Stoichiometric Solvation Effects. Solvolysis of Isopropylsulfonyl Chloride

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Solvolyses of isopropylsulfonyl chloride (IPSC) in water, D_2O, CH_3OD, and in aqueous binary mixtures of acetone, ethanol and methanol are investigated at 25, 35 and 45 °C. The Grunwald-Winstein plot of first-order rate constants for the solvolytic reaction of IPSC with Y_{Cl} (based on 2-adamantyl chloride) shows marked dispersions into three separate lines for three aqueous mixtures with a small slope (m < 0.30). The extended Grunwald-Winstein plots for the solvolysis of IPSC show better correlation. The kinetic solvent isotope effects determined in water and methanol are inconsistent with the proposed mechanism of the general base catalyzed and/or S_AN/S_N2 reaction mechanism for IPSC solvolyses based on mass law and stoichiometric solvation effect studies.

Key Words : Dispersions, Kinetic solvent isotope effects, Stoichiometric solvation effect

Introduction

Sulfonyl halides are known to solvolyze by a borderline mechanism[1] as in the solvolysis of benzyl chloride.[2] There have been, however, much dispute over the mechanism as to whether it is an S_N2[3] or an S_AN[4] process, the former being preferred lately. A particularly important system which contains tetracoordinate sulfur is RSO_2Cl; sulfonyl chlorides are important reagents in organic synthesis and substitution reactions of these compounds bridge inorganic and organic chemistry.

Solvent effects and linear free energy relationships (LFER) in the solvolyses of sulfonyl halides, especially substituted benzenesulfonyl chlorides, have received much experimental attention,[5] but little work has been done on the solvent stoichiometric effect on alcohol-water mixed solvents, especially for the solvolyses of aliphatic sulfonyl chlorides.

In order to examine the quantitative solvent effects, it is necessary to take into account the LFER and the stoichiometric solvation effects based on a third order reaction mechanism.

Dispersion into separate lines in the correlation of the specific rates of solvolysis of a substrate in various binary mixtures was documented[6-10] in early treatment using the Grunwald-Winstein eqn. (1).[11-14]

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

In eqn. (1), k is the rate constant for solvolysis in any solvent relative to 80% ethanol-water (k_o), m is the sensitivity of the substrate to ionizing power (Y) and c is a residual intercept term.

In general, dispersion effects in unimolecular solvolysis[15,16] make smaller contribution to the overall LFER than solvent

nucleophilicity effects in bimolecular solvolysis.[6,17] It was suggested that a second term which is governed by the sensitivity l to solvent nucleophilicity N_T (Kevill's N_T scale; the solvolysis of S-methyl dibenzothiophenium ion),[18-21] should be added to eqn. (1) for bimolecular solvolysis.[17] The resulting eqn. (2) is often referred to as the extended Grunwald-Winstein equation.[17]

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

For solvolyses in alcohol-water mixtures, interpretations based on a third order reaction mechanism are more complex, but significant new information is available because two products are formed. Thus there are four possible third order rate constants in the solvolysis reaction, k_{aa}, k_{aw}, k_{wa}, and k_{ww}.[10,22-25]

In this study, we determined the pseudo first order rate constants for solvolyses of isopropylsulfonyl chloride (IPSC) in alcohol-water mixtures to discuss the reaction mechanism using l/m, third order rate constants, kinetic solvent isotope effects and activation parameters.

Results and Discussion

The rate constants for solvolyses of IPSC in methanol-water, ethanol-water, and acetone-water at 25 °C are summarized in Table 1. The Table 1 reveals that the rate increases in the order acetone-water < ethanol-water < methanol-water, and the rate increases slowly as the water content of the mixtures increases. This implies that the rate is slightly accelerated by the solvent with higher ionizing power, Y, suggesting that bond breaking in the transition state is of little importance. First-order rate constants for solvolysis of IPSC vary over only a thirteen-fold range in alcohol-water mixtures, whereas the observed first-order rate constants for benzyl chloride, p-methoxybenzoyl chloride and

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Table 1. Rate constants for solvolysis of isopropylsulfonyl chloride in aqueous alcohol and acetone binary solvent mixtures at 25 °C

v/v %	MeOH	EtOH	Acetone
	$k \times 10^5$		
100	0.142	0.0636	
90	0.396	0.191	
80	0.778	0.396	0.0915
70	1.04	0.495	0.166
60	1.42	0.717	0.329
50	2.01	1.12	0.539
40	2.69	1.57	0.899
30	2.97	2.49	1.56
20	3.12	2.95	2.27
10	3.24	3.20	2.82
H₂O	3.58	3.58	3.58

thenoyl chloride which are known to react *via* an S_N2 or S_N1 reaction mechanism varying over several thousand-fold range.[27] These results indicate that the rate determining step is not the bond breaking step, which was found in the reaction of S_N1 or S_N2 substrate, but the addition step in for the addition-elimination (S_AN) route where transition state is not sensitive to the solvent ionizing power. These results are very similar to those of solvolytic reactions of *p*-nitrobenzoyl chloride,[28] *p*-nitrobenzenesulfonyl chloride,[29] furoyl chloride,[27a] and phenyl chloroformates,[6] but they are different from the results of solvolytic reactions of benzyl chloride, *p*-methoxybenzoyl chloride and thenoyl chloride.[27a,c]

The Grunwald-Winstein plots (eqn. (1)) of the rates in Table 1 are presented in Figure 1 using the solvent ionizing power scale Y_{Cl} based on 1-adamantyl chloride.[30] The plots are curved upwardly with three separate lines. The slopes (*m*) for the range of relatively good linearity are very small
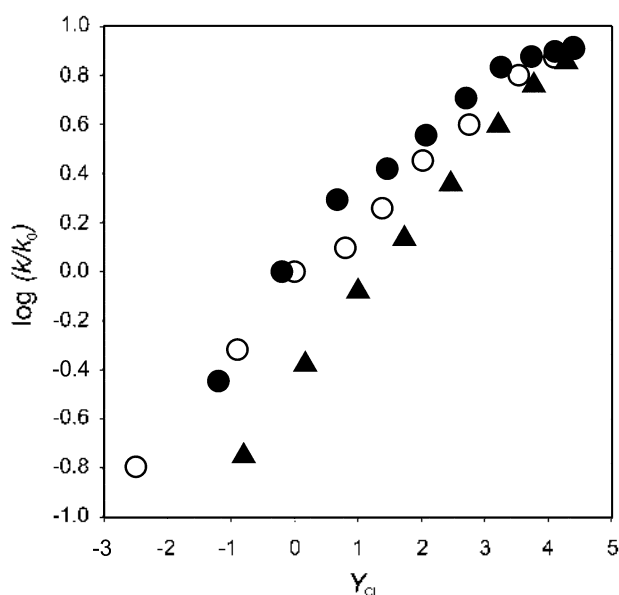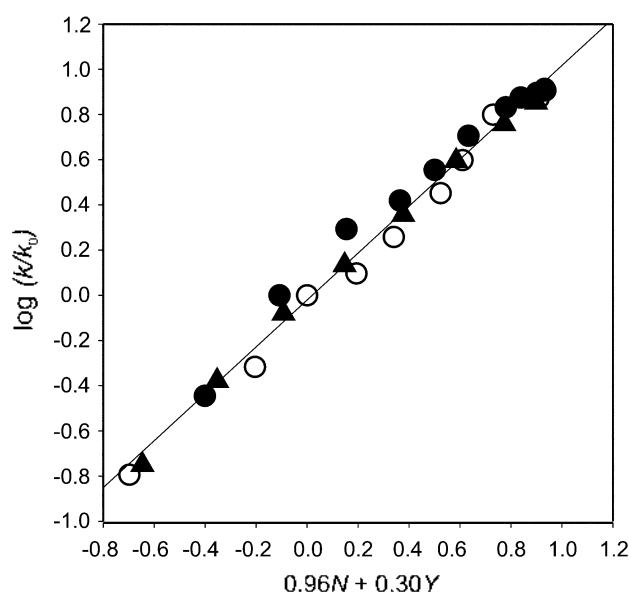
values of $m = 0.22$ ($r = 0.994$), $m = 0.24$ ($r = 0.996$), and $m = 0.30$ (r=0.998) for the ranges of 80M~20M, 90E~20E, and 80A~10A, respectively, implying that the solvolysis of IPSC in the binary mixtures proceeds by addition-elimination (S_AN) or associative S_N2 channel.

In order to examine the cause of dispersion phenomenon, we correlated the rate data in table using eqn. (2). The nucleophilicity parameter (N_T) have been shown to give a good correlation when an lN_T term are added to the original Grunwald-Winstein [eqn. (1)] correlations of solvolysis of IPSC. Therefore such phenomenon can be explained as dispersion effect caused by solvent nucleophilicity parameter. With use of the extended Grunwald-Winstein eqn. (2), the l and m values are 0.96 and 0.30 for the solvolysis of IPSC. The ratio of l and m value (l/m − 3.2) is very similar to those obtained for solvolysis of *p*-chlorobenzoyl chloride ($l/m = 3.2$),[31] *p*-nitrobenzoyl chloride($l/m = 3.3$), and phenyl chloroformate ($l/m = 2.9$),[31] which is independent evidence for the S_AN/S_N2 pathway with the addition step being rate determining.[32]

Logarithm of third-order rate constants for solvolysis of IPSC in acetone-water mixtures (log $k_{ww} = $ log $k_{obs}/[H_2O]^2$) *versus* Y_{Cl} plots are presented in Figure 2. The slope of Figure 2 shows a very small *m* value of near zero (0.075), impling that the k_{ww} terms of solvolysis of IPSC in the binary mixtures is relatively independent of medium. These results indicate that the reaction proceeds through the transition state which is not sensitive to the solvent ionizing power.[28a]

To examine the non-linear Grunwald-Winstein plot, it is necessary to take into account the stoichiometric solvation effects based on third order rate constants. For corresponding solvolyses in alcohol-water mixtures, interpretations based on a third order mechanism are more complex, but significant new information is available because two

Figure 1. Logarithms of first-order rate constants for solvolysis of isopropylsulfonyl chloride at 25 °C log(*k/k₀*) *vs.* Y_{Cl} (solvent codes: ● ; methanol. ○ ; ethanol. ▲ ; acetone).

Figure 2. Plot of log(*k/k₀*) for the solvolysis of isopropylsulfonyl chloride against (0.96*N* + 0.30*Y*) (solvent codes: ● ; methanol. ○ ; ethanol. ▲ ; acetone).

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products are formed. Thus there are four possible third order rate constants in the solvolysis reaction: (i) k_{aa} for a mechanism in which one molecule of alcohol acts as a nucleophile and second molecule acts as a general base; (ii) k_{aw} in which alcohol acts as a nucleophile and water acts as a general base; (iii) k_{wa} in which water acts as a nucleophile and alcohol acts as a general base; (iv) k_{ww} in which water acts as both nucleophile and general base.[22-25] Therefore, observed first-order rate constants in alcohol-water mixtures are given by equation (3).

$$k_{obs} = k_{aa}[\text{alcohol}]^2 + (k_{aw} + k_{wa})[\text{alcohol}][\text{water}] + k_{ww}[\text{water}]^2 \quad (3)$$

The k_{aa} term can be calculated from observed first order rate constants in pure alcohol $(k_{aa} = k_{obs}/[\text{ROH}]^2)$, and k_{ww} can be obtained from the observed first order rate constant in water $(k_{ww} = k_{obs}/[\text{H}_2\text{O}]^2)$.[23,25]

It is impossible to separate k_{aw} and k_{wa} from k_{obs}, but $(k_{aw} + k_{wa})$ can be estimated from $k_{obs}-(k_{ww}[\text{H}_2\text{O}]^2 - k_{aa}[\text{ROH}]^2)$.

The third-order rate constants are summarized in Table 2 for solvolysis of IPSC in aqueous methanol and ethanol. The Table 2 reveals that the k_{ww} terms increase with the increase in water content of the mixtures, but the k_{aa} terms decrease. The contributions of third-order terms $(k_{wa} - k_{aw})$ are larger than those of k_{ww} and k_{aa} terms showing a maximum near 40M and 30E in aqueous alcohol mixtures. Such a upward curve type rate behaviour was often observed[6a,c,10,29b] in the Grunwald-Winstein plot for solvolysis in alcohol mixtures, and this is due to exceptionally greater contribution of $(k_{wa} + k_{aw})$ term, *i.e.*, alcohol is acting as a nucleophile and water is acting as general base catalysis or *vice versa*.

Table 2. Separated third order rate constants for isopropylsulfonyl chloride solvolyses in aqueous methanol (M) and ethanol (E)

Alcohol	$/10^{-6}\,\text{s}^{-1}$		
% (v/v)	k_{aa}	$(k_{aw} + k_{wa})$	k_{ww}
90M	1.15	2.45	0.357
80M	0.910	5.44	1.43
70M	0.697	6.48	3.22
60M	0.512	7.97	5.72
50M	0.355	10.8	8.93
40M	0.227	**13.8**	12.9
30M	0.128	**12.1**	17.5
20M	0.0569	8.24	22.9
10M	0.0142	3.49	28.9
90E	0.514	1.04	0.357
80E	0.406	2.12	1.43
70E	0.311	1.42	3.22
60E	0.228	1.22	5.72
50E	0.159	2.11	8.93
40E	0.101	2.70	12.9
30E	0.0571	**7.34**	17.5
20E	0.0254	**6.57**	22.9
10E	0.00632	3.09	28.9
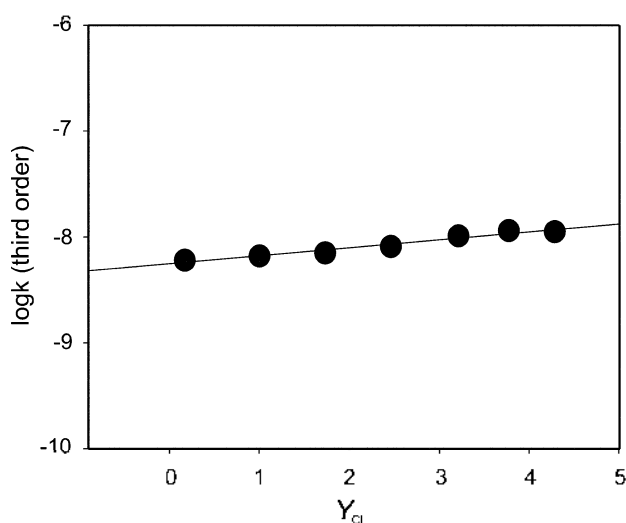
Figure 3. Logarithms of third-order rate constants $(k_{obs}/|\text{H}_2\text{O}|^2)$ for hydrolysis of isopropylsulfonyl chloride in acetone/water at 25 °C *vs.* Y_{Cl}.

We have reported *ab initio* calculation on the hydrolysis and solvolysis of MSC by water methanol, and methanol-water mixtures.[26] In that work, the solvent-catalyzed hydrolysis and methanolysis of MSC with a trigonal bipyramidal transition state in solvent was predicted.

These results are in good agreement with the general base catalysed S_AN/S_N2[33] reaction mechanism proceeding through a tight transition state, where bond formation is much more progressed than bond breaking in the transition state.

A plot of logarithm of rate constants *versus* logarithm of water concentration, which is often referred to as Kivinen plot,[34] is shown in Figure 3 for three aqueous mixtures. The slopes (n) of the linear parts are 1.03 $(r = 0.992)$ for 90M-30M, 1.12 $(r = 0.982)$ for 90E-30E, and 2.05 $(r = 0.991)$ for 80A-30A. Kivinen n values increase in the order methanol-water < ethanol-water < acetone-water. The larger n value of acetone-water mixture indicates that the ionizing power increases with increasing water contents, whereas there is no general base catalysis in acetone-water mixtures, because acetone acts as a cosolvent. These results are in good agreement with S_AN/S_N2[33] reaction mechanism with a slightly progressed bond breaking in the transition state as the water

Table 3. Additional rate constants (k/s^{-1}) for solvolyses of isopropylsulfonyl chloride in aqueous alcohol mixtures and the activation parameters at 25 °C

|	$T/°C$	k/s^{-1}	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
50% EtOH	35 °C	2.89×10^{-5}	17.0	-19.7
50% EtOH	45 °C	7.02×10^{-5}		
30% EtOH	35 °C	6.46×10^{-5}	15.8	-22.0
30% EtOH	45 °C	1.52×10^{-4}		
50% MeOH	35 °C	5.01×10^{-5}	17.0	-18.4
50% MeOH	45 °C	1.43×10^{-4}		
30% MeOH	35 °C	7.83×10^{-5}	16.2	-20.3
30% MeOH	45 °C	1.94×10^{-4}		

Table 4. Rate constants and kinetic solvent isotope effect of isopropylsulfonyl chloride in methanol and water at 25 °C and 35 °C

Temp.	Solvent	k_{SOH}	k_{SOD}	KSIE
		$k \times 10^5$		
25 °C	Methanol	0.142	0.0560	2.54
	Water	3.58	2.16	1.66
35 °C	Methanol	0.391	0.162	2.41
	Water	10.5	7.24	1.45

contents in acetone-water mixtures increased.

The activation parameters for solvolyses of IPSC in aqueous solvents at 25 °C are summarized in Table 3. The large negative $\Delta S^\neq$ and large positive $\Delta H^\neq$ values reveal that the solvolytic reaction proceeds *via* a typical bimolecular reaction.[35] The magnitude of $\Delta S^\neq$ and $\Delta H^\neq$ increase as the water content of the mixtures increases, suggesting that bond formation is very important and bond breaking is of little importance in the transition state.

The solvent isotope effects for reaction of IPSC in methanol and water at 25 °C and 35 °C are summarized in Table 4. The solvent isotope effects are relatively large,
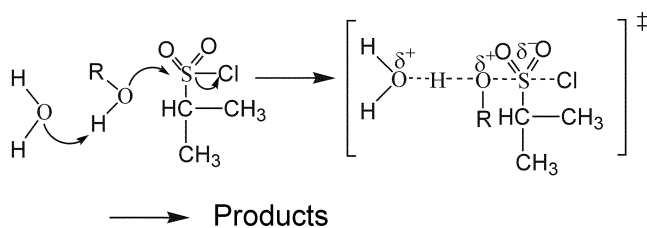
Scheme 1
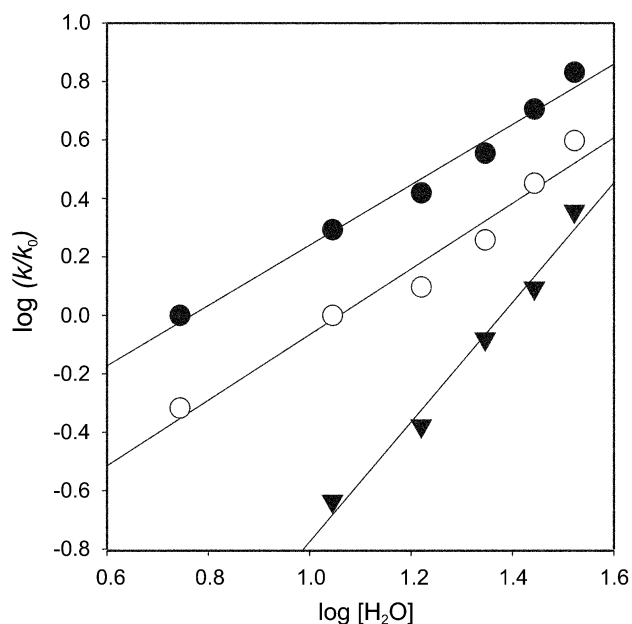
Figure 4. Correlation of logarithms of rate constants for solvolysis of isopropylsulfonyl chloride at 25 °C log(k/k_0) *vs.* log[H₂O] (solvent codes: ● : methanol. ○ : ethanol. ▲ : acetone).

which suggests that the OH bond breaks partially for nucleophilic methanol in the transition state.[6c] This is another piece of evidence in support of the $S_A N/S_N 2$[33] mechanism in methanol and in water, in which methanol and water molecules act as a general base catalyst, as shown in Scheme 1.

Experimental Section

IPSC was commercial grade (Wako Gr-grade >99%). Merk Gr-grade (<0.1% H₂O) acetone, ethanol and methanol were used without further purification. D₂O and CH₃OD were from Aldrich (99.9% D). Distilled water was redistilled with Buchi Fontavapor 210 and treated using ELGA UHQ PS to obtain specific conductivity of less than 1.0 × 10⁻⁶ mhos/cm. Rates were measured conductimetrically at least in duplicate as in previous work.[30]

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33. We used $S_A N/S_N 2$ terminology because nucleophilic substitution reaction with product like transition state is termed as an $S_A N$ or $S_N 2$, in view of addition of nucleophilic or leaving of leaving group. respectively.

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