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Anchoring the gas-phase acidity scale: From formic acid to methanethiol

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ABSTRACT

We have measured the gas-phase acidities of nine compounds: formic acid, acetic acid, 1,3-propanedithiol, 2-methyl-2-propanethiol, 3-methyl-1-butanethiol, 2-propanethiol, 1-propanethiol, ethanethiol, and methanethiol, with acidities ranging from 338.6 to 351.1 kcal mol^{-1} using proton transfer kinetics and the resulting equilibrium constants. These acids were anchored to the well-known acidity of hydrogen sulfide; the measured acidities are in good agreement with previous experimental values, but error bars are significantly reduced. The gas-phase acidity of 3-methyl-1-butanethiol was determined to be 347.1 (5) kcal mol^{-1}; there were no previous measurements of this value. Entropies of deprotonation were calculated and enthalpies of deprotonation were determined.

1. Introduction

The gas-phase acidity of a compound, $\Delta_{\text{acid}}G$, is an important thermochemical property that refers to the amount of energy required to heterolytically cleave an HA bond (HA → A$^-$ + H$^+$). Typical acidities are ∼320–400 kcal mol^{-1} and are therefore not directly measurable, but are determined relative to one another [1]. High pressure mass spectrometry (HPMS) experiments allow for a direct measurement of an equilibrium constant, while flowing afterglow techniques measure a forward and reverse rate constant to determine an equilibrium constant [2]. The Cooks kinetic method also allows for the determination of relative gas-phase acidities [3,4].

Gas-phase acidity measurements carried out using the flowing afterglow technique are determined via ion-molecule equilibrium measurements [5].

$$\mathrm{HA} + \mathrm{B}^- \underset{k_\mathrm{r}}{\overset{k_\mathrm{f}}{\rightleftarrows}} \mathrm{HB} + \mathrm{A}^- \tag{1}$$

HA is the compound of unknown acidity, HB is a reference acid, and A$^-$ and B$^-$ are their respective conjugate bases. The difference in gas-phase acidity [$\Delta(\Delta_{\text{acid}}G)$] between the reference acid and the unknown acid is given by

$$\Delta(\Delta_{\text{acid}}G) = -RT \ln\left(\frac{k_\mathrm{f}}{k_\mathrm{r}}\right) \tag{2}$$

Absolute gas-phase acidities are determined from relative gas-phase acidities by measuring a series of overlapping $\Delta(\Delta_{\text{acid}}G)$ values and constructing an acidity ladder. These ladders must be anchored to a compound whose acidity has been determined accurately and independently of other compounds. This independent value is often determined through the gas-phase negative ion thermochemical cycle, Eqs. (3)–(6), which relates bond energy (Eq. (3)), electron affinity (Eq. (4)), the ionization energy of H (Eq. (5)), and the enthalpy of deprotonation (Eq. (6)). Knowledge of three of these quantities allows for the calculation of the remaining value.

$$\mathrm{HA} \rightarrow \mathrm{H} + \mathrm{A} \qquad D_0(\mathrm{HA}) \tag{3}$$

$$\mathrm{A} + \mathrm{e}^- \rightarrow \mathrm{A}^- \qquad -\mathrm{EA}(\mathrm{A}) \tag{4}$$

$$\underline{\mathrm{H} \rightarrow \mathrm{H}^+ + \mathrm{e}^- \qquad \mathrm{IE}(\mathrm{H})} \tag{5}$$

$$\mathrm{HA} \rightarrow \mathrm{H}^+ + \mathrm{A}^- \qquad \Delta_{\text{acid}}H \tag{6}$$

While electron affinities can be determined extremely accurately using photoelectron spectroscopy, several difficulties exist. The electron affinity must be accessible with a laser, there must be good Franck-Condon overlap between the anion and the neutral in order to measure an adiabatic electron affinity, and the anion must be produced in relatively high concentration [6–8]. Photofragmentation studies, including but not limited to photoionization, laser induced fluorescence, and stimulated emission spectroscopy, can be used to measure bond strengths. These methods often involve complications with Franck-Condon overlap and the observed fragmentation pathways are not necessarily the lowest energy channels [6,9,10].

While these complications often present problems for determining absolute gas-phase acidities for larger molecules, bond strengths and electron affinities have been accurately determined for several smaller molecules. Therefore, the acidities of these molecules, including CH_4, NH_3, H_2O, HF, H_2S, HCN, HCl, HBr, and HI, have been determined very accurately, precisely, and indepen-

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dently of other molecules, and they can serve as anchors for the acidity scale. Gas-phase acidities measured relative to these species can be determined with high accuracy and precision.

We report the acidity of nine neutral reagents: formic acid, acetic acid, 1,3-propanedithiol, 2-methyl-2-propanethiol, 3-methyl-1-butanethiol, 2-propanethiol, 1-propanethiol, ethanethiol, and methanethiol, anchored to the gas-phase acidity of H_2S ($\Delta_{acid}G_{298}$ = 344.89 (2) kcal mol^{-1}) [11]. (We note that, throughout this paper, a parenthetical number indicates the uncertainty in the last digit of the preceding value.) These compounds were chosen since they themselves are often convenient reference acids and therefore the large uncertainty associated with these acidities is propagated to other values. The error bars reported here are reduced from previous work by a factor of 3–4; there are no previous measurements of the acidity of 3-methyl-1-butanethiol.

2. Experimental

Reactions were carried out using a flowing afterglow-selected ion flow tube (FA-SIFT) [12,13]. This instrument has been described in detail elsewhere, so only a brief summary will be given here. Ions are produced in a flowing afterglow source by passing helium buffer gas containing trace amounts of neutral reagents over a heated filament. Using a series of movable and fixed inlets, neutral reagents can be introduced at various reaction distances along the flow tube; target ions are formed from a series of ion-molecule reactions. The desired reactant ions are mass selected using a quadrupole mass filter and injected into the reaction flow tube where they are thermally equilibrated to room temperature through collisions with helium buffer gas (0.5 Torr, $\sim 10^4$ cm s^{-1}). A measured flow of neutral reagent is added at varying distances along the flow tube and allowed to react. The formation of product ions and depletion of the reactant ion are monitored with a quadrupole mass spectrometer coupled to an electron multiplier. Reaction kinetics are determined under pseudo-first order conditions, by changing the position of neutral reagent addition and thereby varying reaction time. Reactions were carried out at 301 ± 2 K. Forward and reverse rate constants were measured on the same day under identical conditions.

Efforts were made to minimize mass discrimination. Estimates of the remaining mass discrimination were carried out through a series of calibration reactions. These reactions were chosen such that a single reactant ion, when allowed to react with a carefully selected neutral reagent, forms a single product ion. Both reactant and product ions were chosen to be similar in mass to those in this study. This correction was verified by summing the total intensities of reactant and product ions and assuring that the signal was constant. Helium buffer gas (99.995%) was purified by passage through a molecular sieve trap immersed in liquid nitrogen. All neutral reagents were purchased from commercial sources and used without further purification. [H_2S, 99.5%; HCOOH, ≥98%; CH_3COOH, >99%; HSC_3H_6SH, 99%; $(CH_3)_3CSH$, 99%; $(CH_3)_2CH(CH_2)_2SH$, 97%; $(CH_3)_2CHSH$, 97 + %; n-C_3H_7SH, 99%; C_2H_5SH, 97%; CH_3SH, 99.5%].

In order to convert gas-phase acidities ($\Delta_{acid}G$) to enthalpies of deprotonation ($\Delta_{acid}H$), the entropy of deprotonation ($\Delta_{acid}S$) must be determined. This can be done experimentally by determining rate constants at different temperatures and preparing a van't Hoff plot. Alternatively, electronic structure calculations are expected to provide accurate $\Delta_{acid}S$ values. We have performed these calculations using Gaussian 03 [14]. Geometries were optimized and frequencies were computed using B3LYP/6-311++G(d,p). This method has been shown to be an effective compromise between cost and accuracy for the determination of frequencies from which entropies are calculated. Heat capacity values are also taken from these calculations to allow for adjustment to $\Delta_{acid}H_0$. The $\Delta_{acid}G$ of methanethiol and 3-methyl-1-butanethiol have been calculated directly as defined by Gaussian-3 (G3) theory [15], a composite technique in which a series of well-defined *ab initio* calculations are executed. This method has been shown to be an accurate method for determining energetics. All optimized geometries and energies are available as supplementary information.

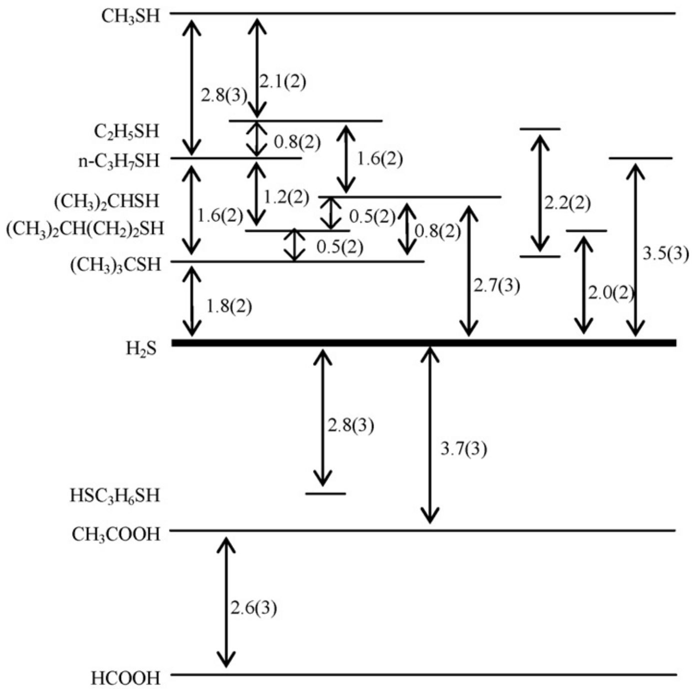

Fig. 1. Measured $\Delta(\Delta_{acid}G)$ values (in kcal mol^{-1}) for the compounds in this study.

3. Results and discussion

The individual $\Delta(\Delta G)$ values measured in this study are shown in Fig. 1. Excellent overlap in the acidity ladder suggests an error of ±0.2 kcal mol^{-1} in the relative acidity measurements. However, several different factors contribute to the total error of each individual rate constant measurement. Absolute uncertainties in the rate constants are ±20%. The errors in the gas-phase acidities are reduced because some systematic errors cancel in the rate constant ratio. These errors are mostly due to uncertainties in the instrument parameters (He flow, pressure, temperature, etc.). The endothermic pathway for these reactions often produces an association product as well as a proton transfer product; the rate constant for proton transfer is determined by multiplying the overall rate constant by the proton transfer branching ratio. The error introduced from the determination of a branching ratio results in a slightly larger error bar for the larger values of $\Delta(\Delta G)$. Uncertainties in product ion branching ratios are ±20%. We also calculated the *total* error, which combines the absolute error in the rate constants, uncertainties in the branching ratios, and the standard deviation of the rate measurements. The errors reported in Fig. 1 are the larger of the total error or the overlap error.

Absolute gas-phase acidities are determined from an acidity ladder with H_2S ($\Delta_{acid}G_{298}$ = 344.89 (2) kcal mol^{-1}) as the anchor acid. This value was taken from the work of Ervin and DeTuri [11], who evaluated twelve anchor compounds. Their evaluation used a careful consideration of thermal corrections to convert an experimental value of $\Delta_{acid}H_0$ [16], measured by threshold ion-pair production spectroscopy (TIPPS), to a value for $\Delta_{acid}G_{298}$.

Our recommended values for the gas-phase acidities and enthalpies of deprotonation for these compounds are given in Table 1. Because these absolute acidities can be determined in

Table 1
Gas-phase acidities (kcal mol^{-1}), entropies of deprotonation (cal mol^{-1} K^{-1}) and enthalpies of deprotonation (kcal mol^{-1}).

	This work				Previous work
	$\Delta_{\text{acid}}G_{298}$	$\Delta_{\text{acid}}S_{298}$[a]	$\Delta_{\text{acid}}H_{298}$	$\Delta_{\text{acid}}H_0$[a]	$\Delta_{\text{acid}}G_{298}$
CH_3SH	351.1 (5)	21.5	357.5 (5)	356.5 (5)	350.6 (20)[b]
C_2H_5SH	349.1 (5)	23.0	356.0 (5)	355.6 (5)	348.9 (20)[b]
n-C_3H_7SH	348.4 (5)	23.1	355.3 (5)	354.4 (5)	347.9 (20)[b]
$(CH_3)_2CHSH$	347.6 (5)	23.4	354.6 (5)	353.8 (5)	347.1 (20)[b]
$(CH_3)_2CH(CH_2)_2SH$	347.1 (5)	23.5	354.1 (5)	353.2 (5)	
$(CH_3)_3CSH$	346.7 (5)	23.4	353.7 (5)	352.9 (5)	346.2 (20)[b]
HSC_3H_6SH	342.1 (5)	24.8	349.5 (5)	348.9 (5)	341.6 (21)[c]
CH_3COOH	341.2 (5)	20.7	347.4 (5)	346.6 (5)	341.1 (20)[d] 341.5 (20)[e] 341.7 (20)[f]
HCOOH	338.6 (5)	24.9	346.0 (5)	345.2 (5)	339.2 (15)[g] 338.3 (20)[h] 338.4 (20)[f] 338.2 (20)[e]

[a] Entropies and heat capacities calculated using B3LYP/6-311++G(d,p).

[b] Ref. [17].

[c] Ref. [19].

[d] Ref. [20].

[e] Ref. [21].

[f] Ref. [22].

[g] Ref. [23].

[h] Ref. [24].

various ways (i.e., the sum and difference of several different combinations of arrows) the resulting absolute acidities vary slightly, due to rounding; these values were averaged to give the recommended values. Additionally, while the gas-phase acidity of H_2S is known to five significant figures, reaction rate constants can only be determined to four significant figures. Due to the combination of these factors, we have reported gas-phase acidities to four significant figures, with slightly more conservative error bars of 0.5 kcal mol^{-1}.

These absolute acidity values are in good agreement with previously published values, and in general have smaller error bars. Many of the thioacids have been previously determined by Bartmess et al. [17] in a series of ICR experiments. An extensive ladder was constructed; the error due to the agreement of the overlap between the relative acidities was reported to be ±0.2 kcal mol^{-1}. However, absolute acidities were determined by performing a multi-compound fit using several anchor points, and determined to within ±2 kcal mol^{-1}. Additionally, while an extensive ladder was constructed, few compounds were anchored directly to H_2S, therefore requiring propagation of error for several relative acidities.

The acidity of methanethiol was determined in this manner by Bartmess et al. [17] to be $\Delta_{\text{acid}}G_{298} = 350.6$ (20) kcal mol^{-1}. This acidity was also determined by Gianola et al. [18] to be $\Delta_{\text{acid}}G_{298} = 351.6$ (4) using a proton transfer equilibrium measurement with pyrrole, which has an independently determined bond strength and electron affinity. Our measurement ($\Delta_{\text{acid}}G_{298} = 351.1$ (5) kcal mol^{-1}) lies between the two values, with our error bars overlapping both values. G3 calculations predict the acidity to be $\Delta_{\text{acid}}G_{298} = 351.2$ kcal mol^{-1}, in best agreement with our value.

The gas-phase acidity of 1,3-propanedithiol was previously measured [19] by a direct equilibrium measurement to H_2S using ICR, where the error on the relative acidity measurement was determined to be 0.4 kcal mol^{-1}. Our relative and absolute acidities agree within experimental error. Additionally, the gas-phase acidity of 3-methyl-1-butanethiol, reported here, has not previously been determined. The measured value ($\Delta_{\text{acid}}G_{298} = 347.1$ (5) kcal mol^{-1}) is in excellent agreement with the value predicted by the G3 calculations ($\Delta_{\text{acid}}G_{298} = 347.1$ kcal mol^{-1}).

The gas-phase acidity of acetic acid has been measured by several different groups. Jinfeng et al. [20] performed direct equilibrium measurements from acetic acid to several substituted phenol compounds. Cumming and Kebarle [21] used direct equilibrium experiments to anchor their entire acidity ladder to HCl with an accuracy of ±2 kcal mol^{-1}. Fujio et al. [22] referenced their acidity ladder, having an internal consistency of ±0.2 kcal mol^{-1}, to phenol; however, they were unable to measure the direct equilibrium to the anchor acid requiring the propagation of individual errors to determine the total error. Our absolute value for the acidity of acetic acid is in agreement with all of these previous measurements within our error bars.

The acidity of formic acid was also measured in the studies of Jinfeng et al. [20] and Fujio et al. [22]. The negative ion cycle (Eqs. (3)–(6)) has allowed for an independent gas-phase acidity of formic acid to be determined [23]. Additionally, a high pressure mass spectrometry study performed by Caldwell et al. [24] measured forward and reverse rate constants to determine the relative gas-phase acidity of formic and acetic acid. Our values are in good agreement with all of these values, but with smaller error bars.

Due to the fact that many "unknown" gas-phase acidities have been determined relative to thiols, the reduced error bars on these measurements will allow for decreased uncertainties throughout the literature [1]. As a specific example, we have recently bracketed the gas-phase acidities of peroxyformic acid and peroxyacetic acid and found their acidities to be between the acidities of 2-methyl-2-propanethiol and acetic acid [25]. The previous acidity measurements for 2-methyl-2-propanethiol and acetic acid gave $\Delta_{\text{acid}}G = 343.7 \pm 4.6$ kcal mol^{-1}. The new acidity values, measured here, instead give the gas-phase acidity of both peroxyacetic acid and peroxyformic acid to be $\Delta_{\text{acid}}G = 344.3 \pm 3.3$ kcal mol^{-1}. This value, when coupled with precise electron affinity measurements, will allow for the determination of bond strengths with smaller error bars than originally possible.

4. Conclusion

The gas-phase acidities measured here have been anchored to H_2S, allowing for their determination with significantly smaller error bars than have previously been reported. The reduced error bars for these gas-phase acidity measurements will allow for decreases in uncertainty throughout the literature. Additionally, the gas-phase acidity of 3-methyl-1-butanethiol has been determined for the first time to be $\Delta_{\text{acid}}G_{298} = 347.1$ (5) kcal mol^{-1}, in excellent agreement with its calculated value.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2009.01.001.

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