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Substituent effects on the formation of sulfonyl cations from sulfonyl chlorides: comparisons of solvolysis kinetic data with calculated gas phase energies

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ABSTRACT: Suitable theoretical methods are validated for organosulfur compounds using experimental data for gas phase enthalpies of formation, proton affinities (PA) and heterolytic bond dissociation enthalpies (HBDEs). From enthalpies of chloride anion transfers from neutral chlorides to acyl, sulfonyl or cumyl cations in the gas phase, it is calculated that (i) similar aromatic substituent effects are expected for heterolyses of acyl, sulfonyl and cumyl chlorides; (ii) HBDEs for loss of chloride increase by over 70 kcal mol^{-1} from 4-$MeOC_6H_4COCl$ to SO_2Cl_2. Rate constants for solvolyses of 4-Z-substituted arenesulfonyl chlorides (Z = OMe, Me, H, Cl, NO_2) in 97% w/w 2,2,2-trifluoroethanol (TFE)–water are reported. Substituent effects are smaller than observed for identical solvolyses of acyl and cumyl chlorides, and are much smaller than those predicted theoretically for gas phase unimolecular heterolysis (explained by variable amounts of nucleophilic solvent assistance). Copyright © 2007 John Wiley & Sons, Ltd.

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KEYWORDS: enthalpies of formation; bond dissociation energies; substituent effects; kinetics; solvolysis; sulfonyl chlorides; sulfonyl cations

INTRODUCTION

Useful insights into the mechanisms of organic reactions involving ions can be achieved by comparing reactivity in solution with reactions in the gas phase, for example for acidity and basicity.[1] In 'highly non-solvating media' (e.g. sulphuric acid), the m^* values used to obtain equilibrium constants by the excess acidity method can be related to gas phase basicities.[1b] Rates of S_N1 solvolyses of bridgehead substrates[2a] and of bicyclic secondary substrates[2b] lead to cationic intermediates, and the energetics correlate well with MO theory and with intrinsic gas phase stabilities of carbocations, obtained by dissociation of protonated alcohols, bromides and chlorides.[2] Less sterically hindered secondary substrates react faster than expected from the correlations,[2b] and reactions in weakly nucleophilic media (e.g. fluorinated alcohols[3a]) more closely parallel gas phase reactivity. These[2b,3a] and similar results[3b,3c] allow insights into reactions in more nucleophilic aqueous media, providing evidence for rate enhancements due to nucleophilic solvation effects.[2b,3]

Substituent effects in benzylic substrates have been investigated extensively in solution, in the gas phase and theoretically,[4] but few comparisons have been made between reactions of aromatic acylium or sulfonylium cations ($ArCO^+$ and $ArSO_2^+$) in solution and in the gas phase, partly because relatively few reliable experimental data are available. Substituent effects on the rates of solvolyses of aromatic acyl chlorides (**1**) in 97% w/w 2,2,2-trifluoroethanol (TFE)–water were initially compared[5] with those for solvolyses of 4-substituted cumyl chlorides (**2**, the basis of σ^+ values[6]), and also with those observed experimentally in mass spectrometry from the appearance potentials of acylium ions from acetophenones. Recent calculations for acylium ions using Hartree–Fock (HF)[7] or density functional theory (DFT)[8] both show larger substituent effects, indicating that the mass spectrometric data include substantial systematic errors.

Previous studies of reactions of arenesulfonyl chlorides have focussed on electron rich substrates,[9] including solvolyses in TFE,[9a,9c] to try to increase the prospects for a cationic reaction pathway. We now report solvolysis rate

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constants for a range of 4-Z-substituted arenesulfonyl chlorides (**3**) in 97% w/w TFE, and compare the results with solvolyses of carboxylic acid (acyl) chlorides, and with theoretical calculations for cumyl, acylium and sulfonyl cations.

Sulfonyl chlorides are important reagents in organic chemistry, but relatively few thermochemical data are available for chlorides and other sulfonic acid derivatives.[10] A few experimental data are available for formation of sulfonyl cations by heterolytic bond dissociation[11] and by protonation of compounds containing S═O bonds;[12,13] these can be used to validate suitable theoretical methods. Calculations of substituent effects then gave enthalpies of formation of a range of sulfonyl chlorides, and also of heterolytic chloride bond dissociation enthalpies (HBDE).

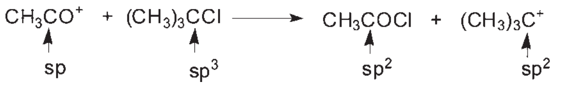
RESULTS

Selection of theoretical methods and procedures

Recent calculations on aromatic acylium ions using two completely different types of lower level calculation, HF/6-31G(d)[7,14] and B3LYP/6-31G(d),[8,14] gave satisfactory agreement for substituent effects. These same two low level methods were also selected for sulfonyl cations, but calculations were supplemented using a much higher level of theory (G3)[15] as a reference point to establish the energetics of reactions for sulfonyl compounds in the gas phase for a selected number of small molecules.

G3 theory has been shown to give reliable thermochemical data for many properties,[15] and a large data base of results is being assembled.[16] We also knew[14] that for chloride ion transfer between two dissimilar cations (*t*-butyl and acetyl, Scheme 1), G3 calculations[17] correctly predicted a thermoneutral reaction (consistent with similar solvolysis mechanisms),[18] whereas the discrepancies in HF/6-31G(d) and B3LYP/6-31G(d) calculations were 4 and 9 kcal mol^{-1}, respectively.[14]

The G3 calculations were compared with (HF/6-31G(d) and B3LYP/6-31G(d)) for hypothetical reactions involving small changes in bonding. Reactions involving the same number and types (i.e. between the same elements) of bonds on each side of the equation are referred to as isodesmic, and if there are also no changes in atom hybridisation the reactions are termed homodesmotic (see also Scheme 1).[19] It is expected (due to both fortuitous[20a] and planned cancellations of errors) that lower level calculations will give satisfactory results for isodesmic and especially for homodesmotic reactions.[19] In many cases, all three methods (G3, HF and B3LYP) agreed well, and results were then considered to be reliable. In cases where G3 was not applied (to limit the amount of computer time required), agreement between HF and B3LYP calculations was taken as a further indication that the lower level results are acceptable (this assumption was supported by experimental data in some cases – see below).



Scheme 1. Chloride ion transfer from the acetyl cation to *t*-butyl chloride; an isodesmic reaction, which is not homodesmotic because of changes in hybridisation at the central carbon atoms[19]

Tests of G3 theory for neutral compounds

Sufficient experimental data are available to show that the G3 calculations are reliable for enthalpies of several hypothetical reactions of neutral S^{VI} organosulfur compounds (Table 1); the largest difference between experiment and theory is only 2.6 kcal mol^{-1} (last entry), which involves substantial changes to four bonds. Similar hypothetical reactions, involving relatively small changes in bonding, were used to obtain two independent G3 calculated values for the enthalpy of formation (ΔH_f^0) of methanesulfonyl chloride (average value of -90.9 kcal mol^{-1}, Table 2), in agreement with the recently published value of -89.7 ± 1.2 kcal mol^{-1}.[10b]

Substituent effects on neutral compounds

The enthalpies of the hypothetical reactions (ΔH_R) shown in Eqn (1) (Table 3) provide a measure of substituent effects on neutral sulfonyl chlorides relative to methane sulfonyl chloride. G3 calculations of ΔH_f^0 for methanesulfonyl chloride (Table 2) 'anchored' the calculations;

Table 1. Validation of G3 calculations (gas phase) for enthalpies of reactions (ΔH_R, kcal mol^{-1}) at 298 K for organosulfur compounds (S^{IV} and S^{VI})

Reaction	ΔH_R (expt)[a]	ΔH_R (calc.)[b]
$SO_2 + 2CH_4 = (CH_3)_2SO + H_2O$	12.9	11.2
$(CH_3)_2SO + H_2O = (CH_3)_2SO_2 + H_2$	4.7	4.9
$SO_3 + 2CH_4 = (CH_3)_2SO_2 + H_2O$	−16.5	−18.6
$SO_2 + Cl_2 = SO_2Cl_2$	−13.9	−14.4
$SO_2Cl_2 + C_2H_6 = (CH_3)_2SO_2 + Cl_2$	15.7	15.1
$SO_2Cl_2 + 2C_2H_6 = (CH_3)_2SO_2 + 2CH_3Cl$	−4.3	−6.9

[a] Enthalpies of reactions (gas phase, 1 atm., 298 K) calculated from experimental data (Ref. 16 and Ref. 21) for enthalpies of formation of products – enthalpies of formation of reactants.

[b] Enthalpies of reactions (gas phase, 1 atm., 298 K) calculated from G3 enthalpy data (from Ref. 16).

Table 2. G3 calculations of enthalpies of reactions (ΔH_R (calc.), kcal mol^{-1}) at 298 K, leading to the enthalpy of formation ($\Delta H_f{}^0$) of methanesulfonyl chloride (gas)[a]

Reaction	ΔH_R (calc.)[b]	ΔH_f^0 (calc.)[c]
$(CH_3)_2SO_2 + Cl_2 = CH_3SO_2Cl + CH_3Cl$	−21.5	−90.6
$(CH_3)_2SO_2 + SO_2Cl_2 = 2CH_3SO_2Cl$	−8.3	−91.1

[a] An independent calculation from experimental data for the liquid and a calculated value of the enthalpy of vapourisation gave ΔH_f^0 of methanesulfonyl chloride (gas) = -89.7 ± 1.2 kcal mol^{-1} (Ref. 10b).

[b] Enthalpies of reactions at 298 K from calculated G3 enthalpy results (from Ref. 16, except for our value for CH_3SO_2Cl).

[c] Enthalpy of formation of methanesulfonyl chloride (kcal mol^{-1}) at 298 K calculated from ΔH_R (calc.) = enthalpies of formation of products − enthalpies of formation of reactants; experimental data for $(CH_3)_2SO_2$, Cl_2, CH_3Cl and SO_2Cl_2 are available from Ref. 16, so ΔH_f^0 for CH_3SO_2Cl can be calculated.

Table 3. Enthalpies of reaction (ΔH_R) from methyl transfer [Eqn (1), kcal mol^{-1}] for sulfonyl chlorides (YSO_2Cl), and enthalpies of formation (ΔH_f^0)

	ΔH_R at various levels of theory[a]			
Species	HF/6-31G(d)	B3LYP/6-31G(d)	G3[b]	ΔH_f^0(g)
HSO_2Cl	−15.3	−16.1	−16.1	−72.5[c]
CH_3SO_2Cl	0.0[d]	0.0[d]	0.0[d]	−90.9[e]
CH_2CHSO_2Cl	−2.6	−2.4	−3.0	−63.0[c]
$PhSO_2Cl$	−1.4	−1.0		−57[f]
$HOSO_2Cl$	+3.3	+3.1	+6.9	−125.6[c]
NH_2SO_2Cl	−3.0	−3.7	+1.1	−77.3[c]
CH_3NHSO_2Cl	−1.5	−2.7		−73[f]
$(CH_3)_2NSO_2Cl$	−7.1			
$ClSO_2Cl$	−18.2	−10.6	−6.5	−84.7[c,g]

[a] Calculated from data for sulfonyl chlorides in Tables S1 and S2, with additional theoretical data for YCH_3 from Ref. 16; HF and B3LYP calculations refer to 0 K, and are not corrected for small changes in zero point energies.

[b] Enthalpy at 298 K.

[c] Based on G3 calculations of ΔH_R, using experimental data for the other terms in Eqn (1).

[d] By definition.

[e] Calculated from hypothetical reactions (Table 2).

[f] Approximate value based on lower level calculations of ΔH_R and experimental data for the other terms in Eqn (1).

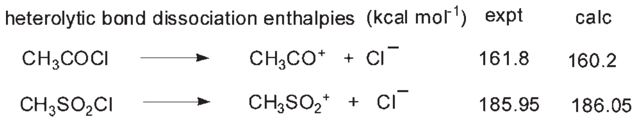
[g] In good agreement with the experimental value of −84.8 (Ref. 16).

combining ΔH_R with the experimental values of ΔH_f^0 for C_2H_6 and YCH_3 gives calculated values of ΔH_f^0 for other sulfonyl chlorides (Table 3).

$$YSO_2Cl + C_2H_6 = YCH_3 + CH_3SO_2Cl \qquad (1)$$

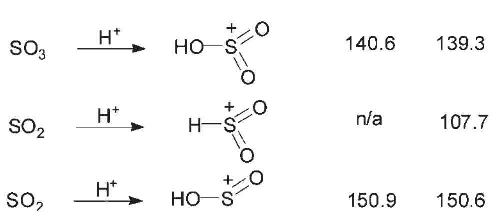
Tests of G3 theory for sulfonylium cations

G3 calculations of bond dissociation enthalpies (Scheme 2)[11] and proton affinities (PA, Scheme 3)[12,13] agree well with experimental data and show the reliability of results for sulfonyl cations, even for reactions in which there are changes in the total number of bonds.



Scheme 2. HBDEs[11] (with additional G3 calculations for acetyl[17])

For dissociation of CH_3SO_2Cl, the quoted value[11b] of 186 kcal mol^{-1} is in good agreement with the published value[11c] of ΔH_f^0 for $CH_3SO_2^+$ of 150.6 kcal mol^{-1} and data for CH_3SO_2Cl (Table 2) and for the chloride anion, which leads to values of 186–187 kcal mol^{-1} for the HBDE. The value quoted in compilations[12,16] for the PA of SO_2 (160.7 kcal mol^{-1}at 298 K) is incorrect, as it is not consistent with data from the original source.[13a] The value quoted for the PA of SO_3[12] is consistent with the



Scheme 3. PA[12] (the change in enthalpy, with a positive sign for energy released on protonation in the gas phase); the experimental value for SO_2 refers to 600 K;[13a] calculated values refer to 298 K, but the temperature dependence is small

Table 4. Enthalpies (kcal mol^{-1}) for transfer of chloride ion to the methanesulfonyl cation from sulfonyl chlorides [YSO_2Cl, Eqn (2)], and HBDEs, $D_{S\text{-}Cl}$, calculated for three levels of theory[a]

Species	HF/6-31G(d)	B3LYP/6-31G(d)	G3[b]	$D_{S\text{-}Cl}$[c]
HSO_2Cl	19.1	18.1	17.9	203.9
CH_3SO_2Cl	0.0[d]	0.0[d]	0.0[d]	186.0[e]
CH_2CHSO_2Cl	−11.3	−9.7	−7.3	178.7
$PhSO_2Cl$	−22.9[f]	−23.2[f]		163[g]
$HOSO_2Cl$	18.2	16.4	16.9	202.9
NH_2SO_2Cl	−12.7	−11.6	−10.2	175.8
CH_3NHSO_2Cl	−21.3	−20.6		165[h]
$(CH_3)_2NSO_2Cl$	−31.9			154[h]
$ClSO_2Cl$	23.4	21.9	19.6	205.6

[a] Calculated from data in Table S1; HF and B3LYP calculations refer to 0 K, and are not corrected for small changes in zero point energies.
[b] Enthalpy at 298 K.
[c] HBDE at 298 K, giving a sulfonyl cation and a chloride anion, based on G3 calculations for the enthalpy of chloride transfer.
[d] By definition.
[e] Anchor point, based on the average of the experimental value of 185.95 (Ref. 11b) and the value of 186.05, calculated by G3 (see Scheme 2).
[f] Data for $PhSO_2Cl$ from Table S2.
[g] Less reliable results, based on HF and B3LYP calculations; the experimental value is 159.7 (Ref. 11b).
[h] Approximate value based on HF/6-31G(d) data.

observation that the PA of SO_3 is less than that of CO,[13b] and with other data.[13c]

Substituent effects on sulfonyl cations

Few, if any, reliable experimental data are available for the feasible (but experimentally difficult to investigate) chloride transfer reactions [Eqn (2)], used to assess the stabilities of sulfonyl cations relative to the methanesulfonyl cation (Table 4). Fortunately, experimental data are available for HBDE (Scheme 2), so best values of HBDE data for methanesulfonyl chloride were (in a similar procedure to Table 3) used as an 'anchor' to minimise differences between the various levels of theory. HBDEs for other acid chorides can then be calculated from the substituent effects (Table 4), based on isodesmic and some homodesmotic reactions (Eqn. 2); agreement between the three levels of theory (Table 4) is quite good (within 4 kcal mol^{-1}). Remarkably, HBDEs cover a range of 52 kcal mol^{-1} from 154 kcal mol^{-1} for Me_2NSO_2Cl to 205.6 kcal mol^{-1} for SO_2Cl_2.

$$YSO_2Cl + CH_3SO_2^+ = YSO_2^+ + CH_3SO_2Cl \qquad (2)$$

The reference substituent was switched from CH_3 to Ph to investigate the substituent effects for both aromatic sulfonyl and aroyl chlorides for homodesmotic reactions (Eqns 3 and 4); as expected from previous work,[7,8,14] HF and B3LYP calculations (Table 5) agree well.

$$\begin{aligned} &4\text{-}ZC_6H_4SO_2Cl + PhSO_2^+ \\ &\qquad = 4\text{-}ZC_6H_4SO_2^+ + PhSO_2Cl \qquad (3) \end{aligned}$$

$$\begin{aligned} &4\text{-}ZC_6H_4COCl + PhCO^+ \\ &\qquad = 4\text{-}ZC_6H_4\,CO^+ + PhCOCl \qquad (4) \end{aligned}$$

Enthalpies of chloride ion transfer between acylium and sulfonyl cations could be obtained from the differences in bond dissociation energies, obtained indirectly using data for methyl derivatives as 'anchors', and adding the calculated substituent effect based on a

Table 5. Enthalpies (kcal mol^{-1}) calculated for chloride ion transfer to $C_6H_5SO_2^+$ from $4\text{-}ZC_6H_4SO_2Cl$ (Eqn 3) and to $C_6H_5CO^+$ from $4\text{-}ZC_6H_4COCl$ [Eqn (4)]

	Sulfonyl chlorides		Aroyl chlorides	
Z	HF/6-31G(d)[a]	B3LYP/6-31G(d)[a]	HF/6-31G[b]	B3LYP/6-311G(d,p)[c]
H	0.0[d]	0.0[d]	0.0[d]	0.0[d]
Me	−4.4		−3.9	−4.5
MeO	−10.2	−11.1	−8.2	−9.5
Cl	3.2		4.2	2.1
NO_2	14.8	12.0	15.5	12.1

[a] Data from Table S2; the equation of a Hammett–Brown (Ref. 6) correlation of HF data is: enthalpy = $(16.1 \pm 1.0)\sigma_p^+ + (1.3 \pm 0.5)$ ($r = 0.994$, $n = 5$).
[b] Data from Ref. 7; the equation of a Hammett–Brown (Ref. 6) correlation is: enthalpy = $(15.5 \pm 1.6)\sigma_p^+ + (2.1 \pm 0.8)$ ($r = 0.984$, $n = 5$).
[c] Includes a correction for zero point energies; data from Ref. 8; the equation of a Hammett–Brown (Ref. 6) correlation is: enthalpy = $(14.0 \pm 0.7)\sigma_p^+ + (0.6 \pm 0.4)$ ($r = 0.997$, $n = 5$).
[d] By definition.

Table 6. Enthalpies for chloride ion transfer between acylium and sulfonyl cations (Eqns 5 and 6) at various levels of theory

Theory Acylium ion	Energy (kcal mol^{-1}) CH_3CO^+	 $PhCO^+$
HF/6-31G(d)	27.5[a]	20.0[b]
B3LYP/6-31G(d)	16.3[a]	10.9[b]
B3LYP/6-311G(d,p)	18.7[c]	12.7[d]
B3LYP/6-311 + G(3df,2p)[e]	21.6[c]	
G3 (enthalpy at 298 K)	25.9[f]	
(Experimental result)	24.2[g]	

[a] Data from Ref. 14 and Table S1.

[b] Data from Ref. 14 and Table S2, excluding small changes in zero point energy of <0.3 kcal mol^{-1}.

[c] The 'big' basis set from Ref. 22.

[d] Data from Ref. 8 and Table S2.

[e] Using HF/6-31G(d) optimised geometries; data from Table S3.

[f] Data from Ref. 17 and Table S1.

[g] Difference in HBDEs (Scheme 2).

homodesmotic reaction. Direct comparisons require isodesmic reactions which are not homodesmotic (e.g. Eqns 5 and 6); G3, HF and various basis sets for B3LYP calculations, illustrated in Table 6 for CH_3 [Eqn (5)] and Ph [Eqn (6)] substituents, now show significant differences depending on the level of theory. The results include calculations of energies using a large basis set (6-311 + G(3df,2p),[22] but at fixed HF/6-31G(d) geometries.

$$CH_3CO^+ + CH_3SO_2Cl = CH_3COCl + CH_3SO_2^+ \quad (5)$$

$$PhCO^+ + PhSO_2Cl = PhCOCl + PhSO_2^+ \quad (6)$$

Kinetic data for solvolyses

First order rate constants for solvolyses of 4-Z-substituted benzenesulfonyl chlorides are shown in Table 7 for solvolyses in 2,2,2-trifluoroethanol (TFE). Reactions were monitored by changes in conductivity and/or by HPLC. Because of the relatively long reaction times, data were obtained at 50 and 75 °C (Table 7), and extrapolated to 25 °C for comparisons with rate constants in 40% ethanol–water (Table 8).

DISCUSSION

Theoretical methods

HF/6-31G(d) takes no account of electron correlation, but is well established as a suitable level for calculating geometries.[19] Extensive HF/6-31G(d) data for a range of small S^{VI} organosulfur compounds were reviewed in 1991.[24] Complete geometry optimisations on larger molecules can be done quickly, and the geometry of 4-nitrobenzenesulfonyl chloride is in satisfactory agreement with the structure recently obtained by X-ray diffraction (Scheme 4).[25]

B3LYP/6-31G(d) is designed to account for the effects of electron correlation, and is known to be a compromise between speed and accuracy;[20c] to quote a recent text, 'we have to be very careful what we can and cannot believe'.[20a] B3LYP/6-31G(d) calculations for **3**, $Z = NO_2$ gave an S—Cl bond length, too long by *ca* 0.1 Å. Initial geometries using G3 are optimised HF/6-31G(d) values, and the effects of electron correlation are later made by further optimising the geometry using MP2;[19] MP2 tends to overestimate bond lengths,[20b] and an S—Cl bond length too long by 0.06 Å is calculated for CH_3SO_2Cl. The geometry optimisation procedure in G2 did not reproduce the experimental geometry of CH_2SO, whereas a larger basis set gave the correct structure.[26a] Calculations on the enthalpy of formation of CH_2SO[26] illustrate the difficulties in obtaining reliable predictions, even using high level calculations.

G2 (the forerunner of G3) calculations[27] gave such good results for PA that theoretical data were used as a

Table 7. Rate constants (k/s^{-1}) for solvolyses of 4-Z-substituted benzenesulfonyl chlorides (3) in 97% w/w TFE–water at 50 and 75 °C[a]

Z	Temp. (°C)	Rate constant k (s^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal K^{-1} mol^{-1})
OMe	75.0	$(1.18 \pm 0.02) \times 10^{-4}$		
	50.0	$(2.25 \pm 0.02) \times 10^{-5}$	14.1	−36
Me	75.0	$(2.82 \pm 0.04) \times 10^{-5}$		
	50.0	$(6.80 \pm 0.02) \times 10^{-6}$	12.1	−45
H	75.0	$(2.00 \pm 0.02) \times 10^{-5}$		
	50.0	$(2.88 \pm 0.08) \times 10^{-6}$	16.7	−32
Cl	75.0	$(1.06 \pm 0.01) \times 10^{-5}$		
	50.0[b]	$(2.20 \pm 0.02) \times 10^{-6}$	13.4	−43
NO_2	75.0[c]	$(1.03 \pm 0.07) \times 10^{-5}$		
	50.0[d]	$(1.51 \pm 0.03) \times 10^{-6}$	16.5	−34

[a] Determined conductimetrically in duplicate, except where stated otherwise; errors shown are average deviations; extrapolations to 25 °C are in Table 8.

[b] One additional rate constant determined by HPLC.

[c] Quadruplicate rate measurements.

[d] Determined by refrigerated HPLC (Ref. 23a).

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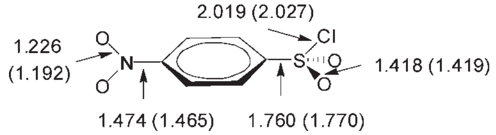
Table 8. Ratios of rate constants (k/s^{-1}) for solvolyses of 4-Z-substituted benzenesulfonyl chlorides (ArSO$_2$Cl, **3**) in 97% w/w TFE–water (97T) and 40% ethanol–water (40E) and k_{40E}/k_{97T} values for corresponding aroyl chlorides (ArCOCl, **1**) at 25 °C[a]

	ArSO$_2$Cl			ArCOCl[a]
Z	k (97% TFE)[b]	k (40% EtOH)	k_{40E}/k_{97T}	k_{40E}/k_{97T}
NO$_2$	1.6×10^{-7}	2.32×10^{-3}[c]	1.5×10^{4}	(8.2×10^{3})[d]
Cl	3.5×10^{-7}	8.5×10^{-4}	2.5×10^{3}	34
H	3.0×10^{-7}	8.82×10^{-4}	2.9×10^{3}	13
Me	1.3×10^{-6}	5.84×10^{-4}[e]	4.5×10^{2}	5.7
OMe	3.3×10^{-6}	9.87×10^{-4}[e]	3.0×10^{2}	4.6
(mesit)[f]	3.5×10^{-5}	5.3×10^{-3}	1.5×10^{2}	

[a] Kinetic data for 97T from Ref. 5, and for 40E from Refs 23b and 23c.
[b] Extrapolated from data in Table 7.
[c] Data from Ref. 23a.
[d] The high ratio is due to a mechanistic change (see Ref. 23b).
[e] Data from Ref. 23d.
[f] Data for 2,4,6-trimethylbenzene sulfonyl chloride is the average from Refs 9a and 23e.



Scheme 4. Comparison of observed (and calculated by HF/6-31G(d)) bond lengths (Å) for 4-nitrobenzenesulfonyl chloride (**3**, Z = NO$_2$)[25]

guide in selecting the best values in the compilation of experimental data.[12] Reassuringly, G3 calculations of PA for a few test molecules were very similar to G2 values.[15]

In considering the reliability of our calculations for enthalpies, it should be emphasised that firm links have been established between experimental data, G3 calculations and the lower level calculations. As each calculation involves a transformation, extensive cancellation of errors can be expected. Also, because Eqns (1–4) are often isodesmic or homodesmotic reactions, it is not surprising that lower level calculations agree well with the G3 calculations. Errors of a few kcal mol^{-1} would not affect our conclusions because the range of substituent effects is huge (it is predicted that HBDEs increase by over 70 kcal mol^{-1} from 4-MeOC$_6$H$_4$COCl to SO$_2$Cl$_2$). A major limitation is that solvation effects are excluded.

Substituent effects on neutral compounds

The G3 results in Table 3 agree with lower levels of theory (HF/6-31G(d) and B3LYP/6-31G(d), except in one case. For SO$_2$Cl$_2$, there is very poor agreement between the three levels of theory, but the G3 value is supported by experimental data (Table 3, footnote g). The results for SO$_2$Cl$_2$ appear to be at the extreme of a trend; agreement between the various levels of theory is less satisfactory when atoms such as O, N or Cl are attached directly to the sulfonyl group [Eqn (1)]. Nevertheless, some values of ΔH_f^0 have been obtained from the lower level theory. For PhSO$_2$Cl, the results are supported indirectly by the G3 calculation for CH$_2$CHSO$_2$Cl; all three levels of theory are in agreement for CH$_2$CHSO$_2$Cl, and the two lower levels of theory agree for PhSO$_2$Cl, for which there are very similar bonding changes.

In contrast to previous calculations for chloroformates (e.g. MeOCOCl),[14] there are no large conjugative effects in neutral sulfonyl chlorides (Table 3), even between the nitrogen atom and the SO$_2$Cl moiety (i.e. sulfamic acid derivatives). Also, for Eqn (7), G3 gives a ΔH_R of only 1.8 kcal mol^{-1}, so there are either small or insignificant conjugative effects between the Cl and SO$_2$ fragments of sulfonyl chlorides. However for Eqn (8), G3 gives $\Delta H_R = 7.1$ kcal mol^{-1} (experimental values of ΔH_f^0 give $\Delta H_R = 6.3$ kcal mol^{-1}), so there is a small conjugative stabilising effect between the Cl and CO fragments of acyl chlorides.

$$CH_3SO_2Cl + CH_3CH_3 = CH_3SO_2CH_3 + CH_3Cl \quad (7)$$

$$CH_3COCl + CH_3CH_3 = CH_3COCH_3 + CH_3Cl \quad (8)$$

Substituent effects and nucleophilic solvent assistance in solvolyses

Aromatic substituent effects for the gas phase (expressed as enthalpies) are calculated to be very similar for acylium ions and for sulfonyl cations (Table 5). There is good agreement between HF and B3LYP calculations, probably because the bonding changes are relatively small (see also above discussion of the G3 calculation for CH$_2$CHSO$_2$Cl). Satisfactory correlations of energies with σ_p^+ are shown in the footnotes to Table 5, and the slopes (14–16) correspond to ρ^+ values of 10–11 when converted to slopes for log rates.

In contrast, the experimental data for rates of solvolyses in 97% TFE for acyl chlorides show $\rho^+ = -3.1$

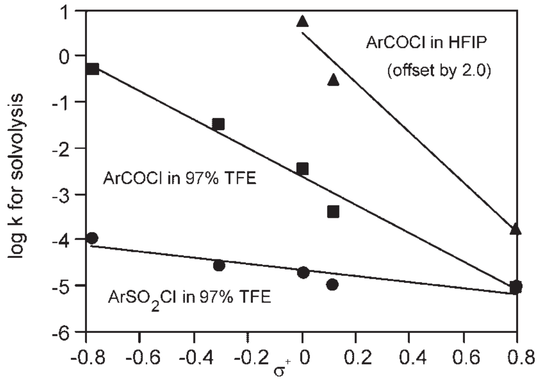


Figure 1. Logarithms of rate constants for solvolyses *versus* σ^+ (Ref. 6) of: (a) sulfonyl chlorides in 97% TFE at 75 °C (data from Table 7): $\log k = -(0.67 \pm 0.19)\rho^+ - (4.65 \pm 0.1)$, $r = 0.895$, $n = 5$; (b, c) acyl chlorides at 25 °C: (b) in 97% TFE (data from Ref. 5): $\log k = -(3.11 \pm 0.23)\rho^+ - (2.62 \pm 0.12)$, $r = 0.992$, $n = 5$; (c) in 97% hexafluoropropanol (HFIP) (data from Ref. 30): $\log k = -(5.4 \pm 0.8)\rho^+ - (1.5 \pm 0.4)$, $r = 0.990$, $n = 3$; note that $(2 + \log k)$ is plotted

−3.1 (Fig. 1); substituent effects are <30% of the calculated values (gas phase), but about fourfold larger than for sulfonyl chlorides ($\rho^+ = ca\ -0.7$, but a shallow curve would fit the data better, Fig. 1).

For comparison, substituent effects for solvolyses of 4-substituted cumyl chlorides (**2**) are 40% of the calculated values (B3LYP/6-31G(d)); heterolytic bond dissociation enthalpies (HBDEs) (kcal mol^{-1}, relative to H) are:[4b] 4-MeO, −11.7; 4-Me, −5.6; 4-Cl, 0.3; 4-NO_2, 13.4, in close agreement with the values for acid chlorides (Table 5). Hence, the extent of attenuation of gas phase substituent effects by solvent (based on rates of solvolyses) is: sulfonyl chlorides > acyl chlorides > cumyl chlorides.[28]

Solvolyses of cumyl chlorides (**2**) proceed by an S_N1 mechanism; the extent of nucleophilic solvent assistance (NSA or S_N2 character) is small[29a] or negligible.[29b,c] Reviewing our earlier comments[5] on solvolyses of acyl chlorides, the gas phase substituent effect is even larger than expected from mass spectrometric data. The earlier proposal that solvolyses of acyl chlorides in 97% TFE proceed through transition states with high cationic character, but are not purely S_N1 processes,[5] was based on the relatively low ρ^+ values of −3.1; it is now supported by more recent data showing a larger substituent effects for solvolyses in 97% hexafluoro-isopropanol ($\rho^+ = -5.4$, Fig. 1), an even more weakly nucleophilic solvent.[3d,31]

The rate ratio of rate constants in 97% TFE and in 40% ethanol–water is a useful guide to the extent of NSA (S_N2 character) in solvolyses.[32] The two solvents have very similar ionizing powers, but TFE is significantly less nucleophilic,[3d,31] so k_{40E}/k_{97T} values >1 are an indication of NSA (see Scheme 1 of Ref. 32). S_N1 solvolyses of aromatic compounds may give k_{40E}/k_{97T} ratios <1,[32] so the value of 13 (Table 8) for solvolyses of benzoyl chloride is consistent with small but significant NSA. Hence, comparing solvolyses of acyl chlorides (**1**) and cumyl chlorides (**2**), the greater extent of attenuation of the calculated (gas phase) substituent effect for the former can be explained by greater NSA.

Now comparing solvolyses of sulfonyl with aromatic carboxylic acid (aroyl) chlorides, the smaller substituent effect for solvolyses in 97% TFE (Fig. 1) can also be explained by greater NSA. The k_{40E}/k_{97T} ratios for sulfonyl chlorides vary 100-fold depending on both electronic and steric effects (Table 8); the highest value for $Z = NO_2$ refers to a strongly electron withdrawing substituent, and the lowest value of 150 refers to a more electron rich and more sterically hindered substrate (2,4,6-trimethyl benzenesulfonyl chloride). The k_{40E}/k_{97T} ratios for aromatic sulfonyl chlorides are typically *ca* 100-fold larger than for corresponding aroyl chlorides (Table 8), consistent with substantial NSA and an S_N2 mechanism for solvolyses of sulfonyl chlorides;[9c,33] also values of $\Delta S^{\neq}$ (Table 7) are much more negative than those for corresponding aroyl chlorides,[5] supporting evidence for a more highly ordered (S_N2) transition state.[9a,9d]

Sulfonyl transfer reactions are usually regarded as concerted bimolecular displacements at the sulfonyl group,[33] but the nature of the 'S_N2' transition state for solvolyses of sulfonyl chlorides has long been a matter of debate and some confusion. Calculations (based on 6-31G(d) geometries and MP2 energies) for methanesulfonyl chloride reacting with one or two water molecules support a concerted process having a transition state with the water nucleophile attacking at the rear of the S—Cl bond (as in the classical S_N2 mechanism).[34a] More recent but lower level PM3 calculations for the gas phase reaction of **3**, Z = H with one water molecule supported an S_AN mechanism and formation of an unstable five-coordinate intermediate.[34b] MP2 and B3LYP calculations for gas phase S_N2 reactions predicted trigonal bipyramidal (TBP) transition states for chloride ion attacking a sulfonyl chloride, but a stepwise mechanism via TBP-type intermediates for sulfonyl transfers between fluorides.[34c]

Differences in solvolysis mechanisms for **1** and **3** can be partly explained by the much greater ease of formation of acylium ions compared with sulfonyl cations (Table 6); the G3 value of 25.9 kcal mol^{-1} for the enthalpy change in Eqn (5) is an indication of the greater stabilization of CH_3CO^+ than $CH_3SO_2^+$. A small correction (*ca* 4 kcal mol^{-1}) for the greater conjugative effects in the neutral acyl chloride [Eqn (8)] than sulfonyl chlorides [Eqn (7)] leads to even larger enthalpy differences between the two cations.

The G3 result (25.9) is also in good agreement with the 24.2 kcal mol^{-1} difference in bond dissociation enthalpies obtained from experimental data (Scheme 2), and the B3LYP results improve significantly as the size of the

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basis set increases; fortuitously in this case, the HF/6-31G(d) result of 27.5 kcal mol^{-1} is also quite good. Because an almost identical pattern of results is calculated for $PhCO^+$ and $PhSO_2^+$, we estimate a best value of 15–18 kcal mol^{-1} for the enthalpy change in [Eqn (6)].

The possibility of mechanistic changes for solvolyses of highly electron rich sulfonyl halides has recently been considered;[9d] reaction of 4-amino benzenesulfonyl chloride (**3**, $Z = NH_2$) with hydroxide is much faster than expected by comparison with other sulfonyl halides, possibly due to deprotonation of an N—H bond in an E1cB mechanism.[9e] Solvolyses of 4-dimethylamino benzenesulfonyl chloride (**3**, $Z = NMe_2$) show the effect of strong electron donation in the absence of deprotonation;[9a,9d] the reaction is much faster than expected from extrapolation of the plot for sulfonyl chlorides in 97% TFE (Fig. 1) to σ^+ (for NMe_2) $= -1.7$, which gives a predicted $k = 3 \times 10^{-4}\,s^{-1}$ at 75 °C, 20-fold less than observed even at 25 °C ($k = 5.5 \times 10^{-3}\,s^{-1}$)[9a] in anhydrous TFE (the kinetic effect of 3% of water in TFE is small).

CONCLUSIONS

G3 theoretical calculations of energies, known to give reliable thermochemical data for many organic compounds,[15] are in good agreement with experimental results for a range of S^{VI} organosulfur compounds (Table 1), and HBDEs (Scheme 2) and the PA′s (Scheme 3). Lower level calculations (HF/6-31G(d) and B3LYP/6-31G(d)) are in agreement with G3 calculations if suitable equations for substituent effects are devised to allow cancellation of some errors (e.g. for the much less demanding calculations of the energies of homodesmotic reactions involving small bonding changes for sulfonyl chlorides and corresponding cations (Eqns 1 and 2, Tables 3 and 4).

Calculated HBDEs (gas phase) vary over 70 kcal mol^{-1} (from 4-methoxy-benzoyl chloride to SO_2Cl_2), but the effects of varying the 4-substituent from OMe to NO_2 for arenesulfonyl cations (Table 5) are almost identical to those for the corresponding acylium ions (Table 5) and cumyl cations.[4b] In contrast, rate constants for solvolyses of aroyl chlorides in 97% TFE show about 30% of the calculated substituent effects, and substituent effects for solvolyses of arenesulfonyl chlorides are a further fourfold smaller (Fig. 1). The variation in extent of attenuation of gas phase substituent effects of 4-substituted aryl cations (in the order: sulfonyl > acylium > cumyl) can be explained by decreases in nucleophilic solvent assistance (S_N2 character).

Changes in HBDE for sulfonyl chlorides (Table 4) are due mainly to substituent effects on stabilisation of the sulfonyl cations, because conjugative effects in the neutral sulfonyl chlorides are relatively small (see Table 3, and Eqns 7 and 8).

EXPERIMENTAL

Calculations

Calculations were performed using Gaussian 03[35] at the Rutherford Appleton laboratory (Columbus service) using the EPSRC National Service for Computational Chemistry software (NSCCS). Linear regressions were performed using Microsoft Excel.

Kinetics

Sulfonyl chlorides were commercial samples; solids were purified by recrystallisation from diethyl ether for **3**, Z = MeO (Lancaster synthesis, mp 41–43 °C), **3**, Z = Me (BDH, mp 68–69 °C) and **3**, Z = Cl (Aldrich, mp 51–52 °C); benzenesulfonyl chloride (Aldrich) was shown to be >99.7% pure by HPLC analysis of methanolysis products. Purification of **3**, $Z = NO_2$, and of solvents and other experimental procedures for kinetics (including new results for 40% ethanol in Table 8) and HPLC were as described earlier.[23a] The accuracy of some of the rate constants obtained by HPLC was improved by incorporating peak areas for both sulfonyl chloride and acid product into the calculations, as described earlier.[36]

SUPPLEMENTARY DATA

Total energies (Hartrees) for new calculations (Tables S1–S3, four pages).

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