Stoichiometric Solvation Effects. Solvolysis of Methanesulfonyl Chloride

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Solvolyses of methanesulfonyl chloride 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 methanesulfonyl chloride with Y_{Cl} (based on 2-adamantyl chloride) shows marked dispersions into three separate lines for three aqueous mixtures with a small m value ($m < 0.30$), and shows a rate maximum for aqueous alcoholic solvents. Stoichiometric third-order rate constants, k_{ww} and k_{aa} were calculated from the observed first-order rate constants and ($k_{aw} + k_{wa}$) was calculated from the k_{ww} and k_{aa} values. The kinetic solvent isotope effects determined in water and methanol are consistent with the proposed mechanism of the general base catalyzed and/or S_AN/S_N2 reaction mechanism for methanesulfonyl chloride solvolyses based on mass law and stoichiometric solvation effect studies.

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 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 stoichio- metric 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 stoichiometric solvation effects based on a third order reaction mechanism. 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}.[6,9]

In this study, we determined the pseudo first order rate constants for solvolyses of methanesulfonyl chloride (MSC) in alcohol-water mixtures, and estimated third order constants, k_{ww}, ($k_{wa} + k_{aw}$) and k_{aa}. We will discuss the mechanism of solvolytic reaction of MSC using third order rate constants and kinetic solvent isotope effects. We will also compare results of solvolytic reaction to that of molecular orbital calculation for the solvolytic reaction of MSC.[10]

Result and Discussion

The rate constants for solvolyses of MSC in methanol-water, ethanol-water, and acetone-water at 25, 35 and 45 °C are summarized in Table 1. Reference to the table reveals that the rate increases in the order acetone-water < ethanol-water < methanol-water at three temperature, and it shows maximum rate constants at near 40% methanol-water (40M) mixtures and at near 30% ethanol-water (30E) mixtures. The rate increases slowly as the water content of the mixtures increases; this means 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 MSC vary over only a fourteen-fold range in alcohol-water mixtures, whereas the observed first-order rate constants for benzyl chloride, para-methoxybenzoyl chloride and thenoyl chloride which are known to react *via* an S_N2 or S_N1 reaction mechanism varying over several thousand-fold range.[11]

These results indicate that the rate determining step is not the bond breaking step, which was found in the reaction of

Table 1. Solvolyses of methanesulfonyl chloride in aqueous alcohol and acetone binary solvent mixtures at 25, 35 and 45 °C

| v/v %	MeOH			EtOH			Acetone		
	$k \times 10^4$								
	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
100	0.267	0.737	1.74	0.149	0.281	0.642			
90	0.695	1.78	4.57	0.403	0.997	2.45			
80	1.14	2.92	7.08	0.673	1.68	3.92	0.199	0.406	0.847
70	1.66	4.04	9.73	0.922	2.29	5.53	0.418	1.00	1.77
60	2.09	5.31	12.5	1.23	3.06	7.29	0.630	1.44	3.34
50	2.33	6.20	14.7	1.61	3.88	9.34	1.05	2.25	5.36
40	2.65	6.74	16.8	2.03	4.87	12.0	1.31	3.33	7.94
30	2.52	6.99	17.7	2.33	5.88	14.5	1.76	4.36	10.6
20	2.36	6.84	17.4	2.37	6.21	15.8	2.16	5.29	13.0
10	2.23	6.32	16.8	2.18	6.12	16.4	2.17	5.79	15.1
0	2.04	5.96	16.4	2.04	5.96	16.4	2.04	5.96	16.4

S_N1 or S_N2 substrate, but the addition step for the reaction of S_AN substrate 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,[12] p-nitrobenzenesulfonyl chloride,[13] furoyl chloride,[11a] and phenyl chloroformates,[14] but they are different from the results of solvolytic reactions of benzoyl chloride, para-methoxybenzoyl chloride and thenoyl chloride.[11a,11c]

The Grunwald-Winstein plots (Eq. 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.[15] Investigation of of Figure 1 shows the plots for the three separate curves with maximum rate constants at near 40M and near 30E. The slopes (m) for the range of relatively good linearity are very small values of $m = 0.26$ ($r = 0.995$), $m = 0.28$ ($r = 0.996$), and $m = 0.27$ ($r = 0.990$) for the ranges of 100M ~60M, 100E ~50E, and 80A ~20A, respectively, implying that the solvolysis of MSC in the binary mixtures proceeds by addition-elimination (S_AN) or associative S_N2 channel.

$$\log(k\,k_o)_{RX} = mY_{Cl} \tag{1}$$

Logarithm of third-order rate constants for solvolysis of MSC 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 show a very small m value of near zero (-0.036), implying that the k_{ww} terms of solvolysis of MSC 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 again.[12a]

In order 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
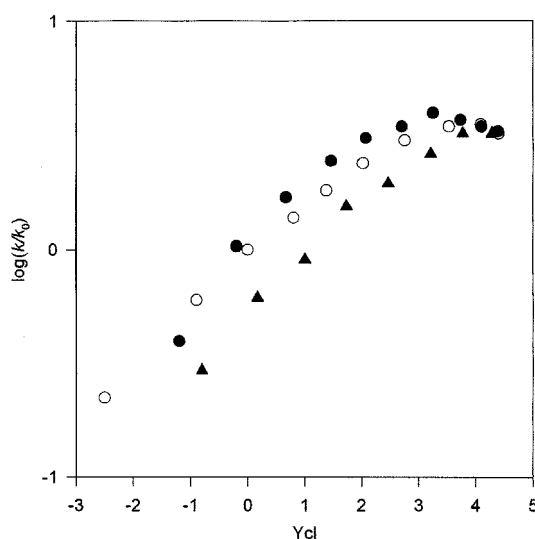
Figure 1. Logarithms of first-order rate constants for solvolyses of methanesulfonyl chloride at 25 °C $\log(k\,k_o)$ vs. Y_{Cl} (solvent codes: ●: methanol, ○: ethanol, ▲: acetone).
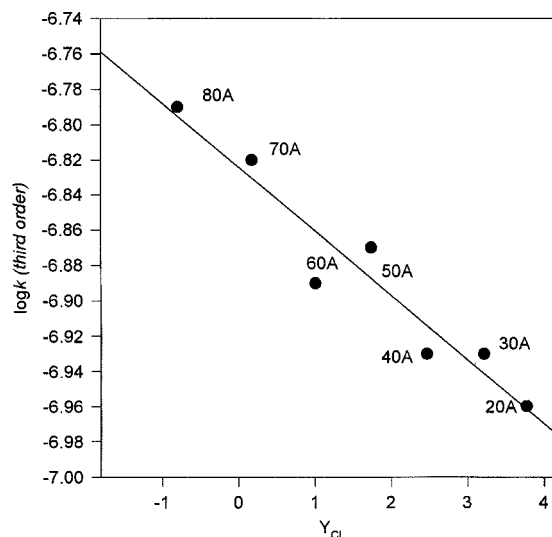
Figure 2. Logarithms of calculated third-order rate constants for hydrolysis of methanesulfonyl chloride in acetone/water at 25 °C vs. Y_{Cl} (slope $m = -0.036$, intercept = -6.824, correlation coefficient = 0.963).

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 nucleophile and alcohol acts as general base: (iv) k_{ww} in which water acts as both nucleophile and general base.[6-9] Therefore, observed first-order rate constants in alcohol-water mixtures are given by Eq. (2).
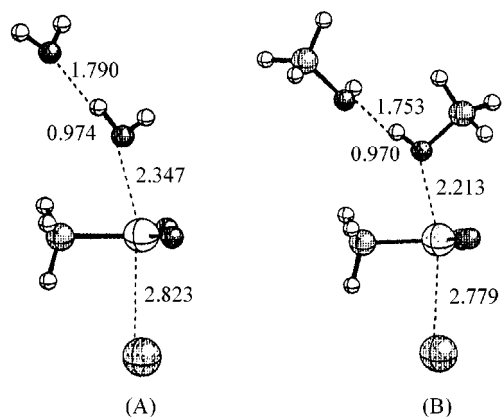
$$k_{obs} = k_{aa}[alcohol]^2 + (k_{aw} + k_{wa})[alcohol][water] + k_{ww}[water]^2 \tag{2}$$

The k_{aa} term can be calculated from observed first order rate constants in pure alcohol ($k_{aa} = k_{obs}/[ROH]^2$): similarly k_{ww} can be obtained from the observed first order rate constant in water ($k_{ww} = k_{obs}/[H_2O]^2$).[7,9]

It is impossible to separate k_{aw} and k_{wa} from k_{obs}, but (k_{aw} + k_{wa}) term can be calculated from $k_{obs}-(k_{ww}[H_2O]^2 + k_{aa}[ROH]^2)$.

The third-order rate constants are summarized in Table 2 for solvolysis of MSC in aqueous methanol and ethanol. Reference to Table 2 reveals that the k_{ww} terms increase with increasing of water content of the mixtures, but the k_{aa} terms decrease. The contributions of third-order terms, (k_{wa} + k_{aw}) are larger than k_{ww} and k_{aa} terms, and show a maximum at near 40M and 30E in aqueous alcohol mixtures. Such a maximum rate behaviour often observed[13b,14a,b,c] in the solvolysis of alcohol mixtures, and this 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*.

Recently, we reported *ab initio* calculation on the hydrolysis and solvolysis of MSC by water methanol, and methanol-water mixtures. In that work, the solvent-catalyzed hydroly-

Scheme 1

Figure 3. Correlation of logarithms of rate constants for solvolyses of methanesulfonyl chloride at 25 °C log(k/k_0) vs. log[H_2O] (40M-90M: slope = 0.77 (r = 0.994); 30E-90E: slope = 0.918 (r = 0.986); 30A-80A: slope = 1.8 (r = 0.997) (solvent codes: ● : methanol, ○ : ethanol, ▲ : acetone).
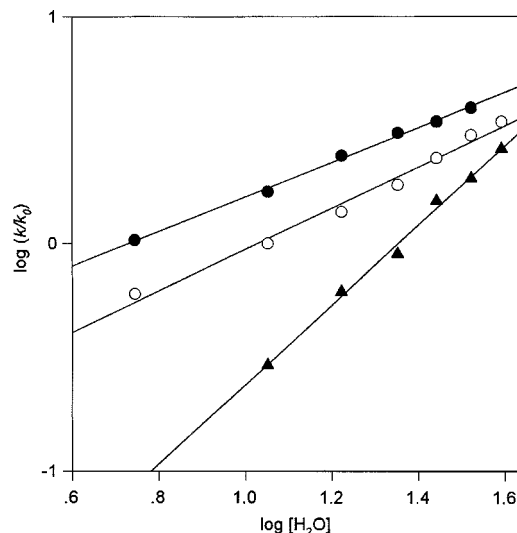
sis and methanolysis of MSC with a trigonal bipyramidal transition state in solvent was suggested (Scheme 1).[10]

These results are in good agreement with the general base catalysis S_AN/S_K2[17] 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,[18] is shown in Figure 3 for three aqueous mixtures. The slopes (n) of the linear parts were 0.77 (r = 0.997) for 90M ~40M, 0.91 (r = 0.986) for 90E ~30E, and 1.8 (r = 0.994) 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 cosolvent. The increase of high ionizing power (Y_{Cl}= 4.57) with water contents in acetone-water mixtures, it mean that bond breaking increases in the transition state. These results are in good agreement with S_AN/S_N2[17] reaction mechanism with a bond breaking slightly more progressed in the transition state which increases with increasing water contents in acetone-water mixtures.

The activation parameters for solvolyses of MSC in aqueous solvents at 25 °C are summarized in Table 3. The large negative $\Delta S^{\neq}$ and large positive $\Delta H^{\neq}$ reveals that the solvolytic reaction proceeds *via* a typical bimolecular reaction.[19] 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 variation of activation

Table 2. Separated rate constants for methanesulfonyl chloride solvolysis in aqueous methanol (M) and ethanol (E)

Alcohol	$/10^{-5} s^{-1}$		
% (v/v)	k_{aa}	$k_{aw} + k_{wa}$	k_{ww}
90M	2.16	6.05	0.204
80M	1.71	10.2	0.817
70M	1.31	14.8	1.84
60M	0.962	19.9	3.27
50M	0.668	24.9	5.10
40M	0.428	26.5	7.36
30M	0.240	25.5	10.1
20M	0.107	21.6	13.1
10M	0.0267	17.0	16.5
90E	1.21	2.62	0.204
80E	0.953	4.96	0.817
70E	0.729	6.65	1.84
60E	0.536	8.49	3.27
50E	0.372	10.6	5.11
40E	0.238	12.7	7.36
30E	0.134	13.2	10.0
20E	0.0596	10.5	13.1
10E	0.0148	5.29	16.5

Table 3. Actiation parameters of the methanesulfonyl chloride in aqueous alcohol and acetone binary solvent mixtures at 25 °C

v/v%	MeOH		EtOH		Acetone	
	$\Delta H^{\neq}$	$-\Delta S^{\neq}$ (e.u.)	$\Delta H^{\neq}$	$-\Delta S^{\neq}$ (e.u.)	$\Delta H^{\neq}$	$-\Delta S^{\neq}$ (e.u.)
100	17.1	22	13.1	37		
90	17.1	20	16.4	24		
80	16.6	21	16.0	24	13.0	36
70	16.1	22	16.3	22	13.0	35
60	16.3	21	16.2	22	15.1	27
50	16.8	19	16.0	22	14.7	27
40	16.8	19	16.1	21	16.4	21
30	17.8	15	16.6	19	16.3	21
20	18.2	14	17.3	17	16.3	21
10	18.4	13	18.4	14	17.7	16
0[H2O]	19.0	12				

Table 4. Kinetic solvent isotope effect of methansulfonyl chloride at 25 °C and 35 °C

Temp.		k_{SOH}	k_{SOD}	KSIE
25 °C	methanol	2.67×10^{-5}	1.67×10^{-5}	1.62
	water	2.04×10^{-4}	1.13×10^{-4}	1.81
35 °C	methanol	7.36×10^{-5}	4.87×10^{-5}	1.51
	water	5.96×10^{-4}	3.89×10^{-4}	1.53

parameters with the change of component of mixed solvents indicates that bond formation is important in the transition state, but bond breaking is negligible at the transition state.

The solvent isotope effects for reaction of MSC in methanol and water at 25 °C and 35 °C are summarized in Table 4. The solvent isotope effects are relatively large, which decreases a little at elevated temperature suggesting that the OH bond breaks partially for nucleophilic methanol in the transition state.[14c] This is another piece of evidence in support of the S_AN/S_N2[17] mechanism in methanol and in water, in which methanol and water molecules act as a general base catalyst, as shown in Scheme 1.

Experiment Section

Methanesulfonyl chloride were commercial grade (Wako Gr-grade > 99%). Merk Gr-grade (< 0.1% H_2O) acetone, ethanol and methanol were used without further purification. D_2O and CH_3OD 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.[15] Activation parameters were determined using Arrehenius equation and Eyring equation.

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17. We used S_AN/S_N2 terminology because nucleophilic substitution reaction with product like transition state is termed as an S_AN or S_N2, in view of addition of nucleophilic or leaving of leaving group, respectively.

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