Sulfur–Chlorine Bond Dissociation Enthalpies in Methane- and Benzene-sulfonyl Chlorides

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Sulfur–chlorine bond dissociation enthalpies in methane- and benzene-sulfonyl chlorides, $D(RSO_2–Cl)$, were measured by photoacoustic calorimetry and were found to be equal within experimental error (295 kJ mol^{-1}). The implicit absence of a stabilizing effect of the phenyl group in $PhSO_2^•$ is consistent with the known spectroscopic properties of sulfonyl radicals but conflicts with the currently accepted thermochemical data. Appearance energy measurements lead to values for the radical ionization potentials, $E_i(MeSO_2^•) = 8.67$ and $E_i(PhSO_2^•) = 7.49$ eV and for the enthalpy changes associated with the heterolytic cleavages $RSO_2Cl \rightarrow RSO_2^+ + Cl^-$ where a substituent effect is observed.

The thermochemistry of sulfur-centred free radicals and heats of formation of sulfur containing molecules are of considerable importance in oil, coal and atmospheric chemistry. Benson critically reviewed the subject in 1978[1] and many of his conclusions have stood the test of time. The heats of formation of sulfur containing compounds that he cited, generally determined by bomb calorimetry, have not been significantly revised in the interim. Bond dissociation energies that were reported were often based on the activation energy for the thermolysis of a sulfur containing molecule to alkyl and sulfur-centred radicals. These require revision to the extent that enthalpies of formation for simple alkyl radicals have been reassessed. The effects of these changes have been fairly substantial and have recently been tabulated.[2] However, the thermochemistry for some of the sulfonyl radicals that appeared in the Benson review[1] appears to be in conflict with the known properties of these species.

It was suggested[1] that bond dissociation energies of $PhSO_2–Me$ was 58.5 kJ mol^{-1} lower than that in $MeSO_2–Me$. One might infer that the result was due to a stabilizing effect of the phenyl group. The conclusion was based on a reinterpretation of existing experimental data.[1] Nevertheless, both the EPR[3] and optical absorption spectra[4] of sulfonyl radicals indicate they are σ species with the unpaired electron being highly localized on the SO_2 moiety.[5] Multiple scattering Xα calculations[4] support these findings and show that the spin distribution for the unpaired electron in $MeSO_2^•$ is 42% on sulfur and 44% on the oxygens while for $PhSO_2^•$ there is very little difference with the corresponding figures being 43% and 39%. The calculations appear to be quite reliable since they predicted the observed optical transitions for both of these sulfonyl radicals with remarkable accuracy.[4]

In general terms, the problem is more significant than the $MeSO_2^•/PhSO_2^•$ dichotomy would suggest, since any deficiencies in the thermochemistry for $MeSO_2^•$ have an impact upon an important process in atmospheric chemistry,[6] reaction (1). We have therefore used photoacoustic calorimetry and appearance energy methods to measure some of the thermodynamic properties of sulfonyl radicals in an attempt to address the problem.

$$Me^• + SO_2 \longrightarrow MeSO_2^• \qquad (1)$$

Results and Discussion

Photoacoustic Calorimetry.—The technique of photoacoustic calorimetry has been used to determine the enthalpies of a variety of free radical reactions in solution and hence bond dissociation enthalpies.[7,8] In non-polar solvents, the results obtained have been in excellent agreement with gas phase data whenever comparison has been possible. We have therefore applied the method to determine sulfur–chlorine bond dissociation enthalpies in methanesulfonyl and benzenesulfonyl chloride to see if there is any special stabilizing effect due to the phenyl group.

Laser photolysis of a mixture of di-*tert*-butyl peroxide (0.1–0.9 mol dm^{-3}), methanesulfonyl chloride (0.5 mol dm^{-3}) or benzenesulfonyl chloride (0.15–0.3 mol dm^{-3}) in triethylsilane as solvent in the photoacoustic sample cell gave rise to reactions (2)–(5).[9,10] Of these processes, reactions (2)–(4) provide a route to measuring the thermochemistry of interest. However, hydrogen abstraction at the ethyl groups of triethylsilane, reaction (5), is a significant side reaction that must also be taken into account.[9,11]

$$Bu^tO–OBu^t \longrightarrow 2\,Bu^tO^• \qquad (2)$$

$$2\,Bu^tO^• + 2\,Et_3SiH \longrightarrow 2\,Bu^tOH + 2\,Et_3Si^• \qquad (3)$$

$$2\,Et_3Si^• + 2\,RSO_2Cl \longrightarrow 2\,Et_3SiCl + 2\,RSO_2^• \qquad (4)$$

$$2\,Bu^tO^• + 2\,Et_3SiH \longrightarrow 2\,Bu^tOH + 2\,Et(-H)Et_2SiH \qquad (5)$$

The heat released in these reactions produced a shock wave that was detected by a transducer clamped to the bottom of the cell. Plots of the wave amplitudes *versus* optical densities of the solutions at different concentrations of di-*tert*-butyl peroxide were linear and their slopes (a_r) were used to define, ΔH_{obs}, the enthalpy change observed, eqn. (6). In this equation 354.8 kJ mol^{-1} represents the energy of the laser photons and the remaining parameter, a_s, is the slope of a plot obtained for a standard solution made up of the appropriate sulfonyl chloride in triethylsilane but in which various concentrations of *o*-hydroxybenzophenone were used in place of di-*tert*-butyl peroxide. This material serves as an excellent calibrant of

$$-\Delta H_{obs} = 354.8 a_r/a_s \text{ kJ mol}^{-1} \qquad (6)$$

Table 1 Values of ΔH_{obs} and D(R–Cl) obtained by photoacoustic calorimetry at 298 K

Compound	$\Delta H_{obs}{}^{a}$/ kJ mol^{-1}	D(R–Cl)^{b}/ kJ mol^{-1}
CCl_4	−274	306^{c}
$MeSO_2Cl$	−290	294
$PhSO_2Cl$	−288	295

[a] Relative error ±2 kJ mol^{-1}. [b] Relative error ±4 kJ mol^{-1}; absolute error ±12 kJ mol^{-1} including a contribution of ±8 kJ mol^{-1} from D(CCl$_3$–Cl). [c] Ref. 14.

the photoacoustic instrument because it converts all of the absorbed radiation into heat within a few nanoseconds.[8a]

The enthalpy change observed is related to the thermochemistry of interest *via* eqn. (7), where Φ is the quantum yield for

$$-\Delta H_{obs} = 354.8 - \Phi\Delta H_r = 345.8 - \Phi[\alpha\Delta H_{2\text{-}4} + (1-\alpha)\Delta H_{2,5}] \quad (7)$$

photolysis of the peroxide in the reaction mixture (Φ = 0.876)[12] and ΔH_r is the net enthalpy change associated with the reactions (2)–(5). $\Delta H_{2\text{-}4}$ and $\Delta H_{2,5}$ represent the combined heats of reactions (2)–(4) and reactions (2) and (5) respectively, *i.e.* $\Delta H_{2\text{-}4} = \Delta H_2 + 2\Delta H_3 + 2\Delta H_4$ and $\Delta H_{2,5} = \Delta H_2 + 2\Delta H_5$. The remaining parameter, α, is the ratio of rate constants $k_3/(k_5 + k_3)$ and defines the extent to which the two reaction channels for the *tert*-butoxyl radicals contribute to the enthalpy change.

The value of α can be estimated from literature data[9,13] to be 0.75. However, the use of eqn. (7) as a means of determining the thermochemistry of interest introduces a good deal of error since additional data on bond dissociation enthalpies such as D(Et$_3$Si–H), D(Bu^{t}O–OBu^t), D(Bu^{t}O–H) and D(Et$_3$Si–Cl) have to be combined with the measured value of ΔH_{obs} to yield D(RSO$_2$–Cl), the result of interest. Moreover, while the value of α indicates that reaction (3) makes up the dominant pathway for loss of *tert*-butoxyl radicals, errors in the published rate constants[9,13] that were used for its derivation have a significant impact on the final result since $\Delta H_{2\text{-}4}$ are highly exothermic while the combination $\Delta H_{2,5}$ is close to being thermoneutral.

To circumvent these difficulties, we chose carbon tetrachloride as a standard because D(Cl$_3$C–Cl) = 306 ± 8 kJ mol^{-1} is reasonably well established.[14] We used it under the same conditions in place of the sulfonyl chlorides, *viz.*[15] reaction (4a).

$$2\,Et_3Si^{\bullet} + 2\,CCl_4 \longrightarrow 2\,Et_3SiCl + 2\,CCl_3^{\bullet} \quad (4a)$$

Once ΔH_{obs} was measured for CCl$_4$ many of the difficulties associated with eqn. (7) were eliminated as shown in eqns. (8)–(11).

$$\Delta H_{obs}(CCl_4) - \Delta H_{obs}(RSO_2Cl) = \Phi\alpha[\Delta H_{2\text{-}4a}(CCl_4) - \Delta H_{2\text{-}4}(RSO_2Cl)] \quad (8)$$

$$\Delta H_{obs}(CCl_4) - \Delta H_{obs}(RSO_2Cl) = \Phi\alpha[\Delta H_{4a}(CCl_4) - \Delta H_4(RSO_2Cl)] \quad (9)$$

since $$\Delta H_4/2 = D(RSO_2\text{–}Cl) - D(Et_3Si\text{–}Cl) \quad (10)$$

$$\Delta H_{4a}/2 = D(CCl_3\text{–}Cl) - D(Et_3Si\text{–}Cl) \quad (10a)$$

then $$D(RSO_2\text{–}Cl) - D(CCl_3\text{–}Cl) = [\Delta H_{obs}(RSO_2Cl) - \Delta H_{obs}(CCl_4)]/2\Phi\alpha \quad (11)$$

The use of CCl$_4$ as a standard allows the relative values of D(PhSO$_2$–Cl) and D(MeSO$_2$–Cl) to be determined with good precision. To convert the relative values to absolute values, one applies the known value of D(CCl$_3$–Cl).[14] In addition, using CCl$_4$ as a standard eliminates any errors in the photoacoustic experiment due to small volume changes that occur in the reactions.[16] Finally, the impact of experimental errors in the value of α are substantially reduced since this parameter modifies the difference between the enthalpies of reaction.

Two critical requirements for the photoacoustic experiment are that the radicals formed have long lifetimes with respect to the response of the instrument and that the heat release, ΔH_{obs}, is fast on this timescale. We have established experimental conditions[7] that satisfy the first criterion by ensuring that the laser flux and hence radical concentrations were sufficiently low that radical–radical processes did not contribute to the heat detected. This was verified in the present work by demonstrating that the amplitudes of the photoacoustic signals were proportional to the laser light intensity, which was varied by the use of neutral density filters. Bimolecular radical reactions would have contributed in a non-linear fashion as the radical concentration was changed.

Chlorine abstraction from sulfonyl chlorides by triethylsilyl radicals is extremely efficient (k_4 = 4 × 10^9 dm^3 mol^{-1} s^{-1}).[10] However, hydrogen abstraction from the silane itself, reaction (3), is a much slower process (k_3 = 5.7 × 10^6 dm^3 mol^{-1} s^{-1})[9] and dictated the use of high concentrations of Et$_3$SiH so that reactions (2)–(4) were complete in a time that was short with respect to the instrumental response.*

Values of the enthalpies for the processes under consideration and the bond dissociation energies of interest are shown in Table 1. The data show that bond dissociation energies in methane- and benzene-sulfonyl chlorides are equal within experimental error and that there is no special stabilizing effect associated with the presence of the aromatic ring. The results are entirely consistent with the assignment of the optical absorption spectra of sulfonyl radicals[4] and with EPR results,[3] both of which show that there is minimal delocalization of the unpaired electron onto the benzene ring of PhSO$_2^{\bullet}$. In addition, our thermochemical measurements are supported by kinetic data which show that the rate constants for fluorine abstraction by triethylsilyl radicals are quite similar for MeSO$_2$F, (1.3 ± 0.1) × 10^6 dm^3 mol^{-1} s^{-1}, and *p*-MeC$_6$H$_4$SO$_2$F, (0.9 ± 0.1) × 10^6 dm^3 mol^{-1} s^{-1}.[10]

The results obtained in this work call into question previous interpretations of literature data on sulfonyl radicals.[1] These interpretations generally attempt to harmonize the results of a wide variety of experiments. In instances where thermodynamic data are inferred from reaction kinetics, *A*-factors are sometimes adjusted in order to make better sense of the experimental results. Such was the case for sulfonyl radicals.[1] This work provides another piece of information for those who seek to solve the more general puzzle of sulfonyl radical thermochemistry. Other pieces include sound thermochemical data on sulfonyl compounds,[17] kinetic data on the thermolysis of RSO$_2$Me,[18] and recent data on the heats of formation of alkyl radicals.[2] A logical starting point for a more general review would be to assume that D(R′SO$_2$–R) are independent of R′ for a given R, as suggested by this work. Other experimental data

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* The instrumental response may not be limited by the response of the transducer but may be affected by the laser beam/sample cell geometry. Accordingly, we established the response time of the instrument by measuring the enthalpy change for the reaction Bu^{t}OOBu^t + 2 PhOH$\rightarrow$2 Bu^{t}OH + 2 PhO$^{\bullet}$ and by establishing the maximum lifetime for the reaction which led to the correct thermochemistry (P. Mulder, O. W. Saastad and D. Griller, *J. Am. Chem. Soc.*, 1987, **91**, 3747).

can be used to look at the thermochemistry for the fragmentation of sulfonyl radicals [reaction (12)][19] and at the reaction (1), which is a process of importance in atmospheric chemistry. We have not explored these possibilities in this paper since they are tangential to this work and are more appropriate to a review than a report of experimental information.[20]

$$\mathrm{RSO_2^{\bullet}} \longrightarrow \mathrm{R^{\bullet}} + \mathrm{SO_2} \qquad (12)$$

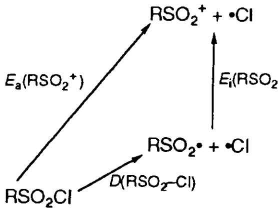
Appearance Energy Measurements.—We measured the appearance energies, E_a, for the reactions (13) (R = Me and Ph) using a mass analyser equipped with an energy-selected electron impact ion source.[21]

$$\mathrm{RSO_2Cl} + \mathrm{e} \longrightarrow \mathrm{RSO_2^+} + \mathrm{Cl^{\bullet}} + 2\mathrm{e} \qquad (13)$$

The E_a values were found to be 11.68 and 10.54 eV for R = Me and Ph, respectively. The kinetic energy release* for these reactions have recently been measured and found to be small, *i.e.* 0.015 and 0.025 eV for $MeSO_2Cl$ and $PhSO_2Cl$, respectively.[22] Therefore, the appearance energies are related to the thermodynamic parameters of interest *via* eqn. (14).

$$E_a(\mathrm{RSO_2^+}) = \Delta H_f(\mathrm{RSO_2^+}) + \Delta H_f(\mathrm{Cl^{\bullet}}) - \Delta H_f(\mathrm{RSO_2Cl}) \qquad (14)$$

A cycle with the connection of appearance energy, bond dissociation enthalpy and ionization potential of the radical can be written as in Scheme 1. The data described above lead to $E_i(\mathrm{MeSO_2^{\bullet}}) = 8.67$ and $E_i(\mathrm{PhSO_2^{\bullet}}) = 7.49$ eV. Interestingly, the result for R = Me is in good agreement with the value of 8.5 eV calculated by Multiple Scattering Xα methods.[22a] However, theory was less reliable for R = Ph where the calculated ionization potential was 6.9 eV.[22a] This reflects the fact that the Xα method is less satisfactory when the molecules under investigation do not have a roughly spherical shape.



Scheme 1

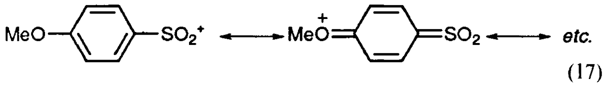
Calculations of thermochemical data on species containing the sulfonyl moiety can be extended by using the data and methods described above and encompass radicals, cations and neutrals. For example, since the heat of formation of the $PhSO_2^{\bullet}$ radical is −160 kJ mol^{-1},[17b,18b] the heats of formation of corresponding sulfonyl chloride and sulfonylium ion are calculated to be −334 and 883 kJ mol^{-1} respectively, using the connection cycle reported in Scheme 1.

While the homolytic bond dissociation enthalpies of the sulfonyl chlorides were obtained by photoacoustic calorimetry, the heterolytic equivalents [reaction (15)] can be calculated by combining the appearance energies with the electron affinity of chlorine,[23] [reactions (13), (15), (16)].

$$\mathrm{RSO_2Cl} \longrightarrow \mathrm{RSO_2^+} + \mathrm{Cl^-} \qquad (15)$$

$$\mathrm{Cl^{\bullet}} + \mathrm{e} \longrightarrow \mathrm{Cl^-} \qquad (16)$$

The data give $\Delta H_{15}(\mathrm{MeSO_2Cl}) = 778$ kJ mol^{-1} and $\Delta H_{15}(\mathrm{PhSO_2Cl}) = 668$ kJ mol^{-1} and lead to the interesting finding that the heterolytic bond dissociation enthalpy is subject to a large substituent effect. Delocalization of the positive charge onto the benzene ring of $PhSO_2^+$ is the most obvious explanation. Some arenesulfonylium ions with a strong stabilizing *para*-substituent such as MeO or Me_2N have been characterized by Olah *et al.*[24] using low temperature NMR experiments and rationalized in terms of additional resonance stabilization [reaction (17)].



(17)

Experimental

Materials.—All of the materials used in this work were commercially available and used as received with the exception of di-*tert*-butyl peroxide. Di-*tert*-butyl peroxide was washed with an aqueous solution of silver nitrate and then with water. It was dried over magnesium sulfate and was finally passed through a column of neutral alumina.

Apparatus for Photoacoustic Calorimetry.—The photoacoustic spectrometer has been described in detail elsewhere.[7] Briefly, pulses from a nitrogen laser (Molectron UV24, 337.1 nm, pulse width 10 ns, output 10 mJ/pulse, repetition rate 5 Hz) were used to photolyze solutions contained in a standard quartz flow cell (Hellma 171 QS). An iris was used to limit the laser light so that only a fine beam passed through the sample cell. Each laser pulse initiated a series of reactions in the solution along the trajectory of the photolyzing beam. The heat evolved in these processes caused a shock wave in the solution that was transmitted at the speed of sound to the cell wall where it caused a vibration. The first vibration and subsequent reflections were detected by using a piezoelectric transducer (Panametrics V101, 0.5 MHz response) and the signals obtained were amplified (Panametrics 5670 preamplifier) and were then stored and averaged in an oscilloscope (Tektronix 7603). From the perspective of this work, only the peak due to the first vibration was of interest. This was recorded in the microsecond time domain and, hence, before the radical products of the reactions under investigation had undergone any significant decay.[7] The amplitude of the signal was shown to be proportional to the amount of heat liberated by changing the concentration of the photolabile substrate and varying the laser light intensity through the use of neutral density filters.

In all experiments, carefully deoxygenated solutions were handled in a flow system. They were first passed through a cuvette situated in a UV–VIS spectrometer (Hewlett-Packard 8450A) where their absorbances were measured and they were then run through a second cuvette that functioned as the sample cell of the photoacoustic calorimeter. The use of a flow system eliminated problems that might have arisen as a result of the formation of light-absorbing products. Signals from 256 laser shots were averaged to produce a data point.

Apparatus for Mass Spectrometry.—Sulfonyl chlorides were ionized in the gas phase (*ca.* 10^{-7} Torr*) by the impact of an

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* The kinetic energy release originates from two different sources: the excess energy of the activated complex and the reverse critical energy; for reviews, see: (*a*) J. L. Holmes, *Org. Mass Spectrom.*, 1985, **20**, 169; (*b*) R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, *Metastable Ions*, Elsevier, Amsterdam, 1973.

* 1 Torr = 133.322 Pa.

electron beam that had been energy resolved (dispersion 0.08 eV) by an electrostatic electron monochromator. Ions were detected by a quadrupole mass spectrometer coupled with a microprocessor data system. The technique has been described in detail elsewhere.[21]

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