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S−H Bond Dissociation Enthalpies in Thiophenols: A Time-Resolved Photoacoustic Calorimetry and Quantum Chemistry Study[†]

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Time-resolved photoacoustic calorimetry (TR-PAC) and quantum chemistry calculations were used to investigate the energetics of sulfur−hydrogen bonds in thiophenol and four *para*-substituted thiophenols, 4-XC_6H_4SH (X = CH_3, OCH_3, Cl, and CF_3). The result obtained for the PhS−H gas-phase bond dissociation enthalpy, derived from the PAC experimental results in solution, is 349.4 ± 4.5 kJ mol^{-1}. This value is significantly higher than recent literature values but agrees with a value suggested some 20 years ago in a widely used review. The PAC result also concurs with the value computed at a high theory level, G3(MP2), 346.8 kJ mol^{-1}. The data obtained for the substituted thiophenols support the idea that substituent effects are less pronounced on the S−H bond dissociation enthalpy than on the O−H bond dissociation enthalpy of the corresponding phenols.

Introduction

The role played by sulfur-centered radicals in the chemistry of coal, oil, atmospheric pollution, and biological systems is well-established.[1] To fully understand this chemistry, reliable thermochemical data are needed, and because we are dealing with radical species, bond dissociation enthalpies are of major importance. A class of sulfur-centered radicals, thiophenoxy radicals, has gained special attention because they can help in understanding the chemistry of the related phenoxy radicals, which is of enormous interest because of their antioxidant activity.[2] These studies involved the comparison between the substituent effects on O−H and S−H bond dissociation enthalpies in substituted phenols and thiophenols, respectively.[3] Central to this discussion is the gas-phase S−H bond dissociation enthalpy in thiophenol itself, *DH*°(PhS−H), defined as the enthalpy of reaction 1 at 298.15 K.

$$\mathrm{PhSH(g)} \rightarrow \mathrm{PhS^{\bullet}(g)} + \mathrm{H^{\bullet}(g)} \qquad (1)$$

The literature values of *DH*°(PhS−H) range from 331 to 349 ± 8 kJ mol^{-1} and were subject to several reevaluations (see Discussion). Given the disparity among the various results for this key value, we decided to investigate the problem using photoacoustic calorimetry (PAC), which is especially suited for the study of transient species in solution. In fact, PAC is probably the most reliable method for obtaining solution-phase bond dissociation enthalpies, which can then be related to the gas-phase values using a well-established procedure.[4] However, this technique has some limitations, one of which is caused by the absorption of the sample molecule at the incident wavelength used to initiate the reaction (see Experimental Section). Although this is the case for thiophenol and substituted thiophenols, we found that the time-resolved version of the technique (TR-PAC) allows the problem to be circumvented. Therefore, in the present study, we report the bond dissociation enthalpies of thiophenol and some substituted thiophenols obtained with TR-PAC. These results were complemented by high-level theoretical methods, using both ab initio and density functional theory calculations.

Theory of Photoacoustic Calorimetry. Although the theory that allows thermochemical data to be extracted from photoacoustic calorimetry experiments is well-established,[5,6] a brief outline is given here for the sake of clarity. The PAC technique involves the measurement of a volume change that occurs when a laser pulse strikes a solution containing the reactants and initiates a chemical reaction. This sudden volume change generates an acoustic wave, which can be recorded by a sensitive microphone such as an ultrasonic transducer. The resulting photoacoustic signal, *S*, is defined by eq 2, where *T* is the solution transmittance, *E* is the incident laser energy, and *K* is a calibration constant, dependent on the instrumental specifications and geometry and on the thermoelastic properties of the solution.

$$S = K\phi_{\mathrm{obs}}(1 - T)E \qquad (2)$$

The parameter ϕ_{obs} is the apparent fraction of photon energy released as heat, which, when multiplied by the molar energy of the laser photons, corresponds to the measured apparent enthalpic change, $\Delta_{\mathrm{obs}}H$. It has been shown that ϕ_{obs} consists of a thermal contribution due to the enthalpy of the reaction and a reaction volume contribution due to the differences between the partial molar volumes of the reactants and products.[7] The latter leads to the introduction of a correction factor in

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calculations of the reaction enthalpy through an energy balance.[6,8]

$$\Delta_r H = \frac{E_m - \Delta_{obs} H}{\Phi_r} + \frac{\Delta_r V}{\chi} \qquad (3)$$

In this equation, E_m represents the molar photon energy, and Φ_r is the reaction quantum yield. The correction term includes the reaction volume change, $\Delta_r V$, and the adiabatic expansion coefficient of the solvent, χ. This parameter depends on its thermoelastic properties, namely the isobaric expansion coefficient α_p, the heat capacity C_p, and the density ρ.

$$\chi = \frac{\alpha_p}{\rho C_p} \qquad (4)$$

Equation 2 is the basis for "classical" photoacoustic calorimetry, usually called non-time-resolved PAC (in the sense that the time dependence of the signal S is not analyzed; see below). Its application is valid only when the process generating the photoacoustic signal is much faster than the transducer response.[9] In this case, the time profile of the photoacoustic wave will depend only on the instrumental response and not on the rate of the process, allowing for a direct correspondence between its amplitude S and the apparent heat fraction ϕ_{obs}. On the other hand, processes that are much slower than the transducer response will give rise to virtually no signal. In the intermediate regime, each process with a different rate will give rise to a unique waveform. For instance, in a system where one or more such processes occur, the signal obtained will be a convoluted waveform that will appear phase-shifted and reduced in amplitude as a result of the presence of components with longer time scales. A deconvolution analysis of such data yields the magnitude of each of the signal-inducing events (as well as information on their rates).[10] This is the basis of time-resolved photoacoustic calorimetry (TR-PAC). The analysis involves the preprocessing of the photoacoustic waveform, which is normalized for its respective absorbance ($1 - T$) and incident laser energy E, as indicated in eq 2. Extraction of ϕ_{obs} for the process(es) is then accomplished by the deconvolution of the waveform, facilitated by the use of commercially available software.[11] Reaction enthalpies for each process are then calculated as before.[5c] For instance, considering a two-step sequential reaction, the enthalpy of the first step is given by eq 3 (with $\Delta_{obs}H = \Delta_{obs}H_1$, calculated from the amplitude $\phi_{obs,1}$ obtained from the deconvolution) and the enthalpy of the second by eq 5 (note that only the first step is light-initiated but the yield of all of the steps is dependent on the quantum yield for the first one).

$$\Delta_r H_2 = \frac{-\Delta_{obs} H_2}{\Phi_r} + \frac{\Delta_r V_2}{\chi} \qquad (5)$$

Experimental Section

Materials. Benzene (Aldrich) was of HPLC grade and was used as received. Thiophenol (Aldrich, >99%) was used as received. Thiocresol (Aldrich) was purified by sublimation. 4-Chlorothiophenol (Aldrich) was recrystalized once from an ethanol−water mixture. 4-Methoxythiophenol (Aldrich, 97%) and 4-(trifluoromethyl)thiophenol (ABCR GmbH, >95%) were vacuum distilled. Di-*tert*-butylperoxide (Aldrich) was purified according to a literature procedure.[12] *o*-Hydroxybenzophenone (Aldrich) was recrystalized twice from an ethanol−water mixture.

Photoacoustic Calorimetry. In this work, we used both time-resolved (TR-PAC) and non-time-resolved (PAC) versions of the photoacoustic calorimetry technique. The photoacoustic calorimeter setup has been described in detail,[6] with the exception of the introduction of an optical trigger in the laser path. This piece of equipment (which was not necessary for the nonresolved technique) is essential for TR-PAC, because it allows for a precise definition of the starting point on the time scale of the photoacoustic wave, as needed for the correct deconvolution of the signal. The experimental technique was also presented before.[6] Briefly, argon-purged solutions in benzene of ca. 0.4 M of di-*tert*-butylperoxide and each thiophenol (in the adequate concentration; see Results and Discussion) were flowed through a quartz flow cell (Hellma 174-QS). The solutions were photolyzed with pulses from a nitrogen laser (PTI PL 2300, 337.1 nm, pulse width 800 ps). The incident laser energy was varied by using neutral-density filters (ca. 5−30 μJ/pulse at the cell, flux < 40 J m^{-2}). Each pulse induced a volume change in solution, producing an acoustic wave that was detected by a piezoelectric transducer (Panametrics V101, 0.5 MHz) in contact with the bottom of the cell. The signals were amplified (Panametrics 5662) and measured by a digital oscilloscope (Tektronix 2430A). The signal-to-noise ratio was improved by averaging 32 acquisitions, and each data point for analysis at each of four different incident laser energies used was determined five times. The apparatus was calibrated by carrying out a photoacoustic run using an optically matched (within 2% absorbance units at 337.1 nm) solution of *ortho*-hydroxybenzophenone (in the same mixtures but without the peroxide),[13] which dissipates all of the absorbed energy as heat.

The experimental procedure for TR-PAC was identical to that described for PAC,[6] but the resulting waveform from each data point (sample and calibration) was recorded for subsequent mathematical analysis. Sample waveforms were deconvoluted with the corresponding calibration waveforms (obtained with the same laser energy) by using the software Sound Analysis by Quantum Northwest.[11]

Theoretical Calculations. Density functional theory (DFT) calculations were carried out for thiophenol, substituted thiophenols, thiophenoxy radical, and substituted thiophenoxy radicals in the gas phase with the Barone and Adamos's Becke style one-parameter functional, using a modified Perdew−Wang exchange and PW91 correlation (MPW1PW91)[14] and the Perdew−Wang exchange and correlation functionals (PW91).[15] Total energies (E) were obtained from eq 6,[16] where V_{NN} is the nuclear−nuclear interaction; H^{CORE} is a monoelectronic contribution to the total energy, including electron kinetic and electron−nuclear interaction energies; and V_{ee} is the Coulombic interaction between the electrons.

$$E = V_{NN} + H^{CORE} + V_{ee} + E_X[\rho] + E_C[\rho] \qquad (6)$$

The terms $E_X[\rho]$ and $E_C[\rho]$ represent the exchange and correlation energies, respectively, which are functionals of the electronic density ρ. The geometries were fully optimized with the aug-cc-pVDZ basis set.[17] Single-point energy calculations with the Dunning triple-ζ correlation-consistent basis set including diffuse functions (aug-cc-pVTZ)[18] were also made. All calculations were corrected with the zero-point energy and with thermal corrections. G3(MP2)[19] and CBS-4M[20] calculations for the S−H bond dissociation enthalpy in thiophenol were also carried out. Gaussian-3 theory is the third in a series of Gn methods for calculating molecular energies with high accuracy. G3 is a composite method in which a sequence of well-defined ab initio molecular calculations is performed and the total energy of the

SCHEME 1

$$t\text{-BuOOBu-}t(\text{sln}) \xrightarrow{h\nu} 2\ t\text{-BuO}^\bullet(\text{sln}) \qquad \Delta_r H_1 \quad (7)$$

$$2\text{PhSH(sln)} + 2\ t\text{-BuO}^\bullet(\text{sln}) \rightarrow 2\text{PhS}^\bullet(\text{sln}) + 2\ t\text{-BuOH(sln)} \qquad \Delta_r H_2 \quad (8)$$

$$t\text{-BuOOBu-}t(\text{sln}) + 2\text{PhSH(sln)} \rightarrow 2\text{PhS}^\bullet(\text{sln}) + 2\ t\text{-BuOH(sln)} \qquad \Delta_r H \quad (9)$$

TABLE 1: Auxiliary Data (kJ mol^{-1})

molecule	$\Delta_f H°$	$\Delta_{sln}H°$ [a]
t-BuOH, l	−359.2 ± 0.8[b]	15.50 ± 0.35
t-BuOOBu-*t*, l	−380.9 ± 0.9[c]	1.21 ± 0.22
PhSH, g	111.3 ± 1.3[b]	
PhSMe, g	97.3 ± 0.8[b]	
H•, g	217.998 ± 0.006[d]	
Me•, g	147 ± 1[e]	

[a] Solution enthalpies in benzene from ref 6. [b] Reference 28. [c] Reference 12. [d] Reference 27. [e] Reference 29.

molecular species is calculated. G3(MP2) is a modification of the G3 theory that uses reduced Mϕller−Plesset order perturbation theory; the basis set extensions are obtained at the MP2 level, eliminating the MP4 calculations. G3(MP2) is based on MP2(full)/6-31G(d) geometries using all electrons. The CBS-4 model is also a composite method that yields the same accuracy as the CBS-q[20] model but has a computationally less demanding MP4(SDQ) higher-order component. This model employs the very fast UHF/3-21G(d) method for geometry optimization and zero-point energies. All calculations were performed with the Gaussian 98 program.[21]

Results and Discussion

The application of the non-time-resolved PAC technique to the general problem of the determination of bond dissociation enthalpies[4,6,22] is illustrated in Scheme 1 for the S−H bond in thiophenol, where the photochemically produced *tert*-butoxyl radical is employed to break that bond, yielding PhS•.

The PAC technique allows for the determination of the net reaction enthalpy in Scheme 1, $\Delta_r H$, through the simple energy balance described by eq 3. For the reactions presented in Scheme 1, the volume change of reaction 9 is assumed to be equal to the volume change for the homolysis of di-*tert*-butylperoxide alone, because the volume change for reaction 8 should be negligible. Wayner et al.[22] made a critical assessment of $\Delta_r V_1$ and recommended $\Delta_r V_1 = 13.4 \pm 4$ mL mol^{-1}. The value for the adiabatic expansion coefficient in benzene is readily calculated from literature data[23] as $\chi = 0.813$ mL kJ^{-1}, and the quantum yield of the peroxide homolysis in this solvent is $\Phi_r = 0.83$.[22] The S−H bond dissociation enthalpy of thiophenol in solution, $DH°_{sln}(\text{PhS} - \text{H})$, can then be derived from $\Delta_r H$. The relationship is established through a thermodynamic cycle, yielding eq 10, which contains several enthalpies of formation and solution enthalpy terms ($\Delta_{sln}H$).[24] With exception of the solvation enthalpy of the hydrogen atom, which can be estimated using the hydrogen molecule as a model,[25] yielding $\Delta_{sln}H°(\text{H}^\bullet,\text{g}) = 5 \pm 1$ kJ mol^{-1} for organic solvents,[26] those quantities are available from the literature (Table 1).[12,27−29]

$$DH°_{sln}(\text{PhS−H}) = \Delta_r H/2 + \Delta_f H°(\text{H}^\bullet,\text{g}) + \Delta_{sln}H°(\text{H}^\bullet,\text{g}) + \Delta_f H°(t\text{-BuOOBu-}t,\text{l})/2 - \Delta_f H°(t\text{-BuOH,l}) + \Delta_{sln}H°(t\text{-BuOOBu-}t,\text{l})/2 - \Delta_{sln}H°(t\text{-BuOH,l}) \quad (10)$$

As mentioned above, the previous approach is valid only if the process being studied (reaction 9) is fast compared to the transducer response. This can be ensured by adequately choosing the concentration of the substrate (thiophenol). Although the actual limit is difficult to define with accuracy, this requirement can be easily verified experimentally, by varying the concentration of substrate until the observed waveform reaches a maximum (or, equivalently, until the final value $\Delta_{obs}H$ reaches a maximum).[6] If this requirement is not met, TR-PAC can be used to derive $DH°_{sln}(\text{PhS} - \text{H})$. Deconvolution of the photoacoustic waveforms obtained in this case affords the amplitudes (ϕ_{obs}) of the two expected sequential processes and the lifetime (τ) of the second, according to the two elementary steps in Scheme 1.[5c] From the enthalpy obtained for the first process, $\Delta_{obs}H_1$, the enthalpy of reaction 7 can be calculated using eq 3. This reaction enthalpy is, by definition, equal to the bond dissociation enthalpy of di-*tert*-butylperoxide in solution, $DH°_{sln}(\text{O} - \text{O})$. The enthalpy of reaction 8 can be calculated from eq 5, assuming that the volume change for this reaction is negligible, i.e., $\Delta_r V_2 = 0$. As the enthalpy of reaction 8 is simply twice the difference between the S−H and O−H bond dissociation enthalpies in thiophenol and *tert*-butyl alcohol in solution, respectively, $DH°_{sln}(\text{PhS} - \text{H})$ can be derived from eq 11.

SCHEME 2

$$\begin{tikzcd}
\text{PhSH (sln)} \arrow[r, "DH°_{sln}(\text{PhS–H})"] & \text{PhS}^\bullet\text{(sln)} \arrow[d, "-\Delta_{sln}H°(\text{PhS}^\bullet\text{,g})"'] & + \text{H}^\bullet\text{(sln)} \arrow[d, "-\Delta_{sln}H°(\text{H}^\bullet\text{,g})"] \\
\text{PhSH (g)} \arrow[u, "\Delta_{sln}H°(\text{PhSH,g})"] \arrow[r, "DH°(\text{PhS–H})"'] & \text{PhS}^\bullet\text{(g)} & + \text{H}^\bullet\text{(g)}
\end{tikzcd}$$

$$DH°_{sln}(\text{PhS−H}) = \Delta_r H_2/2 + DH°_{sln}(t\text{-BuO−H}) \quad (11)$$

The relationship between solution-phase and gas-phase bond dissociation enthalpies is established through the enthalpies of solvation of the species involved. Scheme 2 (or eq 12) illustrates this relationship for the S−H bond dissociation enthalpy in thiophenol.

$$DH°(\text{PhS−H}) = DH°_{sln}(\text{PhS−H}) + \Delta_{sln}H°(\text{PhSH,g}) - \Delta_{sln}H°(\text{PhS}^\bullet\text{,g}) - \Delta_{sln}H°(\text{H}^\bullet\text{,g}) \quad (12)$$

The difficulty in applying eq 12 is the solution enthalpy of the thiophenoxyl radical, which is not experimentally available.[30] This problem can, however, be overcome by using a methodology proposed earlier in a similar PAC study with phenolic compounds. Briefly, Wayner et al.[22] made the sensible assumption that the difference $\Delta_{sln}H°(\text{PhOH,g}) - \Delta_{sln}H°(\text{PhO}^\bullet\text{,g})$ is simply given by the enthalpy of the hydrogen bond between phenol and the solvent, PhOH···S. This enthalpy can be estimated with the ECW model, which contains four parameters that reflect electrostatic ($E_A E_B$) and covalent ($C_A C_B$) contributions to the enthalpies of donor−acceptor interactions, eq 13. Donor (B) and acceptor (A) parameters, optimized by a large database of experimentally determined enthalpies, are available for many substances.[31]

$$-\Delta H(\text{ECW}) = E_A E_B + C_A C_B \quad (13)$$

Using the parameters for the acid thiophenol and the base benzene,[31] the ECW model predicts $\Delta H(\text{ECW}) = \Delta_{sln}H°(\text{PhSH,g}) - \Delta_{sln}H°(\text{PhS}^\bullet\text{,g}) = -2.4$ kJ mol^{-1} with an estimated error of less than 1 kJ mol^{-1}.

The ECW model can also be used together with the experimental gas-phase O−H bond dissociation enthalpy in *tert*-

TABLE 2: PAC and TR-PAC Determination of Solution Bond Enthalpies: DH°_{sln}(S−H) for Thiophenol and Some Substituted Thiophenols and DH°_{sln}(O−O) for Di-*tert*-butylperoxide

substrate	concentration (M)	S/S_{ref}[a]	$\Delta_{\mathrm{obs}}H_1$[b] (kJ mol^{-1})	DH°_{sln}(O−O)[c] (kJ mol^{-1})	$\Delta_{\mathrm{obs}}H_2$[d] (kJ mol^{-1})	DH°_{sln}(S−H) (kJ mol^{-1})
PhSH	0.06	179.0	393.9 ± 10.5[e]			361.7 ± 9.0
	0.006	18.5	246.9 ± 4.8	146.9 ± 7.6	163.6 ± 5.4	356.8 ± 4.4
4-$CH_3C_6H_4SH$	0.006	18.7	253.7 ± 12.4	138.7 ± 15.7	166.9 ± 4.6	354.9 ± 4.1
4-$CH_3OC_6H_4SH$	0.005	19.4	246.8 ± 6.0	147.0 ± 8.8	177.4 ± 4.0	348.5 ± 4.0
4-ClC_6H_4SH	0.006	71.5	263.9 ± 3.4	126.4 ± 6.5	157.8 ± 1.8	360.4 ± 3.5
4-$CF_3C_6H_4SH$	0.005	14.0	239.8 ± 8.7	155.4 ± 11.6	158.6 ± 3.6	359.9 ± 3.9

[a] Typical normalized residual photoacoustic signal ×100 (see text). [b] Measured enthalpic change for the fast process, atributed to reaction 7 (see text), unless indicated otherwise. All values of $\Delta_{\mathrm{obs}}H$ in this table represent the average of at least five independent results. The uncertainties are twice the standard deviation of the mean in each case. [c] O−O bond dissociation enthalpy in the peroxide (reaction 7) "contaminated" by the substrate absorbance (see text). [d] Measured enthalpic change for the sequential slower process, atributed to reaction 8. [e] Measured enthalpic change using non-time-resolved PAC, corresponding to the overall reaction 9.

butyl alcohol,[32] $DH^\circ(t\text{-BuO−H}) = 446 \pm 3$ kJ mol^{-1}, to estimate the O−H bond dissociation enthalpy of *tert*-butyl alcohol in solution (eq 14).

$$\begin{aligned} DH^\circ_{\mathrm{sln}}(t\text{-BuO−H}) &= DH^\circ(t\text{-BuO−H}) - \\ &\quad \Delta_{\mathrm{sln}}H^\circ(t\text{-BuOH,g}) + \Delta_{\mathrm{sln}}H^\circ(t\text{-BuO}^\bullet\text{,g}) + \Delta_{\mathrm{sln}}H^\circ(\mathrm{H}^\bullet\text{,g}) \\ &= DH^\circ(t\text{-BuO−H}) - \Delta H(\mathrm{ECW}) + \\ &\quad \Delta_{\mathrm{sln}}H^\circ(\mathrm{H}^\bullet\text{,g}) \end{aligned} \quad (14)$$

Using $\Delta H(\mathrm{ECW}) = -4.4 \pm 1$ kJ mol^{-1} [33] and $\Delta_{\mathrm{sln}}H^\circ(\mathrm{H}^\bullet,\mathrm{g}) = 5 \pm 1$ kJ mol^{-1},[26] one obtains $DH^\circ_{\mathrm{sln}}(t\text{-BuO} - \mathrm{H}) = 455.4 \pm 3.3$ kJ mol^{-1}.

Our studies began with PAC experiments of thiophenol at a high enough concentration to ensure that reaction 8 (and hence reaction 9) would be fast, so as to allow the application of the non-time-resolved technique. We used the same concentration we had previously established for the analogous study with phenol in our calorimeter,[6] because the hydrogen abstraction from thiophenol should be faster. However, these experiments were hampered by the strong absorption of the substrate at the wavelength used, a fact that can represent a serious limitation of the technique. As eq 2 implies, the photoacoustic signal is related to the transmittance of the photochemically active substance, which, according to Scheme 1, is di-*tert*-butylperoxide. If the substrate (e.g., thiophenol) also absorbs significantly at the same wavelength, the measured photoacoustic signal will reflect this additional input in some measure, and this contribution cannot be resolved from the one due to the peroxide homolysis, reaction 7 (see below, however), thus invalidating Scheme 1 and any thermochemical calculations based on it. To circumvent this limitation, the use of a different excitation wavelength could be tried, but for obvious practical reasons, this is not always possible. Fortunately, TR-PAC also presents a solution to the problem. By lowering the concentration of the substrate, the effect of its absorbance is substantially reduced, but reaction 8 becomes too slow to be studied by classical PAC. However, the deconvolution of the waveform can now be used to extract its enthalpy through eq 5. Furthermore, this alternative not only reduces the interference of the substrate absorbance but it can also allow its influence on the value derived for the enthalpy of reaction 8 to be eliminated. Indeed, if the photochemical or photophysical processes that result from the excitation of the substrate are fast, they will contribute only to the measured amplitude of the first process, but not to the second, which is much slower. Therefore, the amplitude of the second process obtained from the deconvolution is exclusively related to eq 8, allowing for the correct calculation of the S−H bond dissociation enthalpy through eqs 5 and 11. In the same manner, it is expected that, in this case, the O−O bond dissociation enthalpy (reaction 7), calculated through eq 3, will be in error.

The results from the photoacoustic experiments are displayed in Table 2, including the concentrations of substrate used and the corresponding normalized residual photoacoustic signals resulting from the absorption of the substrate (the photoacoustic signal measured with the blank solution containing only the substrate in benzene divided by the signal from a photoacoustic reference system, which provides a simultaneous measure of the laser energy). Classical PAC experiments were attempted with all of the listed compounds, except for 4-trifluoromethylthiophenol because the lower rate of reaction 8 with this compound would require a high concentration to overcome the time constraint, yielding an excessive residual signal. This was confirmed with 4-clorothiophenol, whose very strong absorbance at the laser wavelength used rendered impossible the nonresolved experiments.[34] Because of these experimental difficulties, the only nonresolved experiments completed and presented in Table 2 were those for thiophenol itself. Essentially, the results from both versions of the technique are in good agreement, but the lower precision of the non-time-resolved result is obvious in its uncertainty (more than twice the uncertainty of the TR-PAC result). Thus, only the TR-PAC value will be used in the subsequent discussion.

For the sake of completeness, Table 2 also includes the O−O bond dissociation enthalpy of di-*tert*-butylperoxide in solution, calculated with eq 3 using $\Delta_{\mathrm{obs}}H_1$ retrieved from the TR-PAC experiments. In a previous study of reaction 7 using non-time-resolved PAC, we obtained $DH^\circ_{\mathrm{sln}}(\mathrm{O} - \mathrm{O}) = 156.7 \pm 9.9$ kJ mol^{-1} in benzene.[33] All of the results presented in Table 2 are considerably lower, except for the one derived from the experiments with 4-trifluoromethylthiophenol (the substrate that also presents the lower residual signal), which is in excellent agreement with the previously reported value. According to the interpretation above, this was to be expected, because a strong residual signal causes the measurement of $\Delta_{\mathrm{obs}}H_1$ (but not of $\Delta_{\mathrm{obs}}H_2$) to be in excess. This, in turn, leads to a lower value of $DH^\circ_{\mathrm{sln}}(\mathrm{O} - \mathrm{O})$ while not affecting the calculation of $DH^\circ_{\mathrm{sln}}(\mathrm{PhS} - \mathrm{H})$.[35]

The gas-phase bond dissociation enthalpies can be derived from the solution-phase bond dissociation enthalpies determined by PAC, together with eq 12 and the ECW model, eq 13. Using $\Delta H(\mathrm{ECW}) = \Delta_{\mathrm{sln}}H^\circ(\mathrm{PhSH,g}) - \Delta_{\mathrm{sln}}H^\circ(\mathrm{PhS}^\bullet,\mathrm{g}) = -2.4 \pm 1$ kJ mol^{-1} and $DH^\circ_{\mathrm{sln}}(\mathrm{PhS} - \mathrm{H}), = 356.8 \pm 4.4$ kJ mol^{-1} (Table 2), one finally obtains $DH^\circ(\mathrm{PhS{-}H}) = 349.4 \pm 4.5$ kJ mol^{-1}.

The ECW parameters are not available for the substituted thiophenols. However, more than determining absolute values, we are particularly concerned with the effect of the substituent

TABLE 3: Gas-Phase Relative Bond Dissociation Enthalpies, $\Delta DH°$(S−H), for Substituted Thiophenols[a]

molecule	$\Delta DH°$(S−H)			
	exp[b]	exp[c]	calc[d]	calc[e]
4-$CH_3C_6H_4SH$	−1.9 ± 2.9	−3.3	−4.8	−4.9
4-$CH_3OC_6H_4SH$	−8.3 ± 2.9	−9.2	−12.8	−13.9
4-ClC_6H_4SH	3.6 ± 2.7	0.4	−1.9	−2.3
4-$CF_3C_6H_4SH$	3.1 ± 2.8		7.6	7.3

[a] Values in kJ mol^{-1}. [b] TR-PAC results calculated from the solution values in Table 2 (see text). The uncertainties correspond to the propagated errors, which overestimate the expected uncertainty when the values in the same column are compared. [c] Values from ref 3. [d] MPW1PW91/aug-cc-pVDZ. [e] MPW1PW91/aug-cc-pVTZ; single-point energy calculations with the geometry optimized at MPW1PW91/aug-cc-pVDZ.

on the bond dissociation enthalpies of substituted thiophenols. This effect can be more conveniently addressed by using a relative scale of bond dissociation enthalpies, $\Delta DH°$(S−H), which expresses the change in bond dissociation enthalpy for the substituted thiophenol (ArSH) relative to thiophenol itself (eq 15).

$$\Delta DH°(\mathrm{S{-}H}) = DH°(\mathrm{ArS{-}H}) - DH°(\mathrm{PhS{-}H}) \quad (15)$$

In addition to conveying the substituent effect in an intuitive manner (a positive value means a strengthening of the bond, whereas a negative value means a weakening effect), the relative scale also allows the problem associated with the solvation of the substituted thiophenols to be overcome. Defining a relative solution value $DH°_{\mathrm{sln}}(\mathrm{S-H})$ in the same manner as in eq 15 and recalling eq 12, eq 16 is obtained.

$$\Delta DH°(\mathrm{S{-}H}) = DH°_{\mathrm{sln}}(\mathrm{S{-}H}) + [\Delta_{\mathrm{sln}}H°(\mathrm{ArSH,g}) - \Delta_{\mathrm{sln}}H°(\mathrm{ArS^{\bullet},g})] - [\Delta_{\mathrm{sln}}H°(\mathrm{PhSH,g}) - \Delta_{\mathrm{sln}}H°(\mathrm{PhS^{\bullet},g})] \quad (16)$$

Assuming that the bracketed terms in eq 16 cancel, the substituent effect can be assessed from the solution values, because the relative scales will be equal in solution and in the gas phase. This has proved to be a sensible assumption for the study of substituent effects in phenolic compounds[6,26] and should be even more valid for the thiophenols, which are weaker acids than phenols. As such, the magnitude of the solvation effects is expected to be smaller for this family of compounds.[22] In any case, the difference between the two bracketed terms in eq 16 should be smaller than the typical experimental uncertainties (ca. 5 kJ mol^{-1}).[36] The four relative bond dissociation enthalpies, $\Delta DH°$(S−H), for the substituted thiophenols (ArSH) obtained by TR-PAC are presented in Table 3, together with the values reported by Bordwell et al.[3] and those predicted by DFT calculations. These calculations led to the gas-phase enthalpies of the isogyric and isodesmic reaction 17, which are equal to $\Delta DH°$(S−H). The DFT results are from MPW1PW91/aug-cc-pVDZ optimizations and from single-point energy calculations with the aug-cc-pVTZ basis set.

$$\mathrm{ArSH(g)} + \mathrm{PhS^{\bullet}(g)} \rightarrow \mathrm{ArS^{\bullet}(g)} + \mathrm{PhSH(g)} \quad (17)$$

The TR-PAC results in Table 3 are in good agreement with the *relative* values reported in the electrochemical study by Bordwell et al. and also with the computational results, confirming that the substituent effects on $DH°$(S−H) of thiophenols are significantly smaller than the substituent effects on $DH°$(O−H) of the corresponding phenols. For example, regarding the phenol analogues of the thiophenols presented in Table 3, 4-XC_6H_4OH where X = CH_3, OCH_3, Cl, and CF_3, the O−H bond dissociation values are −8 ± 4, −22 ± 4, −1 ± 4, and 17 ± 4 kJ mol^{-1}, respectively.[26] Nevertheless, the direction of the effects is not changed, i.e., strong electron-donor substituents, such as methoxy, decrease the S−H bond dissociation enthalpy, whereas electron-acceptor substituents, such as trifluoromethyl, strengthen that bond.

As stated in the Introduction, the literature values of $DH°$(PhS−H) range from 331 to 349 ± 8 kJ mol^{-1} and have been subjected to several assessments. The original value was reported by Colussi and Benson,[37] who determined the enthalpy of reaction 18 as 282.4 kJ mol^{-1} using a kinetic method (VLPP).

$$\mathrm{PhSCH_3(g)} \rightarrow \mathrm{PhS^{\bullet}(g)} + \mathrm{CH_3^{\bullet}(g)} \quad (18)$$

Colussi and Benson used their result for the enthalpy of reaction 18 to derive the enthalpy of formation of the thiophenoxy radical, given the enthalpies of formation of the other two species, which were available from the literature. Then, the S−H bond dissociation enthalpy of thiophenol could be calculated from its enthalpy of formation and the enthalpy of formation of the hydrogen atom. The value in the original paper, obtained with the then-existing auxiliary data, was $DH°$(PhS−H) = 343 ± 6 kJ mol^{-1}. Later, McMillen and Golden[38] used newer auxiliary data and reassessed this value as $DH°$(PhS−H) = 349 ± 8 kJ mol^{-1}. However, if one uses the Δ_rH of reaction 18 given in Colussi and Benson's paper together with the auxiliary enthalpies of formation in the literature sources indicated by McMillen and Golden, a value of 335.2 kJ mol^{-1} is obtained for $DH°$(PhS−H). This implies that the enthalpy of reaction 18 in the work by Colussi and Benson was adjusted by ca. 14 kJ mol^{-1}, in keeping with the statement by McMillen and Golden that "a different recombination activation energy assumption was used".[38] Finally, a second reassessment (338 ± 8 kJ mol^{-1}) was made by Griller at al.,[39] simply by taking the enthalpy of reaction 18 reported by Colussi and Benson and using different auxiliary data. If the same exercise is repeated with the most recent auxiliary data (Table 1), $DH°$(PhS−H) = 339.4 ± 8 kJ mol^{-1} is obtained.

The most recent literature value for $DH°$(PhS−H) was determined by Bordwell et al.,[3] using the "electrochemical method" (EC). They obtained $DH°$(PhS−H) = 331 kJ mol^{-1}, matching a PAC result mentioned in their paper.[40] Although absolute uncertainties in the EC data are not given, they should be less than 13 kJ mol^{-1}.[41] Regarding the PAC value, no details are available.[40] This result could be affected by large systematic errors, such as the errors due to the volume change correction and, to a lesser extent, to the enthalpy of the hydrogen bond formation between thiophenol and the solvent (not specified). In conclusion, the more recent values of $DH°$(PhS−H) reported by Bordwell et al. are significantly lower than those reported in early publications and also lower than the result of our PAC study, 349.4 ± 4.5 kJ mol^{-1}. Incidentally, this value is in excellent agreement with the "old" reassessment made by McMillen and Golden, 349 ± 8 kJ mol^{-1}. [38]

To further substantiate our PAC result for $DH°$(PhS−H), the enthalpy of reaction 1 at 298 K was computed at several theory levels, and the results are displayed in Table 4.

DFT calculations show that the PW91 and MPW1PW91 functionals underestimate $DH°$(PhS−H) by more than 35 kJ mol^{-1}, in comparison with our experimental value. A similar difference between the DFT and experimental results for the O−H bond dissociation enthalpy in phenol has recently been observed.[42] This is not unexpected because reaction 1 is not an isogyric and isodesmic reaction, thus not resulting in error cancellation. However, as shown in Table 4, the best theoretical

TABLE 4: S−H Bond Dissociation Enthalpy in Thiophenol[a]

method	*DH*°(PhS−H)
PW91/aug-cc-pVDZ	311.7
MPW1PW91/aug-cc-pVDZ	313.4
MPW1PW91/aug-cc-pVTZ	318.9
CBS-4M	338.1
G3(MP2)	346.8
Exp.	349.4 ± 4.5[b]

[a] Values in kJ mol^{-1}. [b] TR-PAC result calculated from the experimental solution value in Table 2 (see text).

results, CBS-4M and G3(MP2) composite ab initio procedures, predict 338.1 and 346.8 kJ mol^{-1}, respectively, the latter being in good agreement with the PAC result reported here. The average absolute deviation from experiment for thermochemical properties of G3(MP2) theory is 4.94 kJ mol^{-1}.[19] This is a significantly improved value in comparison with the CBS-4M procedure which has an average absolute deviation of ca. 12 kJ mol^{-1}.[43] Thus, we believe that the greater accuracy of the G3(MP2) theory supports our present experimental result for *DH*°(PhS−H).[44]

Conclusions

Time-resolved photoacoustic calorimetry allows for the investigation of the thermochemistry of substrates that have a nonnegligible absorbance at the radiation wavelength, provided that the reaction of interest and the photochemical or photophysical process(es) that result from that absorption occur at different rates. The method was applied to the determination of the gas-phase S−H bond dissociation enthalpies in thiophenol and several substituted thiphenols. The result obtained for thiophenol, supported by high-level quantum chemistry calculations, is significantly higher than the most recent values reported in the literature, but it is in excellent agreement with the value recommended in a widely used review.[38] The bond dissociation enthalpies obtained for the substituted thiophenols are in keeping with the conclusion drawn by Bordwell et al. that substituent effects on the O−H bond are much stronger than those on the less polar S−H bond.[3]

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(34) Aside from invalidating Scheme 1, a strong residual absorbance imposes clear experimental difficulties: the measured photoacoustic signal varies markedly between each laser pulse, and the obtained correlations of photoacoustic signal vs laser energy (eq 2) are generally poor, causing many experiments to be discarded.[6] This overall lack of precision should be related to the fact that, in this case, the signal due to the presence of the peroxide (which brings about the reactions from Scheme 1) is only a fraction of the total signal.

(35) This was supported by another set of experiments, in which we used TR-PAC to study the reactions in Scheme 1 but with phenol as the substrate (to be published). This compound, unlike thiophenol, shows only a small residual absorbance at the concentration needed for nonresolved PAC experiments (typically one obtains $100 \times S/S_{\mathrm{ref}} = 68$ for a 0.06 M solution in benzene, almost three times smaller than the value obtained for thiophenol) and was proposed as a test reaction for that technique, yielding $DH^{\circ}_{\mathrm{sln}}(\mathrm{PhO-H}) = 373.2 \pm 5.2$ kJ mol^{-1}.[6] From TR-PAC experiments, using a 0.005 M solution of phenol in benzene, we obtained $DH^{\circ}_{\mathrm{sln}}(\mathrm{O-O}) = 160.1 \pm 7.0$ kJ mol^{-1} and $DH^{\circ}_{\mathrm{sln}}(\mathrm{PhO-H}) = 380.9 \pm 3.6$ kJ mol^{-1}, in good agreement with previously reported values.[6,33]

(36) We can further substantiate this assumption by calculating the bracketed terms in eq 16 for phenol and substituted phenols in various solvents using the ECW model (as stated, ECW parameters are not available for substituted thiophenols). The results of this exercise for phenol, the weaker acid 4-MeOC$_6$H$_4$OH, and the stronger acid 4-CF$_3$C$_6$H$_4$OH in benzene, are 8.7, 8.0, and 9.3 kJ mol^{-1}, respectively. With the stronger hydrogen-acceptor solvent ethyl acetate, the results are 19.8, 18.2, and 21.3 kJ mol^{-1}. Even in this extreme case, the bracketed terms in eq 16 cancel to within less than 1.6 kJ mol^{-1}.

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