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## S<sub>N</sub>2 Transition State Variation in the Benzenesulfonyl Chloride Solvolysis\*

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For solvolyses of benzenesulfonylchlorides we determined transfer enthalpies of transition states, and solvent (TFE+EtOH) and substituent effects on rates. We have used the More O'Ferrall plots to show that transition states variation caused by solvent and substituent changes is consistent with an associative S<sub>N</sub>2 mechanism for the nucleophilic substitution reaction of benzenesulfonylchlorides.

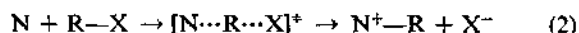
### Introduction

Benzenesulfonyl chloride is known to solvolyze by a borderline mechanism<sup>1</sup> as in the solvolysis of benzyl chloride<sup>2</sup>. There have been however much dispute over the mechanism as to whether it is an S<sub>N</sub>2 or an S<sub>A</sub>N process; Rogne and Lee favor an S<sub>N</sub>2<sup>3</sup> whereas Ciuffarin favors an S<sub>A</sub>N<sup>4</sup> mechanism. Extensive work on the transition state structure for benzyl solvolysis have been reported by Jencks<sup>5</sup> and Harris.<sup>6</sup> Jencks made a detailed analysis of the transition state variation as the medium is changed using the extended Grunwald-Winsten<sup>7</sup> equation (1),

$$\log(k/k_0) = mY + lN \quad (1)$$

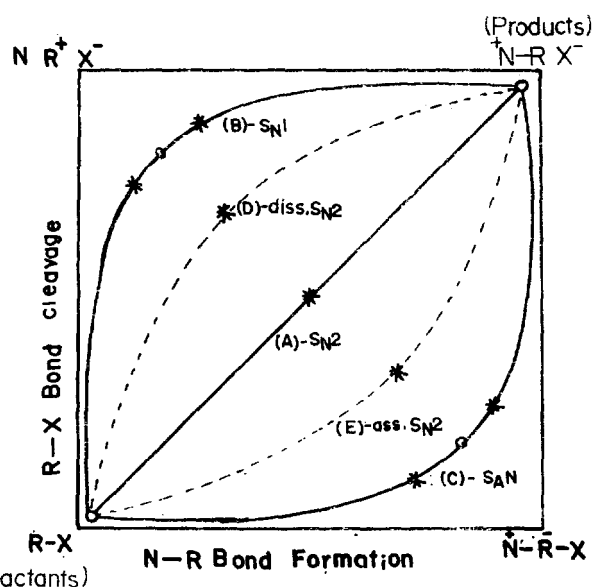
in which *Y* and *N* are the ionizing power and nucleophilicity of the medium, respectively, and *m* and *l* are reaction constants describing the susceptibility to *Y* and *N*.

Harris and coworkers<sup>6</sup>, on the other hand, made use of the More O'Ferrall type of plots<sup>8</sup> in predictions of the S<sub>N</sub>2 transition state variation for a series of substituted benzyl derivatives. Such plots were possible by application of Hammond's postulate<sup>9</sup> and Thornton's theory to direct displacement reactions, (2).



Hammond's postulate<sup>9</sup> can lead us to predictions of new transition state structures along ("parallel" to) the reaction coordinate, while predication of movement of transition state other than that along the reaction coordinate are possible using Thornton's rule.<sup>10</sup>

In the More O'Ferrall approach<sup>8</sup> the two dimensional potential energy diagram (Figure 1) includes two possible



**Figure 1.** A More O'Ferrall plot for a nucleophilic displacement reaction, where *N* is the nucleophile, *X* is the leaving group, and minima and maxima corresponding to the stable intermediates and transition state respectively are represented by circles and star marks. Path A, path B and path C represent the reaction coordinates for an S<sub>N</sub>2, S<sub>N</sub>1 and S<sub>A</sub>N reactions, respectively. Path D and path E represent the reaction coordinates for borderline mechanisms of a dissociative and associative S<sub>N</sub>2 reactions, respectively.

intermediates at two corners (upper left and lower right corners), making it possible to translate substituent and medium effects on intermediate stability into effects on the transition state structure even when the intermediates are not involved in the reaction. The More O'Ferrall plots can be used by applying following three rules:<sup>6</sup> (1) if species corresponding to a corner along the reaction coordinate are

\*This work is taken as Part 14 of the series "Nucleophilic Displacement at Sulfur Center".

stabilized, the transition state along the coordinate moves away from the stabilized corner; (2) if species corresponding to a corner perpendicular to the reaction coordinate are stabilized, the transition state moves toward the stabilized corner; (3) if the stabilization is both along and perpendicular to the reaction coordinate, the transition state movement is determined by the resultant of the vectors for the movements prescribed in rules 1 and 2. The energy surface at the saddle point is often simply assumed symmetrical, so that parallel and perpendicular shifts of the transition state is of equal magnitude for the same amount of corner stabilization.<sup>6</sup>

In this paper we varied both substituent and medium in the solvolysis of benzenesulfonyl chloride, and examined variations in transition state structure by applying the extended Grunwald-Winstein equation, (1), and More O'Ferrall plots. We have shown conclusively that the solvolysis of benzenesulfonyl chloride proceeds *via* an associative  $S_N2$  mechanism.<sup>11</sup>

### Experimental

Solvents and benzenesulfonyl chlorides used were G. R. grades obtained commercially. Water was purified by successive distillation. Rates were determined using conductivity method and pseudo-first order rate constants,  $k_1$ , were obtained by Guggenheim plots as described previously.<sup>12</sup> Average deviation of  $k_1$  was less than  $\pm 5\%$ . Heat of solution were determined using a Calorimeter supplied by Guild Corp.<sup>13</sup>

### Result and Discussion

*Transfer Enthalpies of Transition States.* When reaction medium is changed from a reference solvent to another, transfer enthalpy of the transition state,  $\delta H^\ddagger$ , is defined as,<sup>14</sup>

$$\delta H^\ddagger = \delta \Delta H^\ddagger + \delta \Delta H_s \quad (3)$$

where  $\delta \Delta H^\ddagger$  and  $\delta \Delta H_s$  are the differences in activation enthalpy and in heats of solution for the reactants between the two solvent systems compared. In order to examine the transition state behavior with the variation of solvent for the solvolysis of benzenesulfonyl chloride, we have measured heat of solution,  $\Delta H_s$ , of reactants in MeOH and 50% (v) MeOH-MeCN mixture. The transfer enthalpies of transition states calculated using eq.(3) are summarized in Table 1,

TABLE 1: Transfer Enthalpies for Solvolysis of *p*-CH<sub>3</sub>- and *p*-Cl-Benzenesulfonyl Chlorides from MeOH to 50% (v) MeOH-MeCN mixture\*

	Reaction	
	<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl +CH <sub>3</sub> OH	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl +CH <sub>3</sub> OH
$\delta \Delta H_s$	0.1	0.4
$\delta \Delta H^\ddagger$	-2.2	-1.7
$\delta H^\ddagger$	-2.1	-1.3

\*  $\Delta H_s$  values (average deviations;  $\pm 0.1$  kcal/mol) for CH<sub>3</sub>OH, *p*-CH<sub>3</sub>- and *p*-Cl-C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl in 50% (v) MeOH-MeCN were 0.2, 5.4 and 5.6 kcal/mol, respectively.

where we can clearly see the dominant influence of the transition state in determining activation enthalpies when reaction medium is varied. We can therefore conclude that effect of medium on rates of solvolysis of benzenesulfonyl chlorides is attributed to the effect of medium on the transition state structures.

*Substituent and Medium Effects.* Solvolysis rate constants at 35°C for *para*-substituted benzenesulfonyl chlorides in trifluoroethanol (TFE)-ethanol and ethanol-water mixtures are summarized in Tables 2 and 3. Table 2 shows that rates are faster with electron-withdrawing substituents, which is in contrast with the results for benzyl derivatives. However as TFE content of the TFE-EtOH mixture increases,  $k_1$ , value increases with electron-donating substituent (*p*-CH<sub>3</sub>) but decreases with electron-withdrawing substituent (*p*-NO<sub>2</sub>), (Table 3). This is understandable since TFE is much more ionizing but much less nucleophilic than ethanol, although

TABLE 2: Rate Constants ( $k_1 \times 10^4 \text{ sec}^{-1}$ ) for Solvolysis of *para*-Substituted Benzenesulfonyl Chlorides in EtOH-H<sub>2</sub>O Mixtures at 35°C

EtOH(v)%	Compound			
	<i>p</i> -CH <sub>3</sub>	<i>p</i> -H	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>
100	0.536	0.510	0.572	1.07
90	1.73	1.82	2.31	8.39
80	2.75	3.06	4.13	14.9
70	4.34	4.53	5.90	22.1
60	6.41	6.96	8.23	28.5

TABLE 3: Rate Constants ( $k_1 \times 10^5 \text{ sec}^{-1}$ ) for Solvolysis of *para*-Substituted Benzenesulfonyl Chlorides in EtOH-TFE mixtures at 35°C

EtOH(v)%	Compound			
	<i>p</i> -CH <sub>3</sub>	<i>p</i> -H	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>
100	5.36	5.10	5.72	10.7
80	7.82	6.85	6.85	10.5
70	8.22	7.11	6.41	9.84
60	9.72		5.76	7.61

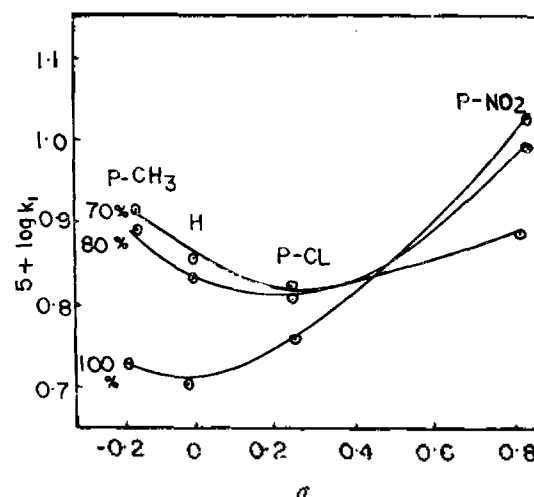
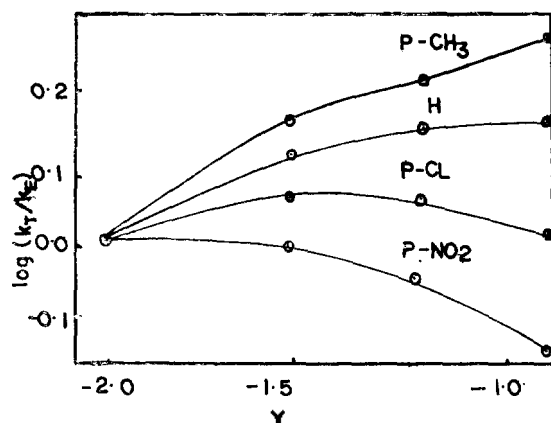


Figure 2. Hammett plot for the solvolysis of *para* substituted benzenesulfonyl chlorides in EtOH-TFE mixtures with various EtOH vol. percents at 35°C.

**TABLE 4:** Selectivity ( $k_E/k_T$ ) for Y-C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl Solvolyses in Trifluoroethanol-Ethanol Mixtures at 35° C.

TEF vol. %	$k_E/k_T$ for Y-C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl			
	Y			
	<i>p</i> -CH <sub>3</sub>	H	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>
0	1.00	1.00	1.00	1.00
20	0.68	0.75	0.87	1.02
30	0.66	0.72	0.89	1.09
40	0.61		0.99	1.41


**Figure 3.** Variation in  $\log(k_T/k_E)$  at 35° C with Y for solvolysis of several substituted benzenesulfonyl chlorides.

the two solvents have similar dielectric constants (26.14 and 24.32 at 25° C, respectively); this implies that for *p*-CH<sub>3</sub> compound bond breaking (increases with ionizing power of the medium) is important in the transition state while for *p*-NO<sub>2</sub> compound bond formation (increases with nucleophilicity of the medium) is important in the transition state.

The Hammett plots (Figure 2) are typically non-linear as obtained for the solvolysis of benzyl derivatives<sup>2</sup>. Ratio of rate constants in EtOH,  $k_E$ , to that in TFE-EtOH mixture,  $k_T$ , ( $k_E/k_T$ ) at 35° C are shown in Table 4, and  $\log(k_T/k_E)$  (note the rate ratio is reversed) versus Y plots are given in Figure 3. It is again clear from this figure that in the transition state bond-breaking is important for *p*-CH<sub>3</sub> while bond formation is important for *p*-NO<sub>2</sub>, since rate increases with the former whereas it decreases with the latter when the TFE content increases;  $k_T$  increases with the former while it decreases with the latter as Y increases. Eq. (1) is an extension of the original Grunwald-Winstein equation<sup>16</sup> (4), where the subscript *GW* on  $m$  is to differentiate the

$$\log(k/k_0) = m_{GW}Y \quad (4)$$

corresponding parameter in the extended form (1). Kaspi and Rappoport<sup>17</sup> have shown that  $N$  and  $Y$  are linearly related, (5).

$$N = aY + b \quad (5)$$

Substitution of (5) into (1) gives,

$$\log(k/k_0) = (m + al)Y + bl \quad (6)$$

**TABLE 5:** Calculated Values of the Grunwald-Winstein Parameters  $m$  and  $l$  for the Solvolysis of Sulfonyl Derivatives in EtOH+H<sub>2</sub>O and EtOH + TFE Mixtures

Sulfonyl derivative	$m_E$	$m_T$	$m$	$l$
<i>p</i> -CH <sub>3</sub>	0.34	0.24	0.35	0.13
H	0.31	0.18	0.32	0.17
<i>p</i> -Cl	0.29	-0.09	0.32	0.49
<i>p</i> -NO <sub>2</sub>	0.25	-0.22	0.29	0.60

Thus

$$m = m_{GW} - al \quad (7)$$

The nucleophilicity of the solvent,  $N$ , changes much more rapidly than ionizing power,  $Y$ , in TFE-EtOH mixtures compared with EtOH-H<sub>2</sub>O mixtures.

It has been shown that the proportionality constant  $a$  in eq. (5) is -0.85 and -0.071, respectively,<sup>7</sup> for these two solvent mixtures. Thus Kaspi and Rappoport's equation (7) for the two solvent mixtures gives

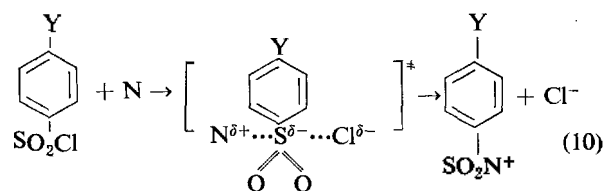
$$l = (m_E - m_T)/0.78 \quad (8)$$

and

$$m = m_E + 0.071l \quad (9)$$

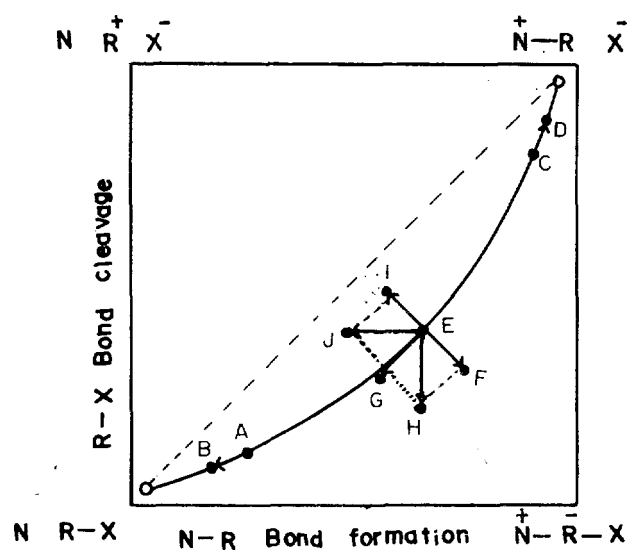
in which  $m_E$  and  $m_T$  are the observed  $m_{GW}$  values in the EtOH-H<sub>2</sub>O and TFE-EtOH mixtures, respectively. The  $m$  and  $l$  values obtained in this work according to eq. (8) and (9) are given in Table 5. The table shows slight decrease in  $m$  and relatively large increase in  $l$  with electron-withdrawing substituents. The values are not exact but they are sufficient to show the trend that there is a progressive increase in the amount of bond formation with the attacking solvent molecule in the transition state with electron-withdrawing substituents. This trend is in good accord with that observed for benzyl derivatives, showing the similarity of the mechanism involved in solvolysis of the two substrates.<sup>5</sup>

**Transition State Variation.** In the present work, we have examined variation of the transition state with changes in  $N$  and  $Y$  in equation (10):  $N = \text{EtOH}$  and TFE;  $Y = p\text{-CH}_3$ , *p*-Cl, H and *p*-NO<sub>2</sub>



Three possible pathways for a nucleophilic substitution are presented in Figure 1: path A ( $S_N2$ ), path B ( $S_N1$ ) and path C ( $S_A N$ ).

The  $S_N2$  reaction coordinate is that expected for a symmetrical process in which R-X bond cleavage and N-R bond formation proceed at the same rate. The transition state for this process will have equal R-X and N-R bonds lengths and no charge development on reaction center of R (in the present work, S). The  $S_A N$  reaction coordinate goes through an intermediate of addition compound



**Figure 4.** A More O'Ferrall plot for an  $S_N2$  process in which N-R bond formation precedes R-X bond cleavage. Energy maxima and minima are shown as closed and open circles, respectively.

( $N^+-R^-X$ ), whereas  $S_N1$  goes through an intermediate of fully broken bonds ( $NR^+X^-$ ).

Table 2 shows that electron-withdrawing substituents on ring accelerate the rates. This indicates that solvolyses of benzenesulfonyl chlorides proceed *via* transition states in which there is significant negative charge development on R, in this case sulfur, (eq. 10). Such transition states result when N-R bond formation proceeds faster than N-X bond cleavage. Therefore the reaction coordinate for this reaction will lie (as shown in Figure 4) somewhere between  $S_N2$  and  $S_{AN}$  processes illustrated in Figure 1. The transition state could lie anywhere, except very late, along this reaction coordinate, because a very late transition state would have essentially no negative charge development on R (in this case, S atom). There are three possibilities which may be considered in determining placements of transition state along the reaction coordinate: early (A), midway (E) and late (C).

Let us examine first the effect expected from increasing the electron withdrawing ability of Y in eq. (10), thus stabilizing addition intermediate,  $N^+-R^-X$ , and lowering the lower right corner of Figure 4. If the transition state lies at the midway point E, then the rule 2 presented earlier predicts movement of the transition state to point F. In this case the transition state will be tighter, involving more N-R formation, less R-X cleavage, more negative charge development on R, and more positive charge development on N. Such a change in transition state would result in higher  $\rho$  (more negative charge development on R),<sup>18</sup> lower  $m$  value<sup>19</sup> (less bond-breaking), less negative  $\Delta S^\ddagger$  value<sup>20</sup> (less charge on X), and increased selectivity (further N-R formation; in this case an increase in reactivity leads to an increase in selectivity)<sup>21</sup>.

For the early transition state at point A, the lower right corner is essentially parallel to the reaction coordinate in this region, and lowering the lower right corner will primarily

**TABLE 6:** Summary of Predictions for Different  $S_N2$  Transition State as a Function of Substitution of Electron-Withdrawing Substituents on R.

Parameter	Prediction			Observed
	Early (A)	Midway (B)	Late (C)	
$m$ (Degree of bond cleavage)	No change	Lower	Higher	Lower
$k_E/k_T$ (Degree of bond formation)	Lower	Higher	No change	Higher
$\rho$ (Negative charge on R)	Lower	Higher	Lower	Higher(21a)
$\Delta S^\ddagger$ (Charge on X)	Less negative	Less negative	More negative	Less negative*

\*There are conflicting reports but in protic solvent  $\Delta S^\ddagger$  values are less negative for electron-withdrawing substituents: O. Rogne, *J. Chem. Soc. (B)*, 1294 (1968) and Ref. 21b.

result in movement along the reaction coordinate to point B (rule 1). The overall effect will be to give a looser transition state, with less N-R formation, essentially unchanged R-X cleavage, and less charge development. The experimental manifestations will be a lower  $\rho$  value, an unchanged  $m$  value, a less negative  $\Delta S^\ddagger$  value and a lower selectivity, ( $k_E/k_T$ ). Finally for the late transition state at point C, the lower right corner lies again essentially along the reaction coordinate. Stabilizing the lower right corner will then result in movement to D (rule 1) to produce a transition state with more R-X cleavage, not much change in N-R formation, and greater dispersal of positive charge onto R. The experimental prediction will be a lower  $\rho$  value, a higher  $m$  value, a more negative  $\Delta S^\ddagger$  value, and an essentially unchanged selectivity, ( $k_E/k_T$ ).

The predictions for the three transition states are summarized in Table 6 together with the experimentally observed variations. As can be seen, the predictions for the midway transition state (point E) are in agreement with experiment.

Let us now examine More O'Ferrall predictions for the effect of medium variation on  $S_N2$  transition state structure. Increasing the stability of the departing anion,  $X^-$ , will result in lowering the top edge of the potential energy surface. The transition state at point E will move to point J, which is the resultant of vectors to points I and G (rule 3), caused by lowering the upper left and upper right corners, respectively.

An increase in TFE content of TFE-EtOH mixtures will result in the stabilization of the leaving group anion,  $X^-$ , and the transition state will move toward point J, accordingly.

The new transition state will have less N-R formation, essentially unchanged R-X cleavage, and less transfer of negative charge from N to R. The experimental results of this change should be a reduction in selectivity ( $k_E/k_T$ ) and an essentially constant  $m$ , which are what we find in Tables 4 and 5.

From the effect of medium variation, predictions regarding

the effects of nucleophile variation can also be made. In this case, an increase in nucleophilicity (by increasing EtOH content of TFE-EtOH mixtures) will result in lowering of the right edge of the diagram in Figure 4.

This will move the transition state at point E to H, which is the resultant of vectors to points F and G (rule 3). The new transition state will be characterized by a reduction in R-X cleavage, essentially no change in N-R formation, and a decrease in charge development on N and X.

Support for this prediction can be obtained from our previous studies on halide exchange kinetics,<sup>21a, 22</sup> where we have shown that as nucleophilicity increases from  $I^-$ ,  $Br^-$  to  $Cl^-$ , R-X (sulfur halogen bond in the study) bond cleavage decreases. Thus the solvent change from TFE to EtOH rich solvent in EtOH-TFE mixtures will shift the transition state from J to H.

The similar consideration leads to the transition state variation from I to F as substituent on the ring is varied from electron-donating ( $p-CH_3$ ) to electron-withdrawing ( $p-NO_2$ ) group.

The experimental manifestations in support of this prediction are relatively large  $m$  and small  $l$  value for  $p-CH_3$  compound and relatively small  $m$  and large  $l$  values for  $p-NO_2$  compound as shown in Table 5. The larger selectivity for  $p-NO_2$  compared with  $p-CH_3$  substituted compound is also in agreement with the prediction of the transition state movement.

Thus we may call the line IF in Figure 4, as a substituent line and JH as a medium line. Similar designations can also be made for a dissociative  $S_N2$  mechanism of benzyl derivatives.<sup>6</sup>

We are now in position to conclude with added confidence that the solvolyses (or the  $S_N$  reactions) of benzenesulfonyl chlorides proceed via an associative  $S_N2$  but not through an  $S_{AN}$  mechanism. Thus, the nucleophilic substitution reactions of benzyl and benzenesulfonyl systems are two important reactions that have been studied extensively owing to their typical but different sort of borderline mechanisms: the former reacts via a dissociative whereas the latter via an associative  $S_N2$  processes.

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