

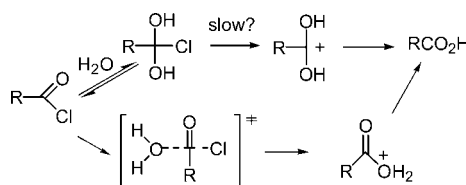
Structural Effects on the Solvolytic Reactivity of Carboxylic and Sulfonic Acid Chlorides. Comparisons with Gas-Phase Data for Cation Formation

T. William Bentley

Chemistry Group, Grove Building, School of Engineering, Swansea University, Singleton Park, Swansea, SA2 8PP Wales, U.K.

t.w.bentley@swansea.ac.uk

Received April 17, 2008



Kinetic data for solvolyses of 28 acid chlorides in 97% w/w trifluoroethanol (TFE)–water spanning over 10^9 in rate constant at 25 °C are obtained directly or by short extrapolation from published values. G3 calculations of the energy required for cation formation in the gas phase are validated from proton affinities and from other experimental data. G3 calculations of heterolytic bond dissociation enthalpies (HBDEs) for formation of cations from acid chlorides in the gas phase show the following trends when compared with the solvolysis rate constants: (i) electron-rich sulfonyl chlorides and most carboxylic acid chlorides, including thione derivatives, give a satisfactory linear correlation with a significant negative slope; (ii) most sulfonyl chlorides and some chloroformates and thio derivatives have higher HBDEs and fit another correlation with a small, negative slope. A significant deviation is observed for the acyl series (RCOCl), for which both solvolysis rates and HBDEs increase in the order $R = \text{Bu}^t < \text{Pr}^i < \text{Et} < \text{Me}$. The deviation may be explained either by a prior hydration mechanism or preferably by electrostatic effects on the formation of small cations. The above results of structural effects support independent evidence from solvent effects that cationic ionization reaction pathways (with nucleophilic solvent assistance or $\text{S}_{\text{N}}2$ character) are involved in the solvolyses of acid chlorides.

Introduction

Acylium ions (RCO^+) are relatively stable under non-nucleophilic conditions;¹ 1:1 addition complexes of RCOF and SbF_5 are ionic (e.g., $\text{CH}_3\text{CO}^+ \text{SbF}_6^-$, $\text{C}_6\text{H}_5\text{CO}^+ \text{SbF}_6^-$),² and in the gas phase the acetyl cation is of comparable stability to the *tert*-butyl cation.³ Nevertheless, for reactions in protic solvents, mechanistic proposals for nucleophilic substitution reactions of carbonyl compounds are dominated by an initial addition step to give tetrahedral intermediates.

Although heterolytic cleavage of the acyl-leaving group bond is more favorable for acid chlorides than for esters or amides,

there are only a few well-established examples of $\text{S}_{\text{N}}1$ nucleophilic substitution reactions involving cation formation in protic solvents; evidence for trapping a cationic intermediate is obtained from the common ion rate depression observed for solvolyses of sterically hindered mesitoyl chloride (**1**, $Z = \text{Me}$) in 95% acetone–water^{4a} and in 99% acetonitrile–water^{4b} and for hydrolysis of the highly electron-rich substrate 4-dimethylaminobenzoyl fluoride (**2**).⁵

Less stable acylium ions than those formed from **1** or **2** react more rapidly in nucleophilic media, and evidence for the formation of cationic intermediates is indirect. Alcohol–water selectivity data for solvolyses of 2,6-dimethylbenzoyl chloride (**1**, $Z = \text{H}$),^{6a} 4-methoxybenzoyl chloride (**3**, $Z = \text{OMe}$),^{6a,b} and *N,N*-diphenylcarbamoyl chloride (Ph_2NCOCl)^{6c} are con-

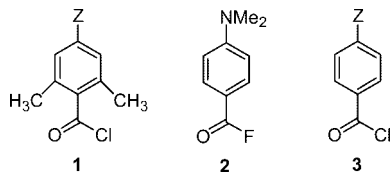
(1) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 146.

(2) Olah, G. A.; Kuhn, S. J.; Tolgyesi, W. S.; Baker, E. B. *J. Am. Chem. Soc.* **1962**, *84*, 2733–2740.

(3) (a) Staley, R. H.; Wieting, R. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 5964–5972. (b) Bentley, T. W.; Llewellyn, G.; McAlister, J. A. *J. Org. Chem.* **1996**, *61*, 7927–7932. (c) Bentley, T. W.; Harris, H. C.; Ryu, Z. H.; Lim, G. T.; Sung, D. D.; Szajda, S. R. *J. Org. Chem.* **2005**, *70*, 8963–8970.

(4) (a) Hudson, R. F.; Moss, G. *J. Chem. Soc.* **1964**, 2982–2985. (b) Bender, M. L.; Chen, M. C. *J. Am. Chem. Soc.* **1963**, *85*, 30–36.

(5) Song, B. D.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8470–8479.



sistent with product formation by solvent attacking a solvent-separated ion pair rather than a more dissociated (“free”) cation.

In general, solvent effects on the rates of solvolyses of acid chlorides are explained by competing “ionization” and addition pathways.^{5,7} Solvolyses of 4-substituted benzoyl chlorides (**3**) in 97% 2,2,2-trifluoroethanol (TFE)–water correlate well with σ^+ , and the negative slope (–3.1) is consistent with an ionization reaction channel.^{8,9a}

As the relative importance of the two mechanistic pathways depends on both the solvent and structure of the acid chloride, structural effects on the solvolytic reactivity of acid chlorides are complex. Recently, we compared^{9a} rates of solvolyses of aroyl, benzenesulfonyl, and cumyl chlorides with the substituent effects calculated for formation of cations in the gas phase.^{9a} Comparisons of experimental and calculated gas-phase thermochemical data⁹ have now been extended to other acyl chlorides and to thio derivatives. The results show that changes in gas-phase heterolytic bond dissociation enthalpies (HBDEs) account for a large part of the observed structural effects on rate constants for solvolyses of a wide variety of acid chlorides in 97% TFE–water, a solvent of relatively low nucleophilicity which favors the ionization pathway.

Results

Solvolysis Rate Constants. Rate constants (k/s^{-1}) for solvolyses of various carboxylic acid, thiocarboxylic acid, and sulfonic acid chlorides in 97% w/w TFE–water at 25 °C were obtained from literature values, sometimes requiring short extrapolations (Table 1); there are conflicting published data for PhSCSCL, and the conductometric value of 2.4×10^{-2} was judged to be the better. Rate constants for aromatic carboxylic acid and sulfonic acid chlorides are compared in Table 2. The results show a 10^9 variation in rate constants for solvolyses of carboxylic acid chlorides and a wide variation in relative rates for different types of acid chlorides having the same substituents. The following calculations were performed to assess the extent to which stabilization of cations can explain the kinetic data.

Theoretical Calculations. Three theoretical methods were applied. G3 is the latest version of the Gaussian n series, which has been tested extensively;¹² experimental data for reactive

TABLE 1. Rate Constants (k/s^{-1}) for Solvolyses of Carboxylic, Thiocarboxylic, and Sulfonic Acid Chlorides in 97% w/w 2,2,2-Trifluoroethanol–Water at 25 °C

substituent R	rate constants		
	RCOCl	RCSCl	RSO ₂ Cl
Me	6.9×10^{-1a}		9.6×10^{-8b}
Et	4.8×10^{-1a}		
Pr ⁱ	2.7×10^{-1a}		
Bu ^t	7.3×10^{-2a}		
Ph	3.63×10^{-3c}		3.0×10^{-7d}
PhO	5.7×10^{-7e}	3.95×10^{-6f}	
EtO	2.5×10^{-7g}		
PhS	3.45×10^{-6h}	2.4×10^{-2i}	
EtS	5.98×10^{-5j}		
Me ₂ N	1.82×10^{-4k}	1.12×10^{-1l}	2.04×10^{-6m}

^a Extrapolated from data at temperatures between –13 and +10 °C; data from ref 10a. ^b Extrapolated from data at 45 °C, assuming $\Delta H^\ddagger = 16.5$ kcal/mol; data from ref 10b. ^c Data from refs 8 and 10c. ^d Extrapolated from data at 50 and 75 °C; data from ref 9a. ^e Data from ref 10d. ^f Data from 10e. ^g Estimated from data (ref 10f) at 24.2 °C. ^h Reference 10g. ⁱ Data from ref 10h; a much lower value (3.24×10^{-3}) is reported in ref 10e. ^j Reference 10f. ^k Reference 10i. ^l Assuming a rate ratio of 617 for Me₂NCSCl/Me₂NCOCl, as observed at 0 °C (ref 10j). ^m Reference 10k.

TABLE 2. Rate Constants (k/s^{-1}) for Solvolyses of Aromatic Carboxylic and Sulfonic Acid Chlorides in 97% w/w 2,2,2-Trifluoroethanol–Water at 25 °C

substituent(s) in Ar	rate constants		
	ArCOCl	ArSO ₂ Cl	ratio
H	3.63×10^{-3a}	3.0×10^{-7b}	1.2×10^4
4-Me	3.49×10^{-2a}	1.3×10^{-6b}	2.7×10^4
4-OMe	5.66×10^{-1a}	3.3×10^{-6b}	1.7×10^5
2,6-diMe	80 ^c		
2,4,6-triMe		3.5×10^{-5d}	
4-NMe ₂	470 ^e	5.5×10^{-3f}	8.5×10^4
4-Cl	4.46×10^{-4a}	3.5×10^{-7b}	1.3×10^3
4-NO ₂	9.9×10^{-6a}	1.6×10^{-7b}	62

^a Data from ref 8. ^b Extrapolated from data (ref 9a) at 50 and 75 °C. ^c Estimated from a correlation with data for 4-methoxy benzoyl chloride (ref 6a). ^d Average from refs 11a and 11b. ^e Estimated by extrapolation of the σ^+ plot shown in ref 9a. ^f Rate constant in 100% TFE, datum from ref 11a (the effect of 3% water is expected to be small; see Table 5 of ref 11c).

organic intermediates in the gas phase (e.g., radicals and cations) are not always reliable,¹³ including the “apparent confirmation of erroneous data”.^{13c} Theory (e.g., G2) has played a significant

(6) (a) Bentley, T. W.; Harris, H. C.; Koo, I. S. *J. Chem. Soc., Perkin Trans. 2* **1988**, 783–789. (b) Bentley, T. W.; Ebdon, D. N.; Kim, E.-J.; Koo, I. S. *J. Org. Chem.* **2005**, *70*, 1647–1653. (c) D’Souza, M. J.; Kevill, D. N.; Bentley, T. W.; Devaney, A. C. *J. Org. Chem.* **1995**, *60*, 1632–1637.

(7) (a) Bentley, T. W.; Carter, G. E.; Harris, H. C. *J. Chem. Soc., Perkin Trans. 2* **1985**, 983–990. (b) Bentley, T. W.; Koo, I. S. *J. Chem. Soc., Chem. Commun.* **1988**, 41–42. (c) Bentley, T. W.; Koo, I. S. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1385–1392. (d) Lee, I.; Sung, D. D.; Uhm, T. S.; Ryu, Z. H. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1697–1701. (e) Liu, K.-T.; Chen, H.-I. *J. Chem. Soc., Perkin Trans. 2* **2000**, 893–898. (f) Kevill, D. N.; D’Souza, M. J. *J. Phys. Org. Chem.* **2002**, *15*, 881–888.

(8) Bentley, T. W.; Harris, H. C. *J. Chem. Soc., Perkin Trans. 2* **1986**, 619–624.

(9) (a) Bentley, T. W.; Jones, R. O. *J. Phys. Org. Chem.* **2007**, *20*, 1093–1101. (b) Krygowski, T. M.; Cyrański, M. K.; Sung, D. D.; Stepień, B. T. *J. Phys. Org. Chem.* **2004**, *17*, 699–706. (c) Liu, K.-T.; Chen, H.-I. *J. Chem. Soc., Perkin Trans. 2* **2000**, 893–898.

(10) (a) Ryu, Z. H.; Lim, G. T.; Bentley, T. W. *Bull. Korean Chem. Soc.* **2003**, *24*, 1293–1302. (b) Kevill, D. N.; Ryu, Z. H.; Niedermeyer, M. A.;

Koyoshi, F.; D’Souza, M. J. *J. Phys. Org. Chem.* **2007**, *20*, 431–438. (c) Bentley, T. W.; Carter, G. E.; Harris, H. C. *J. Chem. Soc., Perkin Trans. 2* **1985**, 983–990. (d) Kevill, D. N.; D’Souza, M. J. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1721–1724. (e) Kevill, D. N.; D’Souza, M. J. *Can. J. Chem.* **1999**, *77*, 1118–1122. (f) Kevill, D. N.; D’Souza, M. J. *J. Org. Chem.* **1998**, *63*, 2120–2124. (g) Kevill, D. N.; Bond, M. W.; D’Souza, M. J. *J. Org. Chem.* **1997**, *62*, 7869–7871. (h) An, S. K.; Yang, J. S.; Cho, J. M.; Yang, K.; Lee, J. P.; Bentley, T. W.; Lee, I.; Koo, I. S. *Bull. Korean Chem. Soc.* **2002**, *23*, 1445–1450. (i) Kevill, D. N.; Oldfield, A. J.; D’Souza, M. J. *J. Chem. Res.* **1996**, 122–123. (j) Kevill, D. N.; Rudolph, T. M.; D’Souza, M. J. *J. Phys. Org. Chem.* **2000**, *13*, 192–196. (k) Kevill, D. N.; Park, B. C.; Park, K. H.; D’Souza, M. J.; Yaakoubd, L.; Mlynarski, S. L.; Kyong, J. B. *Org. Biomol. Chem.* **2006**, *4*, 1580–1586.

(11) (a) Forbes, R. M.; Maskill, H. J. *J. Chem. Soc., Chem. Commun.* **1991**, 854–856. (b) Koo, I. S.; Bentley, T. W.; Kang, D. H.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1991**, 175–179. (c) Bentley, T. W.; Llewellyn, G. *Prog. Phys. Org. Chem.* **1990**, *17*, 121–158.

(12) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764–7776.

(13) (a) Agapito, F.; Cabral, B. J. C.; Simões, J. A. M. *THEOCHEM* **2007**, *811*, 361–372. (b) Traeger, J. C.; Kompe, B. M. In *Energetics of Organic Free Radicals*; Simões, J. A. M., Greenberg, A., Liebman, J. F., Eds.; Chapman and Hall: London, 1996; Chapter 3, pp 59–109. (c) Tsang, W. In ref 13b, Chapter 2, pp 22–58.

TABLE 3. Heterolytic Bond Dissociation Enthalpies (D_{C-Cl}) and Enthalpies (kcal/mol) for Transfer of Chloride Ion to the Acetyl Cation from Carboxylic Acid Chlorides (ZCOCl, eq 3), Calculated by HF/6-31G(d), B3LYP/6-31G(d), and G3 Theory^a

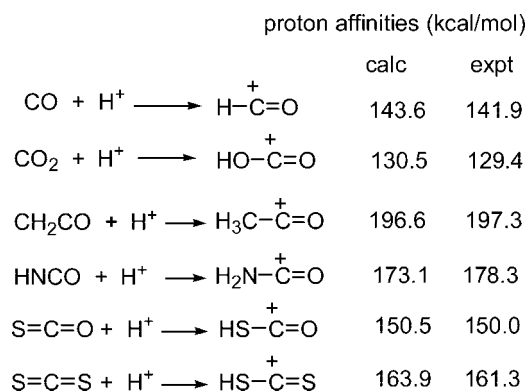
species	HF	B3LYP	G3 ^b	D_{C-Cl} ^c
MeCOCl	0.0 ^d	0.0 ^d	0.0 ^d	161.8 ^e
HCOCl	27.5 ^f	31.0 ^f	26.1	187.9
EtCOCl	-4.4 ^f	-4.7 ^f	-3.6	158.2
Pr ⁱ COCl	-10.5	-10.9	-7.7	154.1
Bu ^t COCl	-14.5	-15.0	-10.8	151.0
CH ₂ CHCOCl	-5.4	-4.9	-1.4 ^g	160.4
PhCOCl	-15.5 ^f	-17.7 ^f	-11.7 ^h	150.1
HOCOCl	29.7	25.7	25.9	187.7
PhOCOCl	1.5	-1.1	4.7 ⁱ	166.5
HSCOCl	11.8	9.9	8.6	170.4
MeSCOCl	3.4 ^f	0.4 ^f	0.8	162.6
EtSCOCl	-1.3 ^j	-5.4 ^j	(159) ^j	(159) ^j
PhSCOCl	-8.8	-12.1	-8.5	153.3
NH ₂ COCl	8.2	6.1	7.3	169.1
MeNHCOCl	0.0	-2.3	0.1	161.9
(Me) ₂ NCOCl	-12.5	-13.0	-9.6	152.2

^a Calculated from data in Tables S1–S3 and S7 (Supporting Information). ^b Enthalpy at 298 K. ^c Heterolytic bond dissociation enthalpy at 298 K, giving an acylium cation and a chloride anion, based on G3 calculations for the energy of chloride transfer. ^d By definition. ^e Anchor point, based on eq 2, the value calculated from experimental data (161.8) and the value (160.2 + 1.5) from G3 data (see also ref 9a). ^f Reference 3c. ^g A value of +0.5 kcal/mol is calculated from hydride transfer, not chloride transfer. ^h Hydride transfer gives -10.1 kcal/mol. ⁱ Hydride transfer gives +13.2 kcal/mol. ^j Approximate result because there is a long S–C bond (breaking) in the cation.

role in resolving discrepancies for cations.¹⁴ G3 was used to provide direct comparisons with experimental data for acylium ions (i.e., absolute values). Two completely different types of lower level calculations (HF/6-31G(d) and B3LYP/6-31G(d)) were used for the less demanding task of calculating substituent effects (i.e., relative values). Comparisons of the two lower level theories and G3 give an indication of how sensitive the results are to the choice of theoretical calculation.

Validation of G3 Calculations for Acylium Cations. Protonation of CO, CO₂, COS, CS₂ and ketene, and HNCO lead to acylium ions or thio derivatives, and calculated proton affinities (PA) are compared with experimental values in Scheme 1.^{15–17} PA refers to the change in enthalpy expressed as a positive value for protonation of a substrate.^{14b} The results were obtained from the G3 enthalpy data at 298 K for the optimized structures of neutral and protonated species, calculated by Gaussian 03, using the NIST database¹⁵ for neutrals and Table S1 (Supporting Information) for cations. The following correction was then added: (5/2)RT = 1.5 kcal/mol at 298 K or 3.0 kcal/mol at 600 K, derived from (3/2)RT for the translational energy of H⁺ plus an extra RT to convert E to H.¹⁶

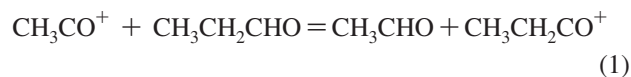
Recent data^{17b} support the PA of ketene;¹⁴ the experimental value^{17c} of 181.3 kcal/mol for HNCO at 298 K is rescaled by 3.0 kcal/mol to a revised PA of NH₃,^{17d} and an even lower value of 176.6 kcal/mol was obtained from appearance potential measurements.^{17d} The other four values in Scheme 1 refer to 600 K.^{17a}

SCHEME 1. Proton Affinities (PA) of Substrates Leading to Acylium Ions**TABLE 4.** Heterolytic Bond Dissociation Enthalpies (D_{C-Cl}) and Enthalpies (kcal/mol) for Transfer of Chloride Ion to the Acetyl Cation from Thion derivatives (ZCSCl, eq 4), Calculated for HF/6-31G(d), B3LYP/6-31G(d), and G3 Theory^a

species	HF	B3LYP	G3 ^b	D_{C-Cl} ^c
MeCOCl	0.0 ^d	0.0 ^d	0.0 ^d	161.8 ^e
HSCSCl	0.4	-6.7	-5.9	155.9
CH ₃ CSCl	-5.4	-11.1	-10.0	151.8
PhOCSCl	-11.5	-18.8	-13.1	148.7
PhSCSCl	-15.1	-23.6	-18.4	143.4
NH ₂ CSCl	-4.2	-10.6	-9.8	152.0
(Me) ₂ NCSCl	-23.1	-27.5	-23.8	138.0

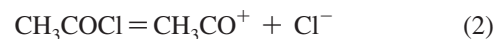
^a Calculated from data in Table S4 (Supporting Information). ^b As for Table 3. ^c As for Table 3. ^d As for Table 3. ^e As for Table 3.

Few reliable thermochemical data for acylium ions are available from other sources. Experimental data for enthalpies of formation of all of the species shown in eq 1 allow the calculation of an “experimental” enthalpy of reaction for hydride transfer from an aldehyde to an acylium ion.



The G3 calculated value of -4.1 kcal/mol is in good agreement with the experimental value of -5.0 kcal/mol; experimental data for the two aldehydes are from ref 18 and for ions are each averages of two values for acetyl^{13b,17b} and propionyl.¹⁹ In this and other cases (Table 3, footnotes g, and h), calculated enthalpies of hydride transfer are in good agreement with those calculated for chloride ion transfer.

G3 calculations have also been used successfully to calculate a wide range of homolytic bond dissociation energies for diatomic species leading to two radicals.²⁰ The heterolytic bond dissociation energy (HBDE) for acetyl chloride (eq 2) can be calculated from experimental enthalpy data to be 161.8 kcal/mol at 298 K, in excellent agreement with the G3 value at 0 K of 160.2 kcal/mol,^{9a} corrected by (5/2)RT to give a value of 161.7 kcal/mol at 298 K.



Substituent Effects on the Formation of Acylium, Thioacylium, and Sulfonyl Cations. These were investigated theoretically by chloride transfer reactions (eqs 3–5). The

(14) (a) Smith, B. J.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 885–888. (b) Hunter, E. P.; Lias, S. G. *J. Phys. Chem. Ref. Data* **1998**, *27*, 413–656.

(15) NIST database accessed in January 2008.

(16) Pokon, E. M.; Liptak, M. D.; Feldgus, S.; Shields, G. C. *J. Phys. Chem. A* **2001**, *105*, 10483–10487.

(17) (a) Szulejko, J. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 7839–7848. (b) Fogleman, E. A.; Koizumi, H.; Kercher, J. P.; Sztáray, B.; Baer, T. *J. Phys. Chem. A* **2004**, *108*, 5288–5294. (c) Wight, C. A.; Beauchamp, J. L. *J. Phys. Chem.* **1980**, *84*, 2503–2506. (d) Hop, C. E. C. A.; Holmes, J. L.; Ruttink, P. J. A.; Schaftenaar, G.; Terlouw, J. K. *Chem. Phys. Lett.* **1989**, *156*, 251–255.

(18) Wiberg, K. B.; Crocker, L. S.; Morgan, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 3447–3450.

(19) (a) Harvey, Z. A.; Traeger, J. C. *J. Mass Spectrom.* **2004**, *39*, 802–807. (b) Kercher, J. P.; Fogleman, E. A.; Koizumi, H.; Sztáray, B.; Baer, T. *J. Phys. Chem. A* **2005**, *109*, 939–946.

TABLE 5. Heterolytic Bond Dissociation Enthalpies (D_{S-Cl}) and Enthalpies (kcal/mol) for Transfer of Chloride Ion to the Methanesulfonyl Cation from Sulfonyl Chlorides (ZSO₂Cl, eq 5), Calculated for HF/6-31G(d), B3LYP/6-31G(d), and G3 Theory^a

species	HF	B3LYP	G3 ^b	D_{S-Cl}^c
MeSO ₂ Cl	0.0 ^d	0.0 ^d	0.0 ^d	187.5 ^e
CH ₂ CHSO ₂ Cl ^f	-11.3	-9.7	-7.3 ^g	180.2 ^h
HOSO ₂ Cl ^h	20.7	18.6	18.8	206.3
NH ₂ SO ₂ Cl ^h	-4.3	-4.8	-4.3	183.2
NHMeSO ₂ Cl	-11.6 ^h	-11.0 ^h	-10.4	177.1
NMe ₂ SO ₂ Cl	-18.1 ^h	-17.6	-16.3 ⁱ	171.2
PhSO ₂ Cl	-22.9	-23.2	-18.6 ^j	168.9

^a Data from Table S5 (Supporting Information). ^b Enthalpy at 298 K. ^c Heterolytic bond dissociation energy, calculated from the value of 186.0 kcal/mol (ref 9a), corrected by $(5/2)RT$ and the substituent effect from G3 (eq 5). ^d By definition. ^e Anchor point. ^f From ref 9a. ^g Hydride transfer gives -7.3 kcal/mol. ^h Revision of values given in ref 9a; revised calculations of stabilization effects on neutral species are given in Table S8 (Supporting Information). ⁱ Hydride transfer gives -17.0 kcal/mol. ^j Hydride transfer gives -19.0 kcal/mol.

TABLE 6. Heterolytic Bond Dissociation Enthalpies (D_{X-Cl}) and Enthalpies (kcal/mol) for Transfer of Chloride Ion to the Benzoyl or Benzenesulfonyl Cations from Corresponding benzene-substituted Acid Chlorides (eqs 6 and 7), Calculated for HF/6-31G(d) and B3LYP/6-31G(d)^a

species	HF	B3LYP	D_{X-Cl}
PhCOCl (Ar = H)			150.1 ^b
Ar = 2,6-diMe	-14.1 ^c	-14.5 ^c	135.8
Ar = 4-NMe ₂	-18.7 ^c	-20.2 ^c	130.7
PhSO ₂ Cl (Ar = H)			168.9 ^d
Ar = 2,4,6-triMe	-11.1 ^{e,f}	-11.4 ^e	157.7
Ar = 4-NMe ₂	-22.4 ^e	-23.3 ^e	146.1

^a Calculated from data in Table S6 (Supporting Information). ^b Anchor point for carboxylic acid chlorides, D_{X-Cl} , from Table 3. ^c Calculated from eq 6. ^d Anchor point for sulfonic acid chlorides, D_{X-Cl} , from Table 5. ^e Calculated from eq 7. ^f Hydride transfer -11.2 kcal/mol.

stabilities of the acylium and thioacylium cations were calculated relative to the acetyl cation, and the HBDE for acetyl chloride (eq 2) was used as an "anchor"; HBDEs for other acyl and thioacyl chlorides were then calculated from the substituent effects (Tables 3 and 4). Similarly, data for sulfonyl cations was obtained from eq 5 (Table 5).



G3 values for the HBDEs of PhCOCl and PhSO₂Cl were employed as anchor points in lower level calculations to estimate HBDEs for acid chlorides containing electron-donating groups (eqs 6 and 7, Table 6).



Discussion

Theoretical Methods. Since G2^{14a} and G2(MP2)²¹ calculations give very good results for the PA of CO, CO₂, and ketene,

(20) M6, O.; Yáñez, M.; Eckert-Maksić, M.; Maksić, Z. B.; Alkorta, I.; Elguero, J. *J. Phys. Chem. A* **2005**, *109*, 4359–4365.

(21) Dechamps, N.; Flammang, R.; Gerbaux, P.; Nam, P.-C.; Nguyen, M. T. *Chem. Phys. Lett.* **2006**, *419*, 139–143.

the agreement for G3 calculations (Scheme 1) is as expected. The discrepancy in the PA of HNCO is surprising because only first row elements are involved and cannot be explained by a more favorable O-protonation;^{17d} as recent G2(MP2) and B3LYP/6-311G++G(d,p) calculations²¹ for H₂NCO⁺ are in good agreement with G3, experimental values^{17c} may be slightly too high; an early DZ-SCF calculation gave a much higher PA (187 kcal/mol)²² than the G3 value of 173.1 kcal/mol. S-Protonation of COS is calculated to be more favorable than O-protonation by 3.5 kcal/mol. Even for CS₂, a more challenging test, the difference between calculated and observed values is only 2.6 kcal/mol. Most of the range of structural types of carboxylic acid chlorides and thio derivatives (Table 1) is covered by the six cations in Scheme 1, but there is only one type of thioacylium ion.

Calculations of PAs are relatively demanding because of the extensive changes in bonding on protonation of a substrate, and the success of G3 is encouraging. The calculation of substituent effects is less demanding, and there is good agreement between G3 and experimental data for eq 1 (see the Results). Consequently, it is expected that the G3 calculations of substituent effects will be reliable, perhaps within 2 kcal/mol.

For substituent effects (Tables 3–5), the lower HF and B3LYP level calculations usually agree within 5 kcal/mol with the G3 calculations and are usually too large (too negative or too positive). Because errors may be systematic, it is expected that the lower level calculations are suitable for calculation of aromatic substituent effects (Table 6).⁹ Comparing HF and B3LYP results with the same 6-31G(d) basis set, the results usually agree within 4 kcal/mol, but there are no clear trends. The least consistent data are for thion derivatives (Table 4).

Overall, B3LYP data are marginally worse than HF, and four of the five discrepancies > 5 kcal/mol are B3LYP (data for PhCOCl and PhOCOC (Table 3), and PhOCSCl and PhSCSCl (Table 4)). The HF and B3LYP results for both benzoyl chloride (Table 3) and benzenesulfonyl chloride (Table 5) agree better than G3 with the corresponding values for D_{X-Cl} calculated from old experimental data,^{23a,b} but substantial corrections (ca. 30 kJ/mol) for precursor internal energy are now considered to be appropriate.^{13b} A very recent correction of the older experimental data for the enthalpy of formation of the benzoyl cation gives a value of 738.8 ± 3.3 kJ/mol,^{23c} 33.8 kJ/mol higher than the previously published value.^{23a} The HBDE for benzoyl chloride is then calculated to be 148 kcal/mol, in satisfactory agreement with the G3 value of 150.1 kcal/mol (Table 3).

Substituent Effects. Logarithms of rate constants for solvolyses of acid chlorides in 97% TFE–water at 25 °C are plotted against D_{X-Cl} in Figure 1. One of the correlation lines (symbol, filled squares) refers to all of the seven substituted benzoyl chlorides (**1**, **3**) for which data are available (Table 2). The other correlation line (symbol, filled circles) refers to five benzene-sulfonyl chlorides (**4**, Z = OMe, Me, H, Cl, and NO₂). These 12 data points are the ones closest to the corresponding correlation lines. Most of the data points for other acid chlorides are close to the line of steeper slope, including chloroformates, thiochloroformates, and a carbamate and their thione derivatives, and the two very electron-rich sulfonyl chlorides (**4**, Z = NMe₂ and the 2,4,6 trimethyl compound, shown with a filled circles symbol and both arrowed in Figure 1). Deviations from the line are surprisingly small, usually less than 6 kcal/mol (in HBDE). Considering the possible errors in the calculations, the diversity

(22) Green, S. *J. Phys. Chem.* **1981**, *85*, 1676–1679.

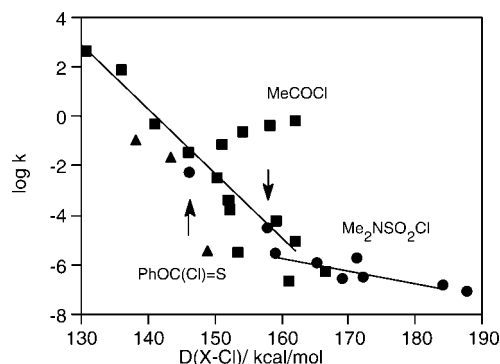
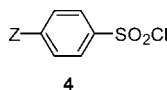


FIGURE 1. Plots of logarithms of rate constants for solvolyses of acid chlorides (RCOCl, squares; RCSCl, triangles; RSO₂Cl, circles) at 25 °C in 97% w/w 2,2,2-trifluoroethanol–water at 25 °C with heterolytic bond dissociation energies (D_{X-Cl}); kinetic data from Tables 1 and 2; D_{X-Cl} from Tables 3–6, and the following additional values (calculated from eqs 6 and 7, and the substituent effects summarized in ref 9); for the acyl series (3), D_{X-Cl} in kcal/mol are: 141, Z = OMe; 146, Z = Me; 152, Z = Cl; 162, Z = NO₂; for the sulfonyl series: (4) D_{X-Cl} in kcal/mol are 159, Z = OMe; 165, Z = Me; 172, Z = Cl; 184, Z = NO₂; the correlation lines refer to benzoyl chlorides ($\log k = (-0.26 \pm 0.02)D_{C-Cl} + 36.7 \pm 2.3$, $r = 0.991$, $n = 7$), and benzenesulfonyl chlorides ($\log k = (-0.052 \pm 0.014)D_{S-Cl} + 2.6 \pm 2.4$ ($r = 0.91$, $n = 5$); the value of D_{C-Cl} for EtOCOCl of 161 kcal/mol is approximate (see ref 3c).

of structures, and the simplicity of the model, the results are encouraging.

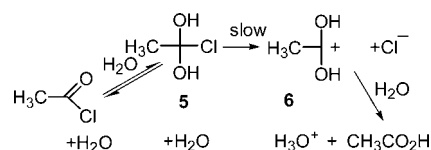


Another correlation having a smaller negative slope is obtained (Figure 1) for sulfonyl chlorides, implying a smaller extent of cleavage of the S–Cl bond in the transition state for solvolysis (possibly decreasing as the S–Cl bond strengthens, because a curve line would fit the data better). The correlation line for 4-substituted benzene sulfonyl chlorides (4) also fits data for Me₂NSO₂Cl and MeSO₂Cl. Rate ratios (RCOCl/RSO₂Cl) vary from almost 10⁷ for R = Me (Table 1) to 62 for R = 4-nitrophenyl (Table 2), reflecting major differences in the extent of X–Cl bond cleavage.

Data for PhOCSCl and PhSCOCl do not fit the carboxylic acid chloride plot (Figure 1), although analyses of solvent effects indicate that both react by an ionization channel in 97T.^{10e-g} These data fit an extrapolation of the sulfonyl plot and may be explained by a change in transition state structure: solvolyses of PhOCSCl are only 7-fold faster than PhOCOCl, whereas two other RCSCl/RCOCl comparisons show values >600 (Table 1).

There are increasingly large deviations for the four data points acyl series from Bu'COCl to MeCOCl (filled squares, Figure 1), and rates increase as HBDE increases, as observed for many S_N2 solvolytic reactions of ethyl and methyl substrates.^{3a,24} Calculations for methanolysis of protonated acetyl chloride support earlier experimental evidence^{3b} for S_N2 solvolyses of

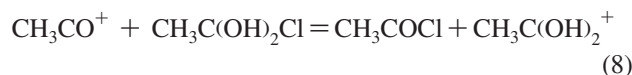
SCHEME 2. Prior Hydration Mechanism for Hydrolysis of Acetyl Chloride²⁶



acetyl chloride.²⁵ Alternatively, solvolysis of acetyl chloride may occur without protonation of the carbonyl group, perhaps by a prior hydration mechanism (Scheme 2).²⁶

We previously^{3b} rejected the possibility that a hydrate (5) could be formed in an initial slow step, because the kinetic solvent isotope effect in methanol of 1.29 is typical of those for S_N1 and S_N2 solvolyses. The alternative possibility of formation of a hydrate (5) in a rapid pre-equilibrium has been rejected in two reviews,²⁷ although it has recently been reconsidered.²⁶

According to G3 calculations (Table S9), addition of water to form 5 is exothermic by 1.8 kcal/mol (cf. 4.4 for addition of MeOH²⁵), and a relatively fast hydration is plausible.²⁶ Chloride ion transfer from 5 to the acetyl cation (eq 8) is favorable by 23.6 kcal/mol.



Assuming that solvolyses of 5 fit the correlation shown in Figure 1 (solvolyses of *tert*-butyl chloride fit within a rate factor of about 2), a rate constant of about 3 s⁻¹ is predicted for solvolyses of 5 in 97% TFE at 25 °C. The value of 3 s⁻¹ is remarkably close to the observed rate constant of 0.69 s⁻¹ for solvolysis of acetyl chloride, consistent with a prior hydration mechanism (Scheme 2). Additional requirements of the prior hydration mechanism are more difficult to evaluate, and it is not expected that loss of chloride ion from 5 could be slow compared with dehydration back to acetyl chloride. Electrostatics provide an alternative explanation of the deviation of the data point for acetyl chloride from Figure 1 (see later discussion of solvent effects).

Substituent Effects on Neutral Substrates. The substituent effects on formation of acylium ions (Table 3) include substantial effects on neutral substrates, which have been evaluated using isodesmic reactions; experimental values (kcal/mol) of ΔH for ketones (eq 9) are -9.9 (Z = H), 6.6 (Z = Cl), 19.6 (Z = NH₂), and 23.4 (Z = OH), values which are reproduced well by theoretical calculations.²⁸ For the above substituents, only calculated data are available for acid chlorides (eq 10); G3 calculations of ΔH (eq 10) in kcal/mol are -11.6 (Z = H), 16.3 (Z = NH₂), and 13.7 (Z = OH).



The negative values for Z = H shows that, relative to hydrogen, the CH₃ group strongly stabilizes a carbonyl group,

(25) Fox, J. M.; Dmitrenko, O.; Liao, L.; Bach, R. D. *J. Org. Chem.* **2004**, *69*, 7317–7328.

(26) Regan, A.; Watt, C. I. F. *J. Phys. Org. Chem.* **2007**, *20*, 180–189.

(27) (a) Kivinen, A. In *Chemistry of Acyl Halides*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1972; Chapter 6. (b) Satchell, D. P. N.; Satchell, R. S. In *Chemistry of Acid Derivatives, Supplement B*; Patai, S., Ed.; Wiley: New York, 1992; Vol. 2, Chapter 13.

(28) Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644–8654.

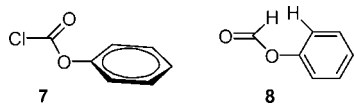
(23) (a) McLoughlin, R. G.; Traeger, J. C. *Org. Mass Spectrom.* **1979**, *14*, 434–438. (b) Chatgililoglu, C.; Griller, D.; Kanabus-Kaminska, J. M.; Lossing, F. P. *J. Chem. Soc., Perkin Trans. 2* **1994**, 357–360. (c) Traeger, J. C. *Eur. J. Mass Spectrometry*, submitted for publication.

(24) Schadt, F. L.; Bentley, T. W.; Scheleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667–7674.

and this substituent effect is incorporated into eq 3 (Table 3). For $Z = \text{Ph}$ (eq 10), the experimental value of $+0.2$ kcal/mol for ΔH is in excellent agreement with the G3 calculated value of $+0.4$ kcal/mol, showing that the same magnitude of stabilizing substituent effects on neutral acid chlorides for $Z = \text{Me}$ and Ph .

The positive values for $Z = \text{OH}$ and NH_2 show that oxygen and nitrogen further stabilize the carbonyl group in neutral ketones²⁸ and acid chlorides^{3c} (eqs 9 and 10), and the same is true for sulfonyl chlorides (Table S8, Supporting Information). Consequently, results such as the relatively high HBDE for NH_2COCl do not imply that NH_2 is destabilizing the cation NH_2CO^+ (also formed by protonation of HNCO (Scheme 1)).

Comparisons of hydride transfer with chloride ion transfer also reveal ground-state effects on neutral substrates; for $Z = \text{Et}$, vinyl, and phenyl (eq 1 and Table 3), the energies agree within 2 kcal/mol, but chloride ion transfer in phenyl chloroformate (**7**) is over 8 kcal/mol less endothermic than hydride transfer (Table 3, footnote i). As the energy calculated for the interconversion of neutral substrates (eq 11) is $+8.5$ kcal/mol, there is a substantial ground-state effect. The formate (**8**) has a low calculated barrier to phenyl rotation, but the chloroformate (**7**) is twisted (in agreement with experimental data in solution²⁹), presumably to avoid repulsion between the Cl and an *ortho*-hydrogen.

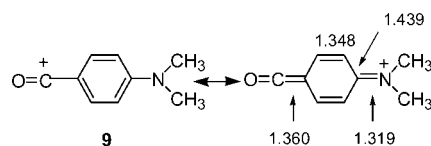


For sulfonyl chlorides, energies for hydride and chloride transfers agree within 1 kcal/mol for $Z = \text{vinyl}$, phenyl and NMe_2 (Table 5, footnotes g, i, and j), and even for the hindered mesitylene derivative (Table 6, footnote f).

Solvent Effects. Good correlations of solution phase rate data with gas-phase energies for carbocations can be observed (e.g., for reactions of α,α -dimethylbenzyl cations with water in TFE/water^{30a} and $\text{S}_{\text{N}}1$ solvolyses of bridgehead substrates^{30b}). However, for acid chlorides, mechanistic changes may occur. Also, the substrates (Tables 1 and 2) contain three types of heteroatom (N, O, and S), in addition to the Cl leaving group, so there will be other complications due to hydrogen bonding and/or protonation between substrates and solvents. Various ion-pair intermediates are also implicated.⁴⁻⁶ Considering the additional complexities of reactions of acid chlorides in solution, only approximate correlations with gas-phase data are expected.

Solvent molecules can be included explicitly in theoretical calculations. A recent study of methanolysis of acetyl chloride included up to six molecules of methanol.²⁵ MO theories have recently been applied to investigate the mechanisms of solvolytic reactions of various aliphatic chlorides.³¹ Necessarily, the methods required are currently much more approximate than G3 theory, but the results provide important new insights.

SCHEME 3. Delocalized Structure of the Dimethylaminobenzoyl Cation (**9**)



Comparisons of gas phase and solution reactivity are also instructive. Free energies of transfer of hydroxide between various carbenium ions (R^+) spanning a 102 kcal/mol range in the gas phase correlate with corresponding values of $\text{p}K_{\text{a}}$ in aqueous solution spanning about 60 kcal/mol.³² Rate constants for solvolyses of cumyl chlorides in 80% acetone–water at 25 °C, the reference reaction for σ^+ constants, show greater attenuation – about 40% of the substituent effect (ρ^+) calculated for gas phase HBDEs (from AM1 geometries and single point B3LYP/6-311+G(2d,2p) energies).³³ Refining the calculations by incorporating various continuum models for solvent effects led to ρ^+ values only 24% greater than experiment.³³

The slope of the line shown in Figure 1 for aroyl chlorides (**3**) corresponds to about 35% of the gas-phase substituent effect,^{9a} but a 50% higher slope is observed for solvolyses in the more weakly nucleophilic solvent, hexafluoropropan-2-ol.^{9a} A nucleophilic component to solvation is consistent with extensive experimental and theoretical evidence, even for solvolyses of relatively hindered substrates such as *tert*-butyl chloride.^{31,34a} It is envisaged that very electron-rich sulfonyl chlorides (e.g., **4**, $Z = \text{NMe}_2$) react by concerted cationic bimolecular mechanisms, in which bond breaking takes place ahead of bond formation.^{11a,34b}

There are well-established effects of molecular size on the stabilization of both cations^{3a} and anions;³⁵ e.g., the acetyl cation is estimated to have an enthalpy of solvation 16 kcal/mol greater than the *tert*-butyl cation in FSO_3H .^{3a} Applying the polar continuum model (PCM),³⁶ the energy difference (Δ) between ions in the gas phase and in a polar solvent such as water decreased from the acetyl cation ($\Delta = 64$ kcal/mol) to 54 for Bu^+CO^+ , 52 for Me_2NCS^+ , and to 48 kcal/mol for the dimethylaminobenzoyl cation (**9**) having a delocalized positive charge (Scheme 3). In contrast, the same PCM calculation for the neutral acid chlorides showed almost identical and small energy decreases of only 4.1 kcal/mol for CH_3COCl and 3.6 kcal/mol for Bu^+COCl . The PCM calculations indicate that when correlations (such as Figure 1) are made between reactivity in the gas phase and in polar solvents, small cations such as acetyl could deviate by about 10 kcal/mol (as observed in Figure 1), simply because of electrostatic effects.

Conclusions

The importance of cationic processes for carboxylic acid chlorides is shown by the negative slope of the correlation (with some deviations, Figure 1) of logarithms of rate constants for solvolyses in 97% w/w trifluoroethanol–water at 25 °C with

(29) Bredikhin, A. A.; Kirillovich, V. A.; Frolova, L. V.; Vereshchagin, A. N. *Russ. Chem. Bull.* **1989**, 38, 2476–2479.

(30) (a) Richard, J. P.; Jagannadham, V.; Amyes, T. L.; Mishima, M.; Tsuno, Y. *J. Am. Chem. Soc.* **1994**, 116, 6706–6712. (b) Abboud, J.-L. M.; Herreros, M.; Notario, R.; Lomas, J. S.; Mareda, J.; Müller, P.; Rossier, J.-C. *J. Org. Chem.* **1999**, 64, 6401–6410.

(31) (a) Ruff, F.; Farkas, Ö. *J. Phys. Org. Chem.* **2008**, 21, 53–61. (b) Martínez, A. G.; Vilar, E. T.; Barcini, J. O.; de la Moya Cerero, S. *J. Org. Chem.* **2005**, 70, 10238–10246.

(32) Herrero, R.; Quintanilla, E.; Müller, P.; Abboud, J.-L. M. *Chem. Phys. Lett.* **2006**, 420, 493–496.

(33) DiLabio, G.; Ingold, K. U. *J. Org. Chem.* **2004**, 69, 1620–1624.

(34) (a) Bentley, T. W.; Garley, M. S. *J. Phys. Org. Chem.* **2006**, 19, 341–349. (b) Thea, S.; Carpanelli, C.; Cevasco, G. *Eur. J. Org. Chem.* **2001**, 151–154.

(35) DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, 14, 146–153.

(36) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, 255, 327–335.

calculated gas-phase heterolytic bond dissociation energies (HBDEs); e.g., for RCOCl, including acyl and carbamoyl chlorides and chloroformates, thio, thione, and dithio-chloroformates, and electron-rich sulfonyl chlorides (RSO₂Cl). Most sulfonyl chlorides and some chloroformates give another correlation of very low negative slope with HBDE, indicating a mechanistic change to a process with relatively little cationic character.

The exceptionally high reactivity of acetyl chloride (Figure 1) is explained either by favorable solvation of the relatively small acetyl cation, and/or by strong nucleophilic solvent assistance (S_N2 character), because nucleophilic attack by solvent on the developing cation is relatively unhindered. A prior hydration mechanism (Scheme 2) is also possible, but less likely.

G3 calculations account well (± 3 kcal/mol) for the enthalpy changes of reactions leading to formation of acylium and sulfonyl cations in the gas phase, including protonation of neutral substrates (Scheme 1) and hydride ion transfer (eq 1). HBDEs for carboxylic acid chlorides (RCOCl) and sulfonyl chlorides (RSO₂Cl) can be calculated from substituent effects (eqs 3–5), relative to values of HBDE for CH₃COCl and CH₃SO₂Cl based on both G3 and experimental data.^{9a}

Calculations

Calculations were performed using the standard Gaussian 03³⁷ at the Rutherford Appleton laboratory (Columbus and Magellan services) using the EPSRC National Service for Computational Chemistry software (NSCCS); the default allocation of memory of 48 MB was increased to as much as 4 GB for the larger systems. For the calculations of proton affinities, it is likely that the vibrational contributions to the thermal enthalpy correction for B and HB⁺ in the protonation equation ($B + H^+ \rightarrow BH^+$) substantially cancel, so the main noncancellable contribution comes from the $(3/2)RT$ translational contribution for the proton plus the extra RT to convert E to H, giving a total of $(5/2)RT$.

Acknowledgment. I thank S. Wilsey for assistance in using NSCCS, J. C. Traeger (ref 23c) and C. I. F. Watt (ref 26) for

preprints and other helpful correspondence, and L. Radom and M. Yanez for helpful comments.

Supporting Information Available: G3 calculations for Scheme 1 (Table S1). G3 calculations for eq 1 (Table S2). G3 calculations for Table 3 (Table S3). G3, HF/6-31G(d), and B3LYP/6-31G(d) calculations for acyl; and thioacyl substrates in Table 4 (Table S4). G3, HF/6-31G(d), and B3LYP/6-31G(d) calculations for sulfonyl substrates in Table 5 (Table S5). HF/6-31G(d) and B3LYP/6-31G(d) calculations for acyl and sulfonyl substrates in Table 6 (Table S6). Total energies for carboxylic acid chlorides and acylium cations, calculated for HF/6-31G(d), B3LYP/6-31G(d), and G3 levels of theory (Table S7). Revised enthalpies of reaction ($ZSO_2Cl + C_2H_6 = ZCH_3 + CH_3SO_2Cl$) for three levels of theory, and revised gas-phase enthalpies of formation at 298 K of sulfonyl chlorides by the procedure described in ref 9a (units: kcal/mol) (Table S8). HF-6-31G(d) and G3 calculations relevant to the prior hydration mechanism for hydrolysis of acetyl chloride (Scheme 2) (Table S9). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO800841G

(37) *Gaussian 03, Revision C.01*: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian, Inc.*, Wallingford, CT, 2004.