Application of the Extended Grunwald-Winstein Equation to the Solvolyses of 4-(Chlorosulfonyl)biphenyl

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ABSTRACT. Solvolyses with the reaction center being the sulfur of 4-(chlorosulfonyl)biphenyl ($C_6H_5C_6H_4SO_2Cl$, **1**) was studied under solvolytic conditions and the extended Grunwald-Winstein equation was applied. The thirty five kinds of solvents gave a reasonable extended Grunwald-Winstein plot with a correlation coefficient (R) of 0.940. The sensitivity values ($l = 0.60$ and $m = 0.47$) of **1** were smaller than those obtained for benzenesulfonyl chloride ($C_6H_5SO_2Cl$, **2**; $l = 1.10$ and $m = 0.61$) proposed to undergo dissociative S_N2 mechanism. These l and m values for the solvolyses of **1** can be considered to support a S_N2 pathway with some ionization reaction. The activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, were determined and they are also in line with values expected for a bimolecular reaction. The kinetic solvent isotope effect (KSIE) of 1.26 is also in accord with a bimolecular mechanism, probably assisted by general-base catalysis.

Key words: 4-(Chlorosulfonyl)biphenyl, Extended Grunwald-Winstein equation, S_N2 pathway, Kinetic solvent isotope effect

INTRODUCTION

Kinetic study is an important method for mechanistic investigation in organic chemistry. Value evidence such as activation parameters, the effect of solvent or substituents, kinetic solvent isotope effects, and evaluating of differences between related structures could provide valuable information about reaction mechanism.

The Grunwald-Winstein equation[1] (eq. 1) is a useful tool for correlating the solvent dependence of rates of solvolysis. The sensitivity (m) can be determined by studying the rates of solvolysis reaction of a standard substrate. However, Fainberg and Winstein[2] found that the plots for some substrates showed a scattering of plots in binary solvent systems due to the solvent nucleophilicity.

$$\log (k/k_o) = mY_x + c \qquad (1)$$

Nucleophilic solvent assistance can be defined as an electron donation from solvent to the developing positive dipole of a reacting C-X bond and an electron acceptance by the solvent of the leaving group (X), *Scheme* 1.
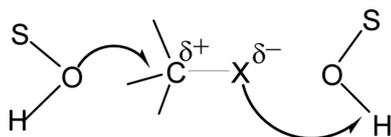
***Scheme* 1.** Nucleophilic solvent assistance and electron acceptance.

Kevill and coworks[3] established a solvent nucleophilicity scale based on the solvolysis of *S*-methyldibenzo- thiophenium ion. They introduced a new term governed by the solvent nucleophilicity. The extended Grunwald-Winstein equation can be expressed as equation 2. In equation 2, k and k_o represent the rate constants of the solvolyses of a substrate R_X in a given solvent and in the standard solvent (80% ethanol), respectively; l is the sensitivity of the solvolysis to changes in solvent nucleophilicity (N_T)[4]; m is the sensitivity of the solvolysis to changes in solvent ionizing power (Y_x, for a leaving group X)[5]; c is a constant (residual). A considerable recent effort

$$\log (k/k_o) = lN_T + mY_x + c \qquad (2)$$

has been to exerted study the extent to which the solvent nucleophilicity and the solvent ionizing power scales, developed for a substitution at carbon, can be applied to the substitution reactions taking place at a hetero atom.[4b]

The nucleophilic substitution reaction of benzenesulfonyl chloride ($C_6H_5SO_2Cl$) has been extensively studied.[6] In this reaction, chloride is displaced by a nucleophile at the sulfur atom (S) on sulfonyl group. Both S_N1[7] and S_N2[8] mechanism have been reported.

In limiting S_N2 mechanism, the nucleophile approaches by donation of its electron pair begins to form a bond to sulfur while the sulfur-leaving group bond is breaking (*Scheme* 1). The reaction is complected in a single step and both the nucleophile and the substrate take part in the transition state
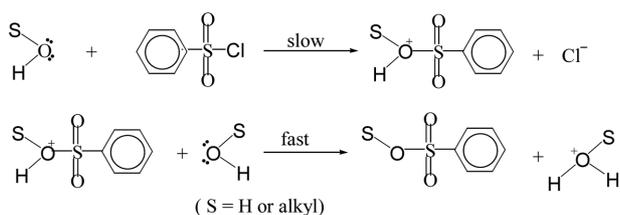
Scheme 2. A limiting S_N2 mechanism.
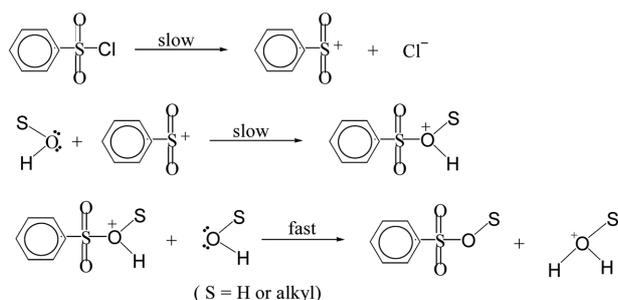
Scheme 3. A limiting S_N1 mechanism.

with the rate is second-order.[9]

On the other hand, the reaction could be a limiting S_N1 mechanism for the solvolysis of benzenesulfonyl chloride, *Scheme* 2, where substrate is ionized without a nucleophilic assistance.[9]

The purpose of this study is to gain a further understanding of the mechanism of sulfonyl transfer. We carried out kinetic investigations of the solvolyses of 4-(chlorosulfonyl)biphenyl ($C_6H_5C_6H_4SO_2Cl$, **1**) in a variety of pure and binary solvents at 55.0 °C, Eq. (3).

$$SOH + \text{[structure]} \longrightarrow \text{Products} \qquad (3)$$
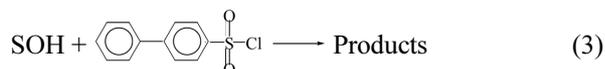
EXPERIMENTAL

Materials

Solvents were purified as previously described.[10] 4-(chlorosulfonyl)biphenyl (**1**, 98%) was used as received. The substrate did not react with the pure acetonitrile within the stock solution.

Kinetic Procedures

The electrical conductance of a solution depends strongly on the concentration and identity of any ion present. The following nucleophilic displacement reaction in solvent has been studied through conductance measurements. The fact that the reactants are neutral and the products are charged, so the conductance increase as the reaction proceeds. Pseudo-first-order rates (k_{obs}) were followed conductimetrically and the k_{obs} values were obtained by the curve fitting method.[10b] The rate (k) values reported are the averages of more than

triplicate runs and were reproducible to within ±3%.

RESULTS AND DISCUSSION

Solvolysis rate constants for 4-(chlorosulfonyl)biphenyl in ethanol, methanol, and binary mixtures of water with eth-

Table 1. Rate constants of solvolysis of 4-(chlorosulfonyl)biphenyl (**1**)[a] in a variety of pure and mixed solvents at 55.0 °C and the N_T and the Y_{Cl} values for the solvents

Solvent[b]	k (s^{-1})	N_T[c]	Y_{Cl}[d]
100%EtOH	4.17×10^{-4}	0.37	−2.52
90%EtOH	1.07×10^{-3}	0.16	−0.94
80%EtOH	1.77×10^{-3}	0.00	0.00
70%EtOH	2.44×10^{-3}	−0.20	0.78
60%EtOH	3.98×10^{-3}	−0.38	1.38
50%EtOH	5.70×10^{-3}	−0.58	2.02
40%EtOH	8.25×10^{-3}	−0.74	2.75
30%EtOH	1.51×10^{-2}	−0.93	3.53
20%EtOH	1.95×10^{-2}	−1.16	4.09
100%MeOH[e]	1.55×10^{-3}	0.17	−1.20
90%MeOH	3.57×10^{-3}	−0.01	−0.20
80%MeOH	5.48×10^{-3}	−0.06	0.67
70%MeOH	9.02×10^{-3}	−0.40	1.46
60%MeOH	1.26×10^{-2}	−0.54	2.07
50%MeOH	1.88×10^{-2}	−0.75	2.70
40%MeOH	2.57×10^{-2}	−0.87	3.25
30%MeOH	3.72×10^{-2}	−1.06	3.73
20%MeOH	4.79×10^{-2}	−1.23	4.10
90%Acetone	6.46×10^{-5}	−0.35	−2.39
80%Acetone	2.94×10^{-4}	−0.37	−0.83
70%Acetone	5.86×10^{-4}	−0.42	0.17
60%Acetone	1.28×10^{-3}	−0.52	1.00
50%Acetone	2.34×10^{-3}	−0.70	1.73
40%Acetone	4.33×10^{-3}	−0.83	2.46
30%Acetone	9.12×10^{-3}	−0.96	3.21
20%Acetone	1.38×10^{-2}	−1.11	3.77
97%TFE[f]	2.57×10^{-3}	−3.30	2.83
90%TFE	2.75×10^{-3}	−2.55	2.85
80%TFE	3.02×10^{-3}	−2.19	2.90
70%TFE	3.43×10^{-3}	−1.98	2.96
50%TFE	5.27×10^{-3}	−1.73	3.16
80T-20E[g]	5.50×10^{-4}	−1.76	1.89
60T-40E	4.11×10^{-4}	−0.94	0.63
40T-60E	3.69×10^{-4}	−0.34	−0.48
20T-80E	2.52×10^{-4}	0.08	−1.42

[a]Unless otherwise indicated, a 1.0 mol dm^{-3} solution of the substrate in the indicated solvent, containing 0.1% CH_3CN. [b]On a volume-volume content at 25.0 °C, other component is water. [c]Values from ref. 4. [d]Values from ref. 5. [e]Values of k [$=1.23\times10^{-3}$s^{-1}] in deuterated methanol (CH_3OD), corresponding to k_{CH3OH}/k_{CH3OD} value of 1.26. [f]Solvent prepared on a weight-weight basis at 25.0 °C, other component is water. [g]TFE-ethanol mixtures.

anol, methanol, acetone, and 2,2,2-trifluroethanol (TFE) and the binary mixtures of TFE with ethanol are summarized in *Table* 1 together with the N_T[4] and the Y_{Cl}[5] values.

Rates were observed to increase in binary aqueous mixture solvents with increasing water content (*Table* 1). These results insisted that the solvolysis of **1** is dominated by a bimolecular reaction mechanism.[11]

The dielectric constants of TFE ($\varepsilon = 26.7$) is about three times smaller than and H_2O ($\varepsilon = 80.0$). The dielectric constant of EtOH ($\varepsilon = 24.3$) is quite similar to that for TFE.[12] The solvent nucleophilicity exhibit a concerted increase in TFE-EtOH mixtures with increasing EtOH content. Although the ionizing power decreases of the similarity in dielectric constants, this effect is counter balanced and swamped out by the change in solvent nucleophilicity. These results showed normal behavior since ionizing power increases as water fraction increases.

The enthalpies ($\Delta H^{\neq}$) and the entropies ($\Delta S^{\neq}$) of activation for solvolysis of **1** are determined in four solvents in *Table* 2. Relatively small $\Delta H^{\neq}$ (12.9~15.2 kcal·mol^{-1}) and a large negative $\Delta S^{\neq}$ (−28.1~−36.0 cal·mol^{-1}·K^{-1}) values are consistent with the proposed bimolecular reactions.[10b]

The application of the extended Grunwald-Winstein equation (2) to the solvolyses of **1** led to only moderate correlation with dispersal for different binary mixtures. For all kinds of solvents, values obtained were 0.60 ± 0.09 for *l*, 0.47 ± 0.03 for *m*; the standard error of the estimate was 0.04; the correlation coefficient (R) value was 0.940 (*Fig*. 1). The sensitivity values, *l* and *m*, are reported in

Table 2. Rate constants and activation parameters for the solvolyses of 4-(chlorosulfonyl)biphenyl (**1**)[a] in pure and aqueous solvents at various temperatures

Solvent (%)	Temp. (°C)	10^4 k (s^{-1})	$\Delta H^{\neq}$ (kcal·mol^{-1})[b]	$-\Delta S^{\neq}$ (cal·mol^{-1}·K^{-1})[b]
100EtOH	35.0	1.09		
	45.0	2.09	12.9±0.2	36.0±0.8
	55.0	4.17		
80EtOH[c]	35.0	3.96		
	45.0	8.85	14.7±0.2	30.0±0.6
	55.0	17.7		
100MeOH	35.0	3.21		
	45.0	7.38	15.2±0.1	28.1±0.3
	55.0	15.5		
80Acetone	35.0	0.639		
	45.0	1.28	14.7±0.5	29.8±1.8
	55.0	2.94		

[a]A 1.0 mol dm^{-3} solution of the substrate in the indicated solvent, also containing 0.1% CH$_3$CN. [b]The activation parameters are accompanied by the standard error. [c]On a volume-volume content at 25.0 °C, other component is water.

Table 3. Extended Grunwald-Winstein equation correlations of the kinetics of solvolytic displacement of chloride

Substrate	n[a]	*l*[b]	*m*[b]	R[c]	l/m
1-AdOCOCl[d]	15	~0	0.47	0.985	~0
2-AdOCOCl[d]	19	~0	0.47	0.970	~0
C$_6$H$_5$CH$_2$OCOCl[e]	11	0.25	0.66	0.976	0.38
(CH$_3$)$_2$CHOCOCl[f]	20	0.28	0.52	0.979	0.54
C$_6$H$_5$CH$_2$SO$_2$Cl[g]	30	0.61	0.34	0.954	1.8
C$_6$H$_5$C$_6$H$_4$SO$_2$Cl[h]	35	0.60	0.47	0.940	1.3
9-Fluorenyl-OCOCl[i]	30	0.95	0.38	0.941	2.5
2,4-(CH$_3$O)$_2$C$_6$H$_3$SO$_2$Cl[f]	30	0.93	0.65	0.918	1.4
(CH$_3$)$_2$NSO$_2$Cl[f]	29	0.92	0.48	0.992	1.9
C$_6$H$_5$SO$_2$Cl[f]	37	1.10	0.61	0.959	1.8

[a]Number of solvents. [b]From eqn. (2). [c]Correlation coefficient. [d]Ref. 13. [e]Ref. 14. [f]Ref. 15. [g]Ref. 12c. [h]This work. [i]Ref. 16.
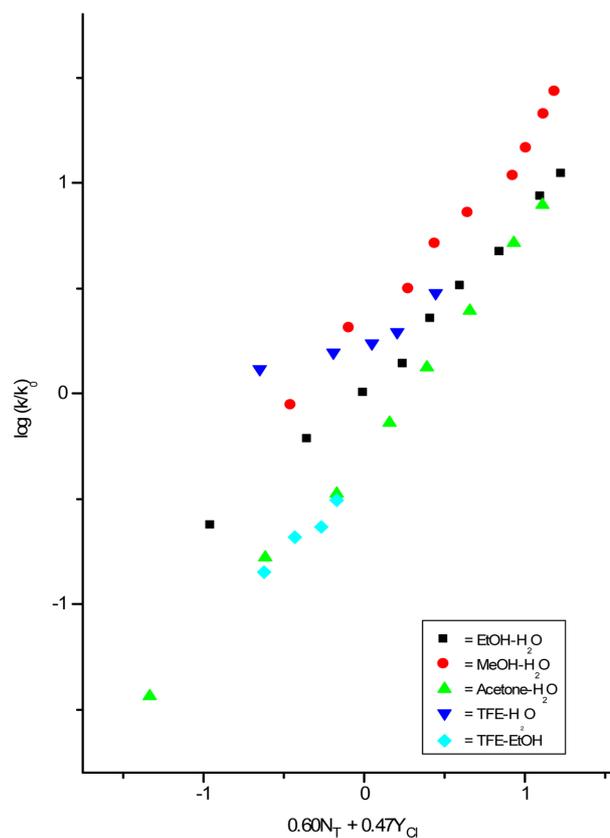
Figure 1. The plot of log (k/k$_0$) for solvolyses of 4-(chlorosulfonyl)biphenyl against $0.60N_T + 0.47Y_{Cl}$ at 55.0 °C.

Table 3, along with the corresponding parameters obtained in the analyses of previously studied substrates, to compare them with literature values for related substrates.

In general, for an S$_N$1 reaction without nucleophilic assistance, *l* value would be zero and *m* value would be close to unity while *l* value would be near unity and *m* value would

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be near 0.5 for a conventional S_N2 mechanism.[10] We compare l value (= 0.60) for the solvolysis of **1** with reported of the solvolysis of 9-fluorenyl chloroformate[16] ($l = 0.95$), dimethoxybenzenesulfonyl chloride[15] ($l = 0.93$), N,N-dimethyl sulfamoyl chloride[15] ($l = 0.92$), and benzenesulfonyl chloride[15] ($l = 1.10$) which are believed to be normal S_N2 mechanism in *Table* 3. The l value of 0.60 for the solvolyses of **1** is smaller than those for the solvolyses proceed through a S_N2 mechanism ($l = 0.92\sim1.10$). This l value (= 0.60) is similar to those previously reported for the solvolyses of benzylsulfonyl chloride (**2**)[16] proposed as S_N2 mechanism with some S_N1 reaction pathway. Therefore, this similarity suggest that the solvolysis of **1** proceed through an S_N2 mechanism involving an attack by solvent at sulfur atom in substrate with some character of S_N1 mechanism.

The l/m values from the extended Grunwald-Winstein equation could be a useful mechanistic criteria; l/m values of 1.4 to 2.5 for bimolecular mechanism; below 0.5 for an ionization pathway[10] (*Table* 3). For solvolysis of **1**, the l/m value was 1.3 which is within the similar range of the proposed bimolecular pathway.

A kinetic solvent isotope effect (k_{CH_3OH}/k_{CH_3OD}) of 1.26 ± 0.04 at 55.0 °C is observed. In general, for the S_N2 reaction, KSIEs are in the range of values from 1.58 to 2.31, whereas for an S_N1 reaction without nucleophilic assistance, KSIEs are close to unity.[16] The lower KSIE value (1.26) for **1** compare to the normal S_N2 mechanism suggests a dissociative S_N2 mechanism with some S_N1 reaction.

CONCLUSION

The solvolysis rate constants of 4-(chlorosulfonyl)biphenyl (**1**) in 35 different solvents are well correlated with the extended Grunwald-Winstein equation, using the N_T solvent nucleophilicity scale and the Y_{Cl} solvent ionizing power scale, with sensitivity values of 0.60 and 0.47 for l and m, respectively. The activation enthalpies ($\Delta H^{\neq}$) were 12.9 to 15.2 kcal·mol^{-1}, the activation entropies ($\Delta S^{\neq}$) were -28.1 to -36.0 cal·mol^{-1}·K^{-1}, and the kinetic solvent isotope effect was 1.26. Based on these results, we suggest that the solvolysis of **1** has a dissociative S_N2 mechanism with some character of S_N1 reaction.

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