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Mechanistic Change-Over in Nucleophilic Solvent Assisted Reactions

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Rate constants of methanolyses of *para-Z*-substituted benzenesulfonyl chlorides have been determined in various 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 methanolyses 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.¹ 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.² 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 reaction³ 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 question³ 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^{3b} and supported by the isolation of hypervalent analogues by Perkins and Martin.⁴ 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.⁵

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

Table 1. Rate Constants ($k_{obs} \times 10^4 \text{ s}^{-1}$) for Solvolyses of *p*-Substituted Benzenesulfonyl Chlorides in MeOH-MeNO₂ at 45°C

Solvents*	Substituents					
	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>p</i> -H	<i>p</i> -F	<i>p</i> -Cl	<i>p</i> -NO ₂
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 ($k_{obs} \times 10^4 \text{ s}^{-1}$) for Solvolyses of *p*-Substituted Benzenesulfonyl Chlorides in MeOH-PhNO₂ at 45°C

Solvents*	Substituents					
	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>p</i> -H	<i>p</i> -F	<i>p</i> -Cl	<i>p</i> -NO ₂
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 reported⁷ 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_N2 through concerted S_N2 to associative S_N2 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 (ZC₆H₄SO₂Cl) were commercially available (Aldrich). The reagents (Z-C₆H₄SO₂Cl) used after distillation or recrystallization according to the literature.⁸ Methanol (MeOH), nitromethane (MeNO₂) and nitrobenzene (PhNO₂) were purified as described previously.⁹

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

Solvents*	Substituents					
	<i>p</i> -OCH ₃	<i>p</i> -CH ₃	<i>p</i> -H	<i>p</i> -Cl	<i>p</i> -NO ₂	
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 method¹⁰ 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_{obs} were obtained by the Guggenheim method.¹¹ 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_{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*-CH₃ < *p*-OCH₃ in MeOH-MeNO₂, *p*-H < *p*-F < *p*-CH₃ < *p*-Cl < *p*-OCH₃ in MeOH-PhNO₂, and *p*-Cl < *p*-H < *p*-CH₃ < *p*-OCH₃ 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*-NO₂. Especially *p*-OCH₃ is shown a higher value of rate constant at any solvent mixtures except *p*-NO₂. This seems that the solvolytic reaction of *p*-OCH₃ 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*-OCH₃ almost certainly involves the generation of a sulfonyllium cation intermediate ($-\text{S}_{\text{O}}^{\text{O}+}$). Therefore the reaction of *p*-OCH₃ seems to be proceeded by S_N1-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*-NO₂) and strong electron-donating substituent (*p*-OCH₃).

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

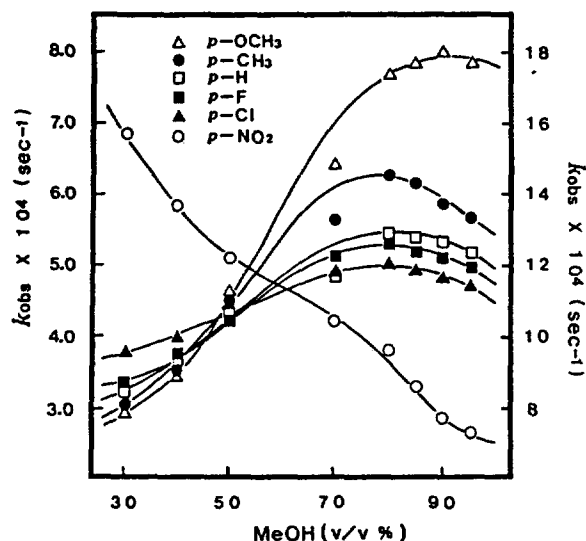


Figure 1. Correlation of methanol content vs. $k_{obs} \times 10^4$ for the solvolyses of *p*-substituted benzenesulfonyl chlorides in MeOH-MeNO₂ solvent mixtures at 45°C. The scale of vertical line of right side indicates for *p*-NO₂ and the left side scale indicates for *p*-OCH₃, *p*-CH₃, *p*-H and *p*-Cl.

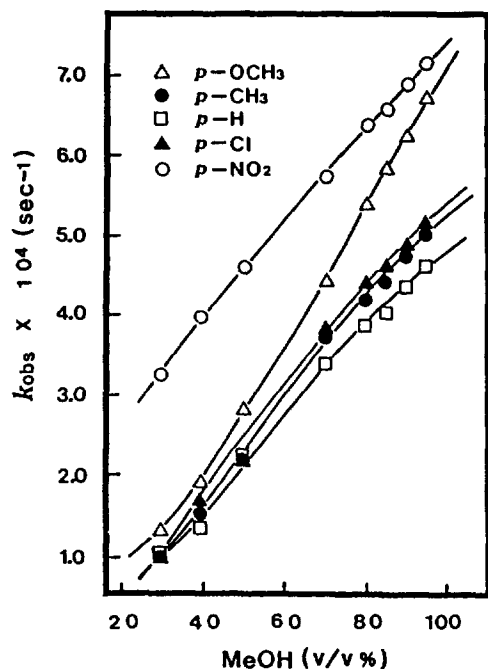


Figure 2. Correlation of methanol content vs. $k_{obs} \times 10^4$ for the solvolyses of *p*-substituted benzenesulfonyl chlorides in MeOH-PhNO₂ solvent mixtures at 45°C.

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*-NO₂) in MeOH-MeNO₂ (Figure 1) is not consistent with the other *p*-substituted benzenesulfonyl chlorides from a mechanistic point of view. *p*-Methoxy benzenesulfonyl chloride (*p*-OCH₃), *p*-toluenesulfonyl chloride (*p*-CH₃), benzenesulfonyl chloride (*p*-H), *p*-fluorobenzenesulfonyl chloride (*p*-F) and *p*-chloro benzenesulfonyl chloride (*p*-Cl) show the rate maxima

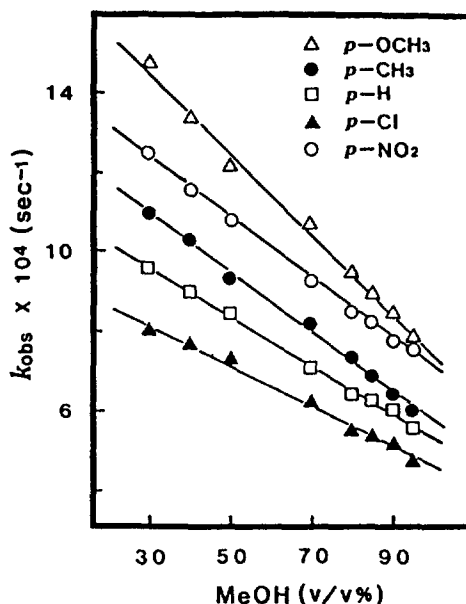


Figure 3. Correlation of methanol content vs. $k_{obs} \times 10^4$ for the solvolyses of *p*-substituted benzenesulfonyl chlorides in MeOH-EG solvent mixtures at 45°C.

at 80-90% MeOH-MeNO₂ binary mixtures. The isodielectric binary solvent mixtures including methanol as a cosolvent are well known to show a phenomenon of rate maximum^{6,7} in the diagram which the rate constants plot against the constant of MeOH. On the other hand there is no rate maximum for *p*-NO₂ and the rate constant decreases steadily as the concentration of cosolvent (MeOH) increases. This trend for *p*-NO₂ indicates that there would exist a higher kinetic order in MeOH-MeNO₂ mixture than the S_N1-S_N2 process. The expected higher kinetic order for *p*-NO₂ would be involved sulfonyllium addition reaction likely to be in accord with the stabilization of the zwitterionic or anionic intermediate¹². 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 dispersion¹³ if there is the zwitterionic or anionic intermediate.

Interpretation of kinetic data for the *para*-substituted benzoyl chlorides with electron-withdrawing substituents was known to be correlated assuming third-order kinetic¹⁴ 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. 1¹⁵ 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-H₂O mixture. However, in practice, Eq. (1) is not well fitted for the nucleophilic solvent assisted reaction¹⁶ 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-

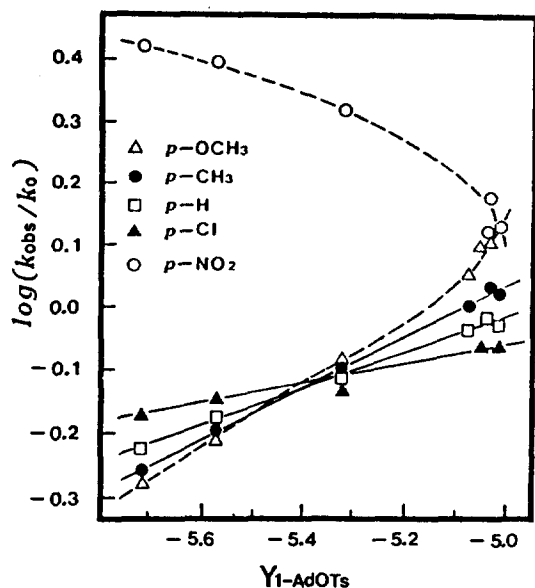


Figure 4. Logarithms of first-order rate constants for solvolyses of *p*-substituted benzenesulfonyl chlorides in MeOH-MeNO₂ binary solvent mixtures at 45°C vs. Bentley-Schleyer's *Y* values. *k*₀ values for *p*-H, *p*-CH₃, *p*-OCH₃, *p*-Cl and *p*-NO₂ in 80% EtOH-H₂O mixtures were quoted from the reference 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: -5.73, 40% MeOH: -5.58, 50% MeOH: -5.53, 70% MeOH: -5.09, 80% MeOH: -5.02, 90% MeOH: -5.03, in MeOH-MeNO₂ solvent mixtures at 45°C respectively.

AdOTs) were selected as a new model substrate for S_N1 behavior because non-bonded interactions would reduce the possibility of nucleophilic attack¹⁷.

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* values¹⁸ based on 1-adamantyl tosylate as shown Figure 4 and 5.

In case of *p*-NO₂, 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*-CH₃ 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.¹⁴ For solvolyses of *p*-nitrobenzenesulfonyl chloride in this research over the whole range of MeOH-MeNO₂ 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*_{aa} is the rate constant for attacking by two methanol molecules, *k*_{nn} refers to the one by nitromethane, *k*_{an} refers to methanol as nucleophile and *k*_{na} 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

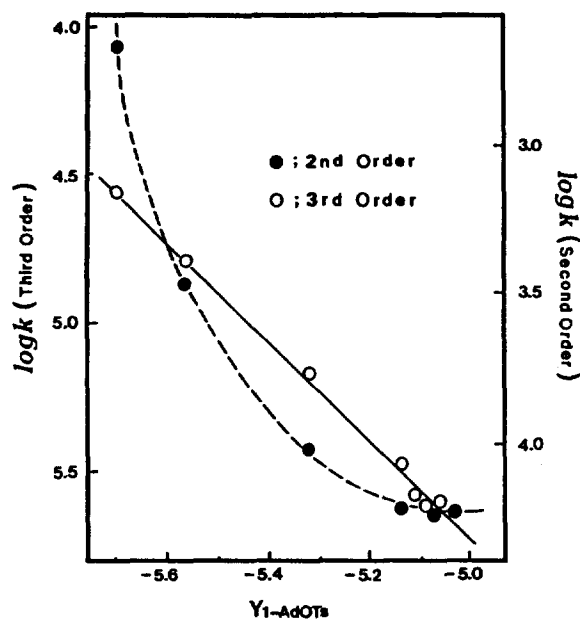


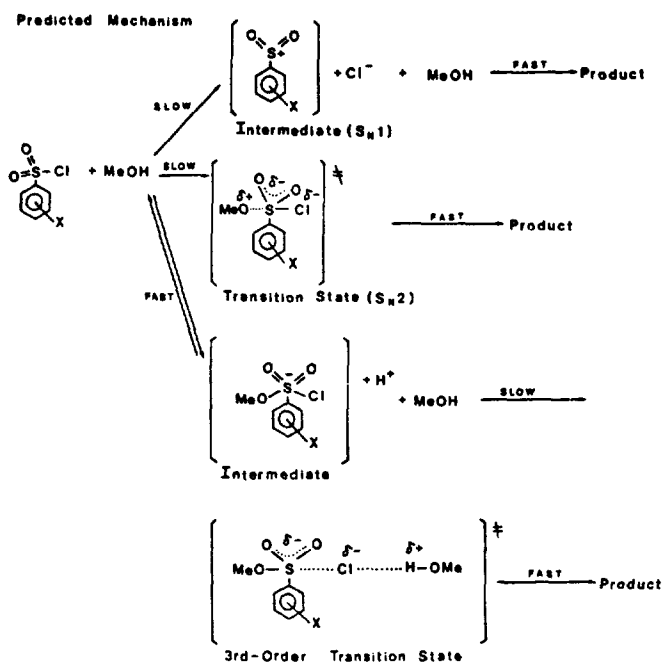
Figure 5. Logarithms of calculated second-, and third-order rate constants for methanolysis of *p*-nitrobenzenesulfonyl chloride in MeOH-MeNO₂ binary solvent mixtures at 45°C vs. Bentley-Schleyer's *Y* values. *Y*_{1-AdOTs} values were scaled by the same values of Figure 4.

evidence to react as nucleophile. Therefore the last two terms are neglected in Eq. (2). Third-order rate constants for methanol (*k*_{aa}) can also be calculated: e.g., *k*_{aa} for MeOH, *k*_{obs}/[MeOH]². The second-order rate constants for methanols can be calculated by a similar method for methanolysis of *p*-nitro benzenesulfonyl chloride in MeOH-MeNO₂ mixtures: e.g., *k*_a for MeOH, *k*_{obs}/[MeOH]. The solvolytic reactions in MeOH-PhNO₂ 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*_{1-AdOTs} values in Figure 5.

Very similar result for the third-order behavior has been reported for solvolysis of *p*-nitrobenzoyl chloride.¹³ 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.¹⁹ Hydrolyses of esters activated in the acyl group are well recognized to proceed *via* a third-order (B_A3) mechanism in which water molecule acts as a general base.²⁰

The predicted S_N1, S_N2 and 3rd-order methanolyses of *p*-substituted benzenesulfonyl chlorides are illustrated in Scheme 1. Electron-donating substituents stabilize S_N1-like intermediate and neutral or weak electron-withdrawing substituents stabilize S_N2-like transition state in Scheme 1. On the other side *p*-NO₂ substituent make possible that a trimolecular collision is pictured as two bimolecular collisions²¹ in rapid succession, then the intermediate²² reacts with the third molecule of MeOH as shown in the 3rd-order inter-



Scheme 1.

mediate in Scheme 1. This observation for *p*-NO₂ 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.²³ 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.²³ 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 halide²⁴ and addition of alcohols to acylium ions²⁵ 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.²⁶ (1). Rappoport and his coworkers²⁷ 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 difference²⁸ 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.²⁹ In that case a negative *m*-value appears because the selectivity does not change but *Y*-value

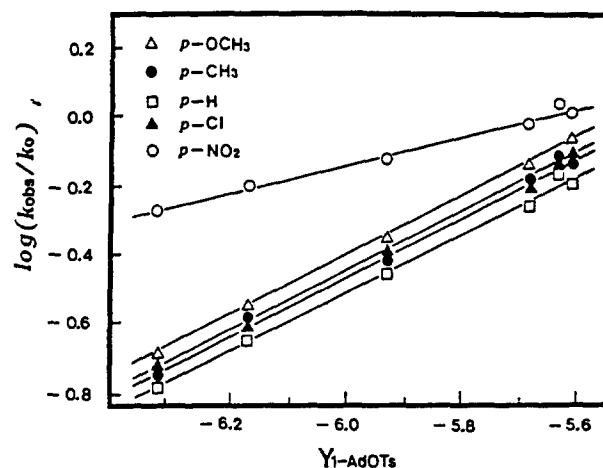


Figure 6. Logarithms of first-order rate constants for solvolyses of *p*-substituted benzenesulfonyl chlorides in MeOH-PhNO₂ binary solvent mixtures at 45°C vs. Bentley-Schleyer's *Y* values. *k*₀ values for *p*-H, *p*-CH₃, *p*-OCH₃, *p*-Cl and *p*-NO₂ in 80% EtOH-H₂O mixtures were quoted from the reference 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: -6.33, 40% MeOH: -6.18, 50% MeOH: -5.93, 70% MeOH: -5.58, 80% MeOH: -5.41, 90% MeOH: -5.64, in MeOH-PhNO₂ solvent mixtures at 45°C respectively.

decreases with increasing the solvent polarity or solvent dielectric constant.²⁹

In this study the isodielectric binary solvent mixture of MeOH-MeNO₂ shows a small difference of *Y*-values (ΔY) according to change the content from 30% (v/v) MeOH to 90% (v/v) MeOH, while a large difference of dielectric constant (ΔD)³⁰ according to change the content variation at the same range comparing with MeOH-PhNO₂ and MeOH-EG binary mixtures.

In MeOH-MeNO₂ mixture ΔY shows 0.71 (see Figure 4) and the difference of dielectric constant (ΔD) shows 6.00, while shows $\Delta Y=0.92$ (see Figure 6), $\Delta D=2.00$ in MeOH-PhNO₂ 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 negative¹⁴ in higher polar solvent and alcohol mixtures relatively because the observed pseudo-first-order rate constants in MeOH-MeNO₂ should depend only on the second power of [MeOH], and the presence of a fixed percentage by volume of [MeNO₂] should not influence the rate constant. The *m*-values based on Bentley-Schleyer's *Y*-values for *p*-H, *p*-CH₃, *p*-OCH₃ and *p*-Cl are shown as *S*_N1-*S*_N2 mixing mechanism likely to be shown *m* = 0.294 for *p*-H, *m* = 0.434 for *p*-CH₃, *m* = 0.523 for *p*-OCH₃ and *m* = 0.138 for *p*-Cl in Figure 4. While the *m*-value for *p*-NO₂ in Figure 5 shows -1.631: this could explain that the more reactive substrate (*p*-NO₂) is involved the third order kinetic behavior as methanol molecule attacks to the

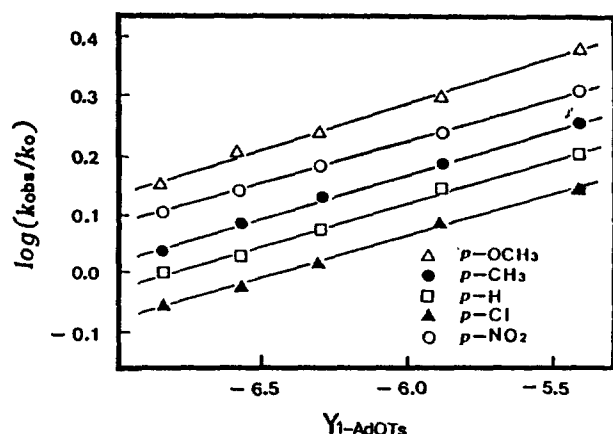


Figure 7. Logarithms of first-order rate constants for solvolyses of *p*-substituted benzenesulfonyl chlorides in MeOH-EG binary solvent mixtures at 45°C vs. Bentley-Schleyer's *Y* values.

k_0 values for *p*-H, *p*-CH₃, *p*-OCH₃, *p*-Cl and *p*-NO₂ in 80% EtOH-H₂O 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-PhNO₂ 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*-NO₂, $m=0.831$ for *p*-OCH₃, $m=0.742$ for *p*-Cl, $m=0.748$ for *p*-CH₃ 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 reactions³¹.

The m -values for the methanolyses in MeOH-EG solvent mixtures show as $m=0.145$ for *p*-OCH₃, $m=0.124$ for *p*-NO₂, $m=0.155$ for *p*-CH₃, $m=0.138$ 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

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Chromium oxide/zirconia catalysts were prepared by dry impregnation of powdered Zr(OH)₄ with (NH₄)₂CrO₄ 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 ZrO₂ 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 ZrO₂ stabilizes supported chromium oxide, chromium oxide was well dispersed on the surface of zirconia, and α-Cr₂O₃ was observed only at the calcination temperature above 1173 K. Upon the addition of only small amount of chromium oxide (1 wt% Cr) to ZrO₂, both the acidity and acid strength of catalyst increased remarkably, showing the presence of two kinds of acid sites on the surface of CrO_x/ZrO₂-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.¹⁻⁵ 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,⁶⁻⁸ and only a little work was studied for the ZrO₂ support.^{9,10}

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 ZrO₂ catalytic activity in the important reactions such as methanol and hydrocarbon syntheses from CO and H₂, from CO₂ and H₂^{11,12}, or from alcohol dehydration.^{13,14} 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.¹⁵⁻¹⁷ ZrO₂ 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-ZrO₂ and ZrO₂ modified with sulphate ion are very active for acid-catalyzed reactions, even at room temperature.¹⁸⁻²⁰ The high catalytic activities in the above reactions were attributed to the enhanced acidic properties