectric binary solvent mixtures including methanol as a cosolvent are well known to show a phenomenon of rate maximum<sup>6,7</sup> in the diagram which the rate constants plot against the constant of MeOH. On the other hand there is no rate maximum for *p*-NO<sub>2</sub> and the rate constant decreases steadily as the concentration of cosolvent (MeOH) increases. This trend for *p*-NO<sub>2</sub> indicates that there would exist a higher kinetic order in MeOH-MeNO<sub>2</sub> mixture than the S<sub>N</sub>1-S<sub>N</sub>2 process. The expected higher kinetic order for *p*-NO<sub>2</sub> would be involved sulfonyllium addition reaction likely to be in accord with the stabilization of the zwitterionic or anionic intermediate<sup>12</sup>. Logarithms of pseudo-first-order rate constants, plotted on ionizing power of solvent, *Y* values would then show a low response to *Y* values and a large dispersion<sup>13</sup> if there is the zwitterionic or anionic intermediate.

Interpretation of kinetic data for the *para*-substituted benzenesulfonyl chlorides with electron-withdrawing substituents was known to be correlated assuming third-order kinetic<sup>14</sup> to be formed the carbonyl addition intermediate during the reaction occur.

In order to find an evidence of mechanistic change-over, the rate constants of *para*-*Z*-substituted benzenesulfonyl chlorides were applied ionizing power parameter (*Y*). The empirical ionizing power parameter, *Y* was introduced by Grunwald-Winstein and was defined by Eq. 1<sup>15</sup> with

$$\log (k/k_o)_{RX} = mY \quad (1)$$

$m=1$  for *tert*-butyl chloride at 25°C;  $k$  is the rate constant for solvolysis in any solvent and  $k_o$  that for solvolysis in 80% (v/v) EtOH-H<sub>2</sub>O mixture. However, in practice, Eq. (1) is not well fitted for the nucleophilic solvent assisted reaction<sup>16</sup> among various solvolytic reactions. In order to resolve the problem that rises at the nucleophilic solvent assisted reaction, a new substrate has been established to fit Eq. (1). 1-Adamantyl tosylate (1-AdOTs) and 2-adamantyl tosylate (2-



**Figure 4.** Logarithms of first-order rate constants for solvolyses of *p*-substituted benzenesulfonyl chlorides in MeOH-MeNO<sub>2</sub> binary solvent mixtures at 45°C vs. Bentley-Schleyer's *Y* values. *k*<sub>0</sub> values for *p*-H, *p*-CH<sub>3</sub>, *p*-OCH<sub>3</sub>, *p*-Cl and *p*-NO<sub>2</sub> in 80% EtOH-H<sub>2</sub>O mixtures were quoted from the reference 16. *Y*<sub>1-AdOTs</sub> values were determined as follows as conductrimetric method of the experimental part in this work in the same solvent compositions: 30% MeOH: -5.73, 40% MeOH: -5.58, 50% MeOH: -5.53, 70% MeOH: -5.09, 80% MeOH: -5.02, 90% MeOH: -5.03, in MeOH-MeNO<sub>2</sub> solvent mixtures at 45°C respectively.

AdOTs) were selected as a new model substrate for S<sub>N</sub>1 behavior because non-bonded interactions would reduce the possibility of nucleophilic attack<sup>17</sup>.

To examine a higher order kinetic behavior the logarithms of pseudo-first-order rate constants and third-order rate constants plotted on Bentley-Schleyer's *Y* values<sup>18</sup> based on 1-adamantyl tosylate as shown Figure 4 and 5.

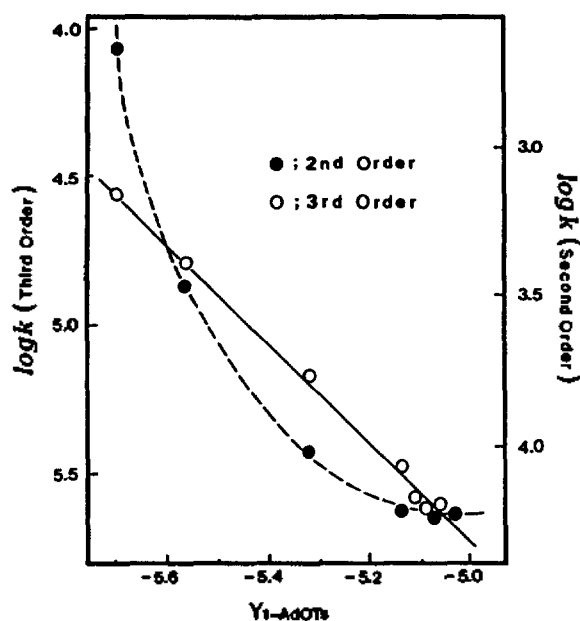
In case of *p*-NO<sub>2</sub>, logarithms of pseudo first-order rate constants show a low response to solvent ionizing power and large dispersion, while *p*-Cl, *p*-H, and *p*-CH<sub>3</sub> are correlated nicely with solvent ionizing power in Figure 4.

These similar mechanistic changes for solvolyses of *p*-chloro benzoyl chloride and *p*-nitro benzoyl chloride in various aqueous media were interpreted that the rates fitted the third-order equation.<sup>14</sup> For solvolyses of *p*-nitrobenzenesulfonyl chloride in this research over the whole range of MeOH-MeNO<sub>2</sub> binary solvent mixtures, the rate applied to the third-order Eq. (2) as shown Figure 5,

$$k_{obs} = k_{aa}[\text{MeOH}]^2 + (k_{an} + k_{na})[\text{MeOH}][\text{MeNO}_2] + k_{nn}[\text{MeNO}_2]^2 \quad (2)$$

in which *k*<sub>aa</sub> is the rate constant for attacking by two methanol molecules, *k*<sub>nn</sub> refers to the one by nitromethane, *k*<sub>an</sub> refers to methanol as nucleophile and *k*<sub>na</sub> refers to nitromethane.

Product analysis showed only sulfonyl ester by reaction of *p*-nitrobenzenesulfonyl chloride with methanol. From the product analysis nitromethane was not shown to have an



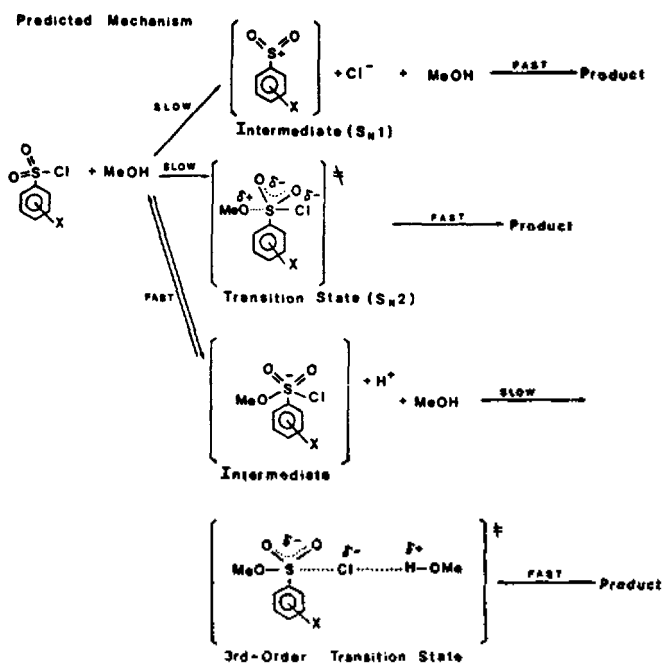
**Figure 5.** Logarithms of calculated second-, and third-order rate constants for methanolysis of *p*-nitrobenzenesulfonyl chloride in MeOH-MeNO<sub>2</sub> binary solvent mixtures at 45°C vs. Bentley-Schleyer's *Y* values. *Y*<sub>1-AdOTs</sub> values were scaled by the same values of Figure 4.

evidence to react as nucleophile. Therefore the last two terms are neglected in Eq. (2). Third-order rate constants for methanol (*k*<sub>aa</sub>) can also be calculated: e.g., *k*<sub>aa</sub> for MeOH, *k*<sub>obs</sub>/[MeOH]<sup>2</sup>. The second-order rate constants for methanols can be calculated by a similar method for methanolysis of *p*-nitro benzenesulfonyl chloride in MeOH-MeNO<sub>2</sub> mixtures: e.g., *k*<sub>a</sub> for MeOH, *k*<sub>na</sub>/[MeOH]. The solvolytic reactions in MeOH-PhNO<sub>2</sub> and MeOH-EG binary mixtures are also obeyed Eq. (2) and results of product analyses are shown the same.

All of the third-order rate constants and second-order rate constants are plotted as shown in Figure 5. *p*-Nitrobenzenesulfonyl chloride shows a good correlation to the third-order behavior, while the second-order behavior is not consistent with the rate profile to show many dispersed points along with *Y*<sub>1-AdOTs</sub> values in Figure 5.

Very similar result for the third-order behavior has been reported for solvolysis of *p*-nitrobenzoyl chloride.<sup>13</sup> Chloride ion from the reaction of *p*-nitrobenzoyl chloride and *p*-nitrobenzenesulfonyl chloride can act as a general base catalyst replacing one of the alcohol molecules in the transition state.<sup>19</sup> Hydrolyses of esters activated in the acyl group are well recognized to proceed via a third-order (B<sub>AC</sub>3) mechanism in which water molecule acts as a general base.<sup>20</sup>

The predicted S<sub>N</sub>1, S<sub>N</sub>2 and 3rd-order methanolyses of *p*-substituted benzenesulfonyl chlorides are illustrated in Scheme 1. Electron-donating substituents stabilize S<sub>N</sub>1-like intermediate and neutral or weak electron-withdrawing substituents stabilize S<sub>N</sub>2-like transition state in Scheme 1. On the other side *p*-NO<sub>2</sub> substituent make possible that a trimolecular collision is pictured as two bimolecular collisions<sup>21</sup> in rapid succession, then the intermediate<sup>22</sup> reacts with the third molecule of MeOH as shown in the 3rd-order inter-



Scheme 1.

mediate in Scheme 1. This observation for *p*-NO<sub>2</sub> is caused by the unshared electron pairs of nitro group. It gives an explanation when the reaction center is adjacent to the aromatic ring involves with nitro group and the Hammett equation breaks down.<sup>23</sup> For example, the *para*-nitro group has a much greater influence on the ionization constant of phenols in water at 25°C than it does on that of benzoic acids.<sup>23</sup> In that case, the opposite side groups of the aromatic ring including nitro group can stabilize negative charge by strong electron-withdrawing resonance effects require an additional or enhanced resonance effect.

Hydration of acyl halide<sup>24</sup> and addition of alcohols to acylium ions<sup>25</sup> also involve general base catalytic reaction.

Medium effects on the first-order and third-order rate constants can be incorporated into *m*-values of Grunwald-Winstein equation. The solvolytic reactions involved nucleophilic solvent assistance (NSA) and acidity of the solvent contribute to show a different behavior of *m*-value in Eq.<sup>26</sup> (1). Rappoport and his coworkers<sup>27</sup> reported *m* = -0.3 for solvolytic reaction of 3-fluorobenzyl bromide in trifluoroethanol (TFE) and ethanol (EtOH) mixtures. If highly unstable anionic intermediate is formed during solvolytic reaction occurs, a constant selectivity observes even though the solvent composition changes. This kind of intermediate is well formed in the isodielectric binary solvent mixture such as the dielectric constants (*D*) show a wide difference<sup>28</sup> between the two solvents and contributes to keep up a constant selectivity irrespective of the solvent composition.

Especially a constant selectivity also observes in case that the leaving group is not only connected closely with aromatic ring which is influenced strongly by an electron-withdrawing substituent, but also the leaving group and the substituent are surrounded with an isodielectric solvent mixture composing with the two solvents have a wide difference between two dielectric constants.<sup>29</sup> In that case a negative *m*-value appears because the selectivity does not change but *Y*-value

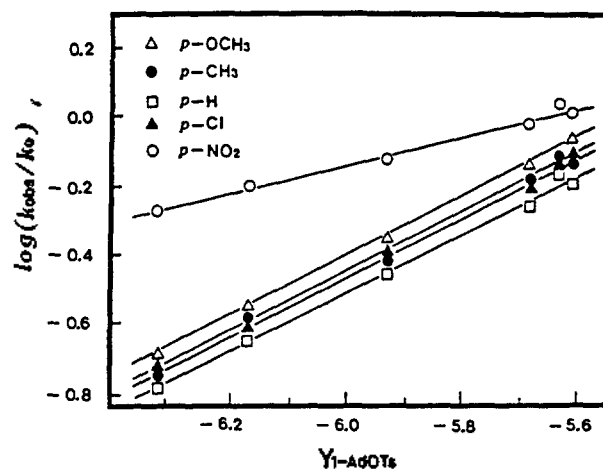


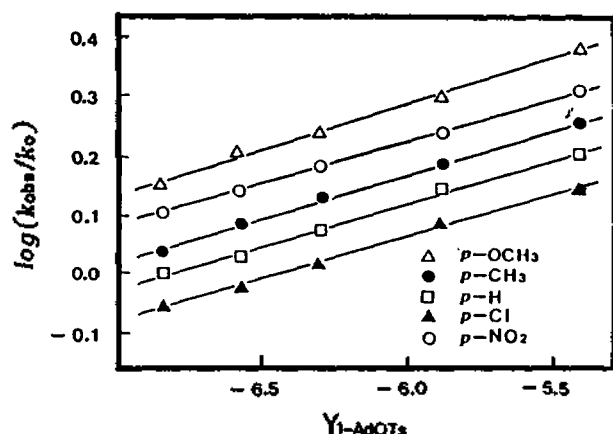
Figure 6. Logarithms of first-order rate constants for solvolyses of *p*-substituted benzenesulfonyl chlorides in MeOH-PhNO<sub>2</sub> binary solvent mixtures at 45°C vs. Bentley-Schleyer's *Y* values. *k*<sub>0</sub> values for *p*-H, *p*-CH<sub>3</sub>, *p*-OCH<sub>3</sub>, *p*-Cl and *p*-NO<sub>2</sub> in 80% EtOH-H<sub>2</sub>O mixtures were quoted from the reference 16. *Y*<sub>1-AROTs</sub> values were determined as follows as conductrimetric method of the experimental part in this work in the same solvent compositions; 30% MeOH: -6.33, 40% MeOH: -6.18, 50% MeOH: -5.93, 70% MeOH: -5.58, 80% MeOH: -5.41, 90% MeOH: -5.64, in MeOH-PhNO<sub>2</sub> solvent mixtures at 45°C respectively.

decreases with increasing the solvent polarity or solvent dielectric constant.<sup>29</sup>

In this study the isodielectric binary solvent mixture of MeOH-MeNO<sub>2</sub> shows a small difference of *Y*-values ( $\Delta Y$ ) according to change the content from 30% (v/v) MeOH to 90% (v/v) MeOH, while a large difference of dielectric constant ( $\Delta D$ )<sup>30</sup> according to change the content variation at the same range comparing with MeOH-PhNO<sub>2</sub> and MeOH-EG binary mixtures.

In MeOH-MeNO<sub>2</sub> mixture  $\Delta Y$  shows 0.71 (see Figure 4) and the difference of dielectric constant ( $\Delta D$ ) shows 6.00, while shows  $\Delta Y=0.92$  (see Figure 6),  $\Delta D=2.00$  in MeOH-PhNO<sub>2</sub> and  $\Delta Y=1.43$  (see Figure 7),  $\Delta D=5.10$  in MeOH-EG respectively. The higher ratio of  $\Delta Y/\Delta D$  contributes to keep up a constant selectivity during the solvolytic reaction occurs from the ground state to the activated state and the ratio increases the possibility of the formation the anionic intermediate.

Therefore the *m*-values for the solvolytic reaction of *p*-nitro benzenesulfonyl chloride would require negative<sup>14</sup> in higher polar solvent and alcohol mixtures relatively because the observed pseudo-first-order rate constants in MeOH-MeNO<sub>2</sub> should depend only on the second power of [MeOH], and the presence of a fixed percentage by volume of [MeNO<sub>2</sub>] should not influence the rate constant. The *m*-values based on Bentley-Schleyer's *Y*-values for *p*-H, *p*-CH<sub>3</sub>, *p*-OCH<sub>3</sub> and *p*-Cl are shown as *S*<sub>N1</sub>-*S*<sub>N2</sub> mixing mechanism likely to be shown *m* = 0.294 for *p*-H, *m* = 0.434 for *p*-CH<sub>3</sub>, *m* = 0.523 for *p*-OCH<sub>3</sub> and *m* = 0.138 for *p*-Cl in Figure 4. While the *m*-value for *p*-NO<sub>2</sub> in Figure 5 shows -1.631: this could explain that the more reactive substrate (*p*-NO<sub>2</sub>) is involved the third order kinetic behavior as methanol molecule attacks to the



**Figure 7.** Logarithms of first-order rate constants for solvolyses of *p*-substituted benzenesulfonyl chlorides in MeOH-EG binary solvent mixtures at 45°C vs. Bentley-Schleyer's *Y* values.

$k_0$  values for *p*-H, *p*-CH<sub>3</sub>, *p*-OCH<sub>3</sub>, *p*-Cl and *p*-NO<sub>2</sub> in 80% EtOH-H<sub>2</sub>O mixtures were quoted from the reference 16.  $Y_{1-AdOTs}$  values were determined as follows as conductrimetric method of the experimental part in this work in the same solvent compositions; 30% MeOH: -5.42, 50% MeOH: -5.90, 70% MeOH: -6.31, 80% MeOH: -6.59, 90% MeOH: -6.85, in MeOH-EG solvent mixtures at 45°C respectively.

reaction center before departing the leaving group and then, is formed the sulfonyl additional intermediate like an anionic structure.

The correlation between  $\log(k/k_0)$  and Bentley-Schleyer's *Y* value in MeOH-PhNO<sub>2</sub> mixtures has been shown in Figure 6.

The correlation lines explained to show  $S_N1$ - $S_N2$  mixing mechanism as shown  $m=0.326$  for *p*-NO<sub>2</sub>,  $m=0.831$  for *p*-OCH<sub>3</sub>,  $m=0.742$  for *p*-Cl,  $m=0.748$  for *p*-CH<sub>3</sub> and  $m=0.652$  for *p*-H in Figure 6. Because the  $m$ -values have been varied from 0.326 to 0.831 so that the value of 0.326 is nearly close to be slanted  $S_N2$  mechanism and the values of 0.742 to 0.831 are oppositely close to be slanted  $S_N1$  mechanism.

A mechanistic criterion based on the  $m$ -value might be estimated likely that  $S_N1$  mechanism is favored to approach to  $m=1.00$  and  $S_N2$  mechanism is well fit on when  $m=0.00$  to apply the  $m$ -values to the solvolytic reactions<sup>31</sup>.

The  $m$ -values for the methanolyses in MeOH-EG solvent mixtures show as  $m=0.145$  for *p*-OCH<sub>3</sub>,  $m=0.124$  for *p*-NO<sub>2</sub>,  $m=0.155$  for *p*-CH<sub>3</sub>,  $m=0.138$  for *p*-H and  $m=0.141$  for *p*-Cl in Figure 7.

These values in MeOH-EG are close to  $S_N2$  mechanism rather than  $S_N1$ - $S_N2$  mixing mechanism since the  $m$ -values are lower approaching to 0.00.

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## Preparation and Characterization of Chromium Oxide Supported on Zirconia

Jong Rack Sohn<sup>\*</sup>, Sam Gon Ryu, Man Young Park, and Young Il Pae<sup>†</sup>

<sup>\*</sup>Department of Industrial Chemistry, Kyungpook National University, Taegu 702-701

<sup>†</sup>Department of Chemistry, National Science College Ulsan University, Ulsan 680-749

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Chromium oxide/zirconia catalysts were prepared by dry impregnation of powdered Zr(OH)<sub>4</sub> with (NH<sub>4</sub>)<sub>2</sub>CrO<sub>4</sub> aqueous solution. The characterization of prepared catalysts was performed using FTIR, XPS, XRD and DTA methods, and by the measurement of surface area. The addition of chromium oxide to zirconia shifted the transitions of ZrO<sub>2</sub> from amorphous to tetragonal phase and from tetragonal to monoclinic phase to higher temperature due to the strong interaction between chromium oxide and zirconia, and the specific surface area of catalysts increased in proportion to the chromium oxide content. Since the ZrO<sub>2</sub> stabilizes supported chromium oxide, chromium oxide was well dispersed on the surface of zirconia, and α-Cr<sub>2</sub>O<sub>3</sub> was observed only at the calcination temperature above 1173 K. Upon the addition of only small amount of chromium oxide (1 wt% Cr) to ZrO<sub>2</sub>, both the acidity and acid strength of catalyst increased remarkably, showing the presence of two kinds of acid sites on the surface of CrO<sub>2</sub>/ZrO<sub>2</sub>-Brønsted and Lewis.

### Introduction

Supported chromium oxide catalysts are being used for the polymerization, hydrogenation, dehydrogenation, oxidation-reduction reactions between environmentally important molecules such as CO and NO.<sup>1-5</sup> Recently, many efforts have involved the characterization of these catalysts in an attempt to find the appropriate reaction mechanisms. The titrations to determine the oxidation state of the chromium used in conjunction with infrared and electron paramagnetic resonance spectroscopies have provided much information dealing with these questions. So far, however, they have been studied mainly on silica and alumina,<sup>6-8</sup> and only a little work was studied for the ZrO<sub>2</sub> support.<sup>9,10</sup>

Zirconia is an important material due to its interesting

thermal and mechanical properties and so has been investigated as a support and catalysts in recent years. Different papers have been devoted to the studies of ZrO<sub>2</sub> catalytic activity in the important reactions such as methanol and hydrocarbon syntheses from CO and H<sub>2</sub>, from CO<sub>2</sub> and H<sub>2</sub><sup>11,12</sup>, or from alcohol dehydration.<sup>13,14</sup> Zirconia has been extensively used as a support for metals or incorporated in supports to stabilize them or to make them more resistant to sintering.<sup>15-17</sup> ZrO<sub>2</sub> activity and selectivity highly depend on the methods of preparation and treatment used. In particular, in the previous papers from this laboratory, it has been shown that NiO-ZrO<sub>2</sub> and ZrO<sub>2</sub> modified with sulphate ion are very active for acid-catalyzed reactions, even at room temperature.<sup>18-20</sup> The high catalytic activities in the above reactions were attributed to the enhanced acidic properties