Solvolyses for Phenyl Methanesulfonyl Chloride

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Application of the Extended Grunwald-Winstein Equation to the Solvolyses of Phenyl Methanesulfonyl Chloride in Aqueous Binary Mixtures

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This report shows the rates of solvolyses for phenyl methanesulfonyl chloride ($C_6H_5CH_2SO_2Cl$, **I**) in ethanol, methanol, and aqueous binary mixtures incorporating ethanol, methanol, acetone, 2,2,2-trifluroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) are reported. Three representative solvents, studies were made at several temperatures and activation parameters were determined. The thirty kinds of solvents gave a reasonably precise extended Grunwald-Winstein plot, coefficient (R) of 0.954. The sensitivity values ($l = 0.61$ and $m = 0.34$, $l/m = 1.8$) of phenyl methanesulfonyl chloride (**I**) were smaller than those obtained for benzenesulfonyl chloride ($C_6H_5SO_2Cl$, **II**; $l = 1.01$ and $m = 0.61$) and 2-propanesulfonyl chloride (($CH_3)_2CHSO_2Cl$, **III**; $l = 1.28$ and $m = 0.64$). As with the two previously studied solvolyses, an S_N2 pathway with somewhat ionization reaction is proposed for the solvolyses of **I**. 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 mechanism. The kinetic solvent isotope effect of 2.34 in CH_3OH/CH_3OD is in accord with a bimolecular mechanism, probably assisted by general-base catalysis.

Key Words : Solvolyses for phenyl methanesulfonyl chloride, Extended grunwald-winstein equation, S_N2 pathway, Kinetic solvent isotope effect

Introduction

Sulfonyl chlorides are important reagents in organic chemistry for activating alcohol groups,[1] and their substitution reactions bridge inorganic and organic chemistry.[2] The nucleophilic substitution of sulfonyl halide is an extensively studied of class of reaction in organic chemistry.[3]

Nucleophilic substitution reactions of benzyl halides (eq. 1) have been extensively studied.[4] In this reaction, halides (Z) are displaced by a nucleophile (Nu) at the benzylic (Ca)

$$\text{(1)}$$
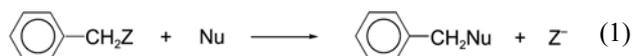
carbon. On the other hand, nucleophilic substitution reactions of benzenesulfonyl halides (eq. 2) have also attracted much interest;[3] in this case the displacement of halides (Z)

$$\text{(2)}$$

occurs at the sulfur atom on sulfonyl group (S). There are similarities and differences in the mechanisms of these two nucleophilic reactions. The two reactions are notable examples of the S_N2 reaction with a borderline mechanism exhibiting U-shaped nonlinear Hammett plots,[3d,e,4b] with an uncharged neutral nucleophile (Nu), the former reaction (eq. 1) proceeds by a dissociative S_N2 mechanism in which the bond breaking is relatively more advanced than the bond formation,[4c] while the latter reaction (eq. 2) proceeds by an associative S_N2 mechanism with its bond formation being more extensive than bond breaking in the transition state (TS).[3f]

To gain further understanding of the mechanism of sulfonyl transfer, we carried out a kinetic investigation of the solvolysis of phenyl methanesulfonyl chloride ($C_6H_5CH_2SO_2Cl$, **I**) in a variety of pure and binary solvents at 35.0 °C, eq. (3).

$$\text{(3)}$$
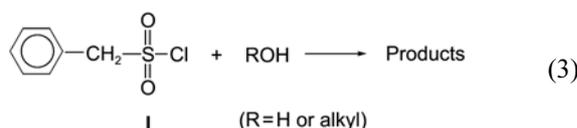
In addition to the application of the extended Grunwald-Winstein equation[5] to the rate constants, the influence of the temperature on the rate constant (for three solvents) allows enthalpies and entropies of activation to be calculated. Measurements in deuterated methanol (CH_3OD) also allow the determination of the kinetic clarifying the sulfonyl transfer mechanism, to compare the reactivities among benzenesulfonyl chloride ($C_6H_5SO_2Cl$, **II**) and 2-propanesulfonyl chloride (($CH_3)_2CHSO_2Cl$, **III**).
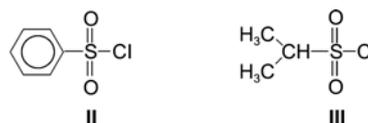
Results and Discussion

The rate constants of solvolysis of **I** have been determined in the thirty kinds of solvents at 35.0 °C. The solvents consisted of ethanol, methanol, and binary mixtures of water with ethanol, methanol, acetone, 2,2,2-trifluoroethanol (TFE)

Table 1. Rate constants of solvolysis of phenyl methanesulfonyl chloride ($C_6H_5CH_2SO_2Cl$, **I**)[a] in a variety of pure and mixed solvents at 35.0 °C and the N_T and the Y_{Cl} values for the solvents

Solvent[b]	$10^4 k^c (s^{-1})$	N_T[d]	Y_{Cl}[e]
100%EtOH	0.276 ± 0.002	0.37	−2.52
90%EtOH	1.22 ± 0.03	0.16	−0.94
80%EtOH	1.58 ± 0.02	0.0	0.0
70%EtOH	2.45 ± 0.03	−0.20	0.78
60%EtOH	2.55 ± 0.02	−0.38	1.38
50%EtOH	3.93 ± 0.04	−0.58	2.02
40%EtOH	6.32 ± 0.05	−0.74	2.75
20%EtOH	8.97 ± 0.07	−1.16	4.09
100%MeOH[f]	0.708 ± 0.005	0.17	−1.20
90%MeOH	1.67 ± 0.04	−0.01	−0.20
80%MeOH	2.88 ± 0.02	−0.06	0.67
70%MeOH	3.65 ± 0.03	−0.40	1.46
50%MeOH	6.75 ± 0.07	−0.75	2.70
40%MeOH	9.35 ± 0.08	−0.87	3.25
20%MeOH	11.5 ± 0.3	−1.23	4.10
90%Acetone	0.302 ± 0.003	−0.35	−2.39
80%Acetone	0.751 ± 0.004	−0.37	−0.83
70%Acetone	1.37 ± 0.03	−0.42	0.17
60%Acetone	1.84 ± 0.04	−0.52	1.00
50%Acetone	3.02 ± 0.03	−0.70	1.73
40%Acetone	4.68 ± 0.05	−0.83	2.46
30%Acetone	6.50 ± 0.04	−0.96	3.21
20%Acetone	8.13 ± 0.07	−1.11	3.77
90%TFE[g]	0.295 ± 0.003	−2.55	2.85
80%TFE	0.380 ± 0.003	−2.19	2.90
70%TFE	0.501 ± 0.004	−1.98	2.96
50%TFE	1.66 ± 0.03	−1.73	3.16
90%HFIP[g]	0.447 ± 0.004	−3.84	4.31
70%HFIP	0.708 ± 0.006	−2.94	3.83
50%HFIP	1.23 ± 0.03	−2.49	3.80

[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]With associated standard deviations. [d]Values from ref. 23b. [e]Values from ref. 7,18a. [f]Values of k [= 3.03(± 0.04) × $10^{-5}s^{-1}$] in deuterated methanol (CH_3OD), corresponding to k_{CH_3OH}/k_{CH_3OD} value of 2.34 ± 0.03 (with associated standard error).[32] [g]Solvent prepared on a weight-weight basis at 25.0 °C, other component is water.

and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). The same rate constants are presented in Table 1, together with the solvent nucleophilicity N_T[6] and the solvent ionizing power Y_{Cl}[7] values.

For three solvents, their rate constants of solvolysis were measured at three additional temperatures, and these values are reported in Table 2. The enthalpies and entropies of activation for each solvolysis calculated using all four values, they are also presented in Table 2.

Benzenesulfonyl chloride (**II**) is known to solvolyze by a borderline mechanism[8] as in the solvolysis of benzyl chloride.[9] There has been, however, much dispute over the mechanism as to whether it is an S_N2 or an S_AN process; Rogne and Lee favor an S_N2[3e,10] whereas Ciuffarin favors an S_AN[3g] mechanism. Also, the mechanism of solvolysis of 2-

Table 2. Rate constants and activation parameters for the solvolyses of phenyl methanesulfonyl chloride ($C_6H_5CH_2SO_2Cl$, **I**)[a] in pure and aqueous solvents at various temperatures

Solvent (%)	Temp. (°C)	$10^4 k^b (s^{-1})$	$\Delta H^{\neq}$ (kcal·mol^{-1})[c]	$-\Delta S^{\neq}$ (cal·mol^{-1}·K^{-1})[c]
100EtOH	25.0	0.120 ± 0.002	16.4 ± 0.6	28.1 ± 2.0
	35.0	0.276 ± 0.003		
	45.0	0.635 ± 0.004		
	55.0	1.59 ± 0.04		
80EtOH[d]	25.0	0.658 ± 0.005	17.6 ± 0.4	21.2 ± 1.3
	35.0	1.58 ± 0.02		
	45.0	3.79 ± 0.04		
	55.0	9.20 ± 0.07		
100MeOH	25.0	0.308 ± 0.002	16.5 ± 0.4	27.1 ± 1.2
	35.0	0.708 ± 0.004		
	45.0	1.69 ± 0.03		
	55.0	3.91 ± 0.04		

[a]A 1.0 mol dm^{-3} solution of the substrate in the indicated solvent, also containing 0.1% CH_3CN. [b]Averages of three or more runs, with standard deviation. [c]The activation parameters are accompanied by the standard error. [d]On a volume-volume content at 25.0 °C, other component is water.
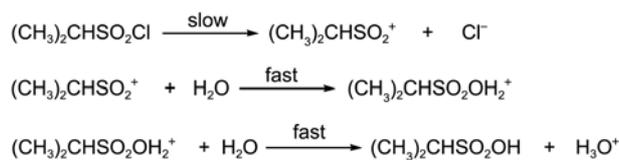
Scheme 1

propanesulfonyl chloride (**III**) has been described[11] as controversial, and, indeed, both S_N1[12-14] and S_N2[15,16] mechanism have been proposed.

The reaction proposed an S_N1 mechanism for the hydrolyses of **III** (Scheme 1). Ko and Robertson[14] accepted the bimolecular nature of the superimposed reaction with azide ion[15] but, reasonably, argued that the underlying hydrolysis could be S_N1 in character.

On the other hand, the reaction will be expected an S_N2 mechanism for the solvolyses of **III** (Scheme 2). Lee *et al.*[16] measured the rate constants for solvolysis of *N,N*-dimethylsulfamoyl chloride in aqueous solvent mixtures, were measured by Lee *et al.*, and then, these solvolysis were proposed as S_N2 in character, but with bond breaking
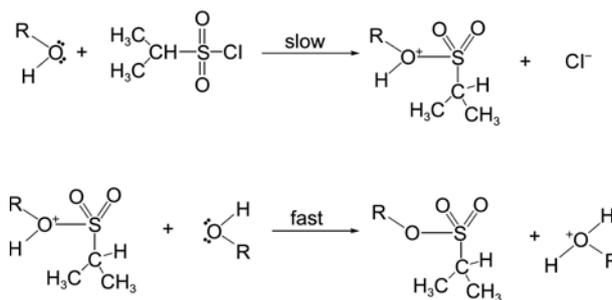
(R=H or alkyl)

Scheme 2

running ahead of bond making. An S_N2 reaction with ionic character was also proposed based upon the way salt effects the rate constant of solvolysis in 50% acetone.[17]

In the present study, we are concerned with the rate constants of the solvolyses represented in eq. (3). In most solvents, the reactions were reasonably fast, and therefore an apparatus allowing a rapid response to the changes in conductivity[18] was a convenient way of following the extent of reaction a function time. In order to promote a rapid dissolution in the solvent, the substrate was added to a concentrated stock solution of acetonitrile, such as to show that the reaction solution contained about 0.1% acetonitrile.

Table 1 shows that the rate is faster in a solvent of higher ionizing power, i.e., higher H_2O content.[19] This case could be caused by the dominant electrophilic solvation of the leaving group by water molecule. This provides further support for the theoretical conclusion that the reactivity follows after the leaving group ability.[20]

The extended Grunwald-Winstein equation[5-7,21] is used to correlate the rate constants of solvolysis reactions in terms of solvent ionizing power[7,18a] and solvent nucleophilicity.[6,21b] The multiple regression analysis for those reaction is attempted by extended Grunwald-Winstein equation (4) to decide. In equation (4), k and k_o, they represent the rate constants of solvolysis in a given solvent and in a standard solvent (80% ethanol), respectively; l represents the sensitivity to changes in solvent nucleophilicity (N_T); m represents the sensitivity to changes in the solvent ionizing power (Y_X, for a leaving group X); and c represents a constant (residual) term.

$$\log (k/k_o) = l\,N_T + m\,Y_X + c \qquad (4)$$

Initially applied to unimolecular and bimolecular solvolytic substitution reactions at a saturated carbon atom, the equation has also been applied, with considerable success to solvolytic substitution at a carbonyl carbon and at the sulfur of sulfonyl chlorides[5i,21] and sulfonic anhydrides.[5g,h]

The application of eq. (4) to the solvolyses of **I** also led to only moderately good correlations, with dispersal for different binary mixtures. For thirty kinds of solvents, values were obtained of 0.61 ± 0.04 for l, 0.34 ± 0.02 for m; the standard error of the estimate was 0.04, and the R value was 0.954. The sensitivity values, l and m, are reported in Table 3, along with the corresponding parameters obtained in the analyses of previously studied substrates, where they can be compared with literature values for related substrates.

The extended Grunwald-Winstein equation is a very useful indicator of the extent of nucleophilic participation by the solvent, as expected in the parameter, l, which, in turn, is directly related to whether a substituted reaction is a unimolecular or a bimolecular pathway. In general, for an ionization reaction without nucleophilic assistance, l will be zero and m close to unity. Therefore, the determinization of these values will be a valuable source of information concerning the structure of the transition state for these solvolyses.[23]

The l and m values for the solvolysis of **I** are smaller than

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

Substrate	n^a	l^b	m^b	R^c	l/m
$C_6H_5CH_2SO_2Cl$	30	0.61 ± 0.04	0.34 ± 0.02	0.954	1.8
i-PrOCOCl[28]	20	0.28 ± 0.05	0.52 ± 0.03	0.979	0.54
1-AdOCOCl[29]	15	~0	0.47 ± 0.03	0.985	~0
BzOCOCl[30]	11	0.25 ± 0.05	0.66 ± 0.06	0.976	0.38
2-AdOCOCl[29]	19	~0	0.47 ± 0.03	0.970	~0
$C_6H_5SO_2Cl$[5g]	37	1.10 ± 0.17	0.61 ± 0.04	0.959	1.8
$(CH_3SO_2)_2O$[5g]	41	0.95 ± 0.04	0.61 ± 0.03	0.973	1.6
CH_3SO_2Cl[5g]	43	1.20 ± 0.05	0.52 ± 0.03	0.969	2.2
$(CH_3)_2NSO_2Cl$[5g]	32	1.20 ± 0.04	0.72 ± 0.03	0.985	1.7
$(CH_3)_2CHSO_2Cl$[5g]	19	1.28 ± 0.05	0.64 ± 0.03	0.988	2.0
n-OctOCOF[29]	23	1.89 ± 0.13	0.79 ± 0.06	0.959	2.3
CH_3OCOCl[31]	19	1.59 ± 0.09	0.58 ± 0.05	0.977	2.7
p-$NO_2C_6H_4OCOCl$[29]	39	1.68 ± 0.06	0.46 ± 0.04	0.976	3.7
$((CH_3)_2N)_2POCl$[5b]	27	1.14 ± 0.05	0.63 ± 0.03	0.982	1.6
$(PhO)_2POCl$[5e]	29	1.31 ± 0.10	0.61 ± 0.04	0.960	2.1

[a]Number of solvents. [b]From eq. (4) and with associated standard error. [c]Multiple correlation coefficient.

those recently reported (Table 3) in expected for normal S_N2 mechanism or addition-elimination mechanism. The l ($= 0.61$) value is higher than ionization pathway ($l = 0$-0.28) but smaller than S_N2 or addition-elimination pathway ($l = 0.95$-1.89). Also the m ($= 0.34$) value is smaller than ionization mechanism ($m = 0.47$-0.66) in Table 3. They are believed to solvolyze by an S_N2 mechanism involving an attack by the solvent at a-carbon with some ionization pathway. Solvolyses of **I**, where bond making ($l = 0.61$) is more progressed than bond breaking ($m = 0.34$), is also indicated to proceed by a bimolecular pathway, reflecting nucleophilic assistance from a solvent nucleophile.[23] The enthalpies and entropies of activation, determined in three of the solvents (Table 2), are consistent with the proposed bimolecular pathway.[23b]

The l to m ratios have been also suggested as a useful mechanistic criteria. The l/m values from the extended Grunwald-Winstein equation could be classified into three classes of mechanism, l/m values of 1.2 to 2.0 for bimolecular mechanism, 2.3 to 3.5 for an addition-elimination pathway, and below 0.7 for an ionization pathway.[23] For solvolysis of **I**, the l/m value was 1.8 which is very similar to those of previous studies investigating the solvolyses of isopropylsulfonyl chloride,[23b] *N,N*-dimethyl sulfamoyl chloride,[22b] 2-phenyl-2-ketoethyl-tosylate,[24] dimethyl thiophosphorochloridate,[5c] and *N,N,N′,N′*-tetramethyl-diamidophosphorochloridate,[5b] and these similarities suggest the S_N2 mechanism.

The ratio of the constants ($k_{80\%EtOH}/k_{100\%EtOH}$) to be proposed bimolecular reactions are compared with reported results for the rate constants of solvolyses of methyl chloroformate ($k_{80\%EtOH}/k_{100\%EtOH} = 4.0$),[5a] ethyl chloroformate ($k_{80\%EtOH}/k_{100\%EtOH} = 3.2$),[5a] benzyl chloroformate ($k_{80\%EtOH}/k_{100\%EtOH} = 3.4$),[23f] *p*-methylbenzoyl chloride ($k_{80\%EtOH}/k_{100\%EtOH} = 5.3$),[25] *p*-nitrobenzyl chloroformate ($k_{80\%EtOH}/$

$k_{100\%EtOH} = 4.0$),[23f] These values ($k_{80\%EtOH}/k_{100\%EtOH}$) have less sensitivity due to the solvent ionizing power. For the solvolyses of **I**, the $k_{80\%EtOH}/k_{100\%EtOH}$ value of 5.7 is similar for five substrates studied earlier which are believed to be S_N2 in character with some ionic character was proposed. In contrast that it's the reaction of the ionization pathway, previous $k_{80\%EtOH}/k_{100\%EtOH}$ value has usually been larger with values of 95 for *t*-butyl chloride,[21] 92 for 1-adamantyl *p*-toluensulfonate[26] and 320 for 1-adamantyl chloride.[27]

In methanol and deuterated methanol (CH_3OD), a kinetic solvent isotope effect (k_{CH_3OH}/k_{CH_3OD}) of 2.34 ± 0.05 at 35.0 ℃ is observed. This result is in the range of values from 1.58 to 2.31 which have been observed for the corresponding methanolyses of a series of benzenesulfonyl chlorides at 25.0 ℃, in which the reactions are believed to be S_N2 in character.[23b]

In summary, the solvolyses of phenyl methanesulfonyl chloride (eq. 3) in ethanol, methanol, and aqueous binary mixture incorporating ethanol, methanol, acetone, TFE and HFIP at 35.0 ℃ proceed the dissociative S_N2 pathway with somewhat of the ionization pathway process. The result was drawn on the base; (1) smaller sensitivities ($l = 0.61$ and $m = 0.34$, $l/m = 1.8$) than those obtained for previously studied solvolyses; (2) small H with the large negative S values; (3) the small $k_{80\%EtOH}/k_{100\%EtOH}$ value (= 5.7) and (4) the large kinetic solvent isotope effects (= 2.34).

Experimental

Solvents were purified as previously described.[23] The substrate did not react with the pure acetonitrile within the stock solution. The phenyl methanesulfonyl chloride (Aldrich 98%) was used as received.

The kinetic experiments were carried out by allowing a conductivity cell containing 12.5 mL of solvent to equilibrate, with stirring, in a constant-temperature water bath. A 12 μL portion of a 1.0 mol dm^{-3} stock solution of **I** in acetonitrile was then added. The monitoring of increases in conductivity with time and the calculation of the rate constants (first-order coefficients) were conducted as previously reported.[23b] The multiple regression analyses were performed using commercially available packages.

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