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Gas-phase acidities of thiocarboxylic acids

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We are pleased to dedicate this paper to Dr. Jean Futrell, a great scientist, leader, and friend.

Abstract

The gas-phase acidity of thioacetic acid, determined using ion–molecule equilibrium reactions, was found to be $\Delta G_{\text{acid}} = 329.0 \pm 1.5\,\text{kcal mol}^{-1}$. The gas-phase acidity of thiobenzoic acid was determined by ion–molecule bracketting reactions to be $\Delta G_{\text{acid}} = 323 \pm 5\,\text{kcal mol}^{-1}$. Gas-phase acidities of these compounds, as well as of thioformic acid, were calculated; our calculations and experiments are in good agreement. The calculated value of the enthalpy of deprotonation of thioformic acid is consistent with previously published computational results.

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1. Introduction

Gas-phase studies allow exploration of the reactivities of molecules and ions without the effects of a solvent. An important measure of a compound's gas-phase reactivity is its gas-phase acidity, ΔG_{acid}; the free energy change for reaction (1) is defined as the gas-phase acidity of HA:

$$\text{HA} \rightarrow \text{H}^+ + \text{A}^- \tag{1}$$

Extensive gas-phase acidity ladders have been measured experimentally and calculated theoretically [1–6].

Gas-phase acidities are often determined via ion–molecule equilibrium measurements or through ion–molecule bracketting reactions. Ion–molecule equilibrium measurements require the unknown acidity to be measured relative to a compound with a known acidity. Through the use of Eq. (2), one can calculate the difference in gas-phase acidity between the reference acid and the unknown acid.

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

where, k_f and k_r are rate constants measured for the two reactions shown in Eq. (3).

$$\text{HA} + \text{B}^- \underset{k_\text{r}}{\overset{k_\text{f}}{\rightleftarrows}} \text{HB} + \text{A}^- \tag{3}$$

HA is the compound of unknown acidity and HB is a reference acid. A^- and B^- are their respective conjugate bases.

Ion–molecule bracketting provides an estimate of the gas-phase acidity of a compound by simply examining the occurrence or non-occurrence of proton transfer with several acids. In this manner, the acidity of the compound can be determined to lie between two known values, with an error bar that spans the difference in values. Often this technique is used when ion–molecule equilibrium reactions are not possible. This may be the case when one of the reactions necessary for an equilibrium measurement is highly endothermic or when the conjugate base of the unknown acid cannot be readily formed.

Another important measure of gas-phase reactivity, enthalpy of deprotonation (ΔH_{acid}), is related to other thermodynamic values through a thermochemical cycle.

$$\begin{array}{lll}
\text{HA} \rightarrow \text{H} + \text{A} & D_0\,(\text{HA}) & (4) \\
\text{A} + \text{e}^- \rightarrow \text{A}^- & \text{-EA (A)} & (5) \\
H \rightarrow H^+ + e^- & IE\,(H) & (6) \\
\hline
\text{HA} \rightarrow \text{H}^+ + \text{A}^- & \Delta H_{acid} & (7)
\end{array}$$

Consequently, knowing enthalpies of deprotonation has allowed determination of bond strengths [D(H–A)] or elec-

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tron affinities [EA(A)] without their direct measurement. These enthalpies of deprotonation can be converted into gas-phase acidities if the change in entropy for the reaction is known.

The properties of carboxylic acids in the gas-phase have been well characterized [7–10]. In comparison, less is known about carboxylic acids in which an oxygen atom has been replaced by another element. The stability and structure of sulfur, selenium, and tellurium substituted carboxylic acids have been investigated computationally [11–14]. These substituted carboxylic acids have been experimentally investigated in solution [15]. Silicon substituted carboxylic acids, where silicon replaces a carbon, have also been investigated theoretically [12–14].

Of all substituted carboxylic acids, thiocarboxylic acids (RCOSH) have received the most attention. They have long been of interest due to their application in biochemistry and pharmaceuticals [16–20]. Thioacids can also be used in synthesizing proteins [21] as well as in polymer assembly [22]. Thioacetic acid, in particular, is often used as a starting material in the synthesis of a large number of sulfur containing organics [23]. More recently, thioacetic acid has been identified as a contaminant in water extracted along with oil during oil production [24]. While the structure and physical properties of these thiocarboxylic acids have been investigated in detail [25–31], little is known about the gas-phase reactivity of thioacids.

Although acidities of thioacids have been calculated, only a single compound has been experimentally investigated. The gas-phase acidity of trifluorothioacetic acid, $CF_3C(O)SH$, has been determined both computationally ($\Delta G_{acid} = 308.2\ \mathrm{kcal\,mol^{-1}}$) [4] and experimentally ($\Delta G_{acid} = 312.5\ \mathrm{kcal\,mol^{-1}}$) [5]. In addition, Kass and DePuy [32] have estimated the “acidity” of thioformic acid, HC(O)SH, to be $345\ \mathrm{kcal\,mol^{-1}}$. This value was neither experimentally measured nor calculated, but instead approximated to be the same as that of formic acid; moreover, this value was intended to represent the enthalpy of deprotonation of HC(O)SH (ΔH_{acid}) rather than ΔG_{acid} (S. Kass, Personal Communication, 2007). The NIST WebBook [6] cites Ref. [32] and lists ΔG_{acid} (HC(O)SH) $= 343.0 \pm 3.0\ \mathrm{kcal\,mol^{-1}}$ and ΔH_{acid} (HC(O)SH) $= 350.7 \pm 3.1\ \mathrm{kcal\,mol^{-1}}$. However, recent calculations produce lower values. Remko et al. [12–14] have calculated the enthalpy of deprotonation of thioformic acid using both density functional theory (DFT) and ab initio methods with a series of basis sets. The enthalpy of deprotonation has been determined to be significantly lower than that of formic acid, between 328.8 and $334.0\ \mathrm{kcal\,mol^{-1}}$, depending on the method employed. These studies also examined the enthalpy of deprotonation of thioacetic acid, which was found to be between 333.3 and $335.9\ \mathrm{kcal\,mol^{-1}}$. Additional studies of the structures of these thiocarboxylic acids, as well as selenium and tellurium substituted acids, have been carried out in recent years [11,15].

2. Experimental

We have measured the gas-phase acidities of both thioacetic acid, $CH_3C(O)SH$ (Aldrich, 96%), and thiobenzoic acid, $C_6H_5C(O)SH$ (Aldrich, 90%). HCl (Scott, 99.999%) was used as a reference acid. These studies were carried out using the flowing afterglow-selected ion flow tube (FA-SIFT) at the University of Colorado [33]. Thioacetate reactant anions are made by allowing hydroxide, produced from electron impact on N_2O in the presence of CH_4, to interact with thioacetic acid. Chloride anions were produced by carrying out electron impact on CCl_4. Bromide anions were produced by allowing hydroxide to react with an alkyl bromide. The desired reactant ions were mass selected using a quadrupole mass filter and injected into the reaction flow tube where they become thermally equilibrated to room temperature through collisions with He buffer gas (∼0.5 Torr, ∼298 K). A known flow of neutral reactants was added to the reaction flow tube through a series of inlets. The flow of HCl was determined by measuring the pressure change in a calibrated volume as a function of time. Due to complications in measuring the flow of thioacetic acid, which is viscous and adhesive on surfaces, the rate constant for the reaction of chloride with thioacetic acid was measured relative to the rate constant for the reaction of hydroxide with thioacetic acid. It was assumed that the reaction of thioacetic acid with hydroxide proceeds at 90 ± 10% of the collision rate [34]. The depletion of the reactant ion and formation of the product ions were monitored using the detection quadrupole mass filter coupled to an electron multiplier.

3. Theory

The enthalpies of deprotonation, ΔH_{acid}, of thioformic acid, thioacetic acid, and thiobenzoic acid were calculated. Entropies of thioformic acid, thioacetic acid, and thiobenzoic acid and their product ions were calculated to allow for conversion of ΔH_{acid} to ΔG_{acid}. Electronic structure calculations were carried out using the Gaussian 98 program package [35]. Geometries were optimized and frequencies were computed as defined by Gaussian-3 (G3) theory [36,37], a composite technique in which a series of well-defined ab initio calculations are executed. Optimized geometries are available as supplementary information.

4. Results and discussion

Ion–molecule bracketting was used to determine the gas-phase acidity of thiobenzoic acid. In reactions of thiobenzoic acid with chloride anion, only a proton transfer product was observed. No reaction was observed when thiobenzoic acid was allowed to interact with bromide anion. We therefore estimate the acidity of thiobenzoic acid to be $\Delta G_{acid} = 323 \pm 5\ \mathrm{kcal\,mol^{-1}}$, between that of HCl ($\Delta G_{acid} = 328.1 \pm 0.1\ \mathrm{kcal\,mol^{-1}}$) and HBr ($\Delta G_{acid} = 318.3 \pm 0.2\ \mathrm{kcal\,mol^{-1}}$). Due to difficulties in generating and injecting the thiobenzoate ion, the reverse reactions with HCl and HBr were not studied.

Forward and reverse reaction rate constants were measured for the reaction of thioacetic acid, with HCl as the reference acid.

$$Cl^- + CH_3C(O)SH \underset{k_r}{\overset{k_f}{\rightleftarrows}} HCl + CH_3C(O)S^- \tag{8}$$

For the reverse reaction, the anion was produced by the reaction of thioacetic acid with hydroxide. While it is possible that the enolate form of the anion was present (ΔG_{acid} of the methyl group was calculated to be $360.5\ \mathrm{kcal\,mol^{-1}}$), it is unlikely.

Due to the large difference in acidity between the two sites and the high concentration of neutral-reagent in the production region, it is expected that a neutral-reagent catalyzed isomerization takes place in which the most stable anion is formed. Each rate constant is an average of at least six individual measurements; the reported error is the standard deviation of the measurements. The products of the forward reaction were the proton transfer product, CH_3COS^-, and an association product, $Cl^-(CH_3COSH)$. The observation of an association product suggests that this reaction is the endothermic pathway. The proton transfer branching fraction (83%) was measured in order to determine the proton transfer rate constant, which was found to be $k_f = 1.76\ (\pm 0.06) \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. Due to the corrections applied to this rate constant, the absolute uncertainty in this measurement is ±40%. The rate constant for the reverse reaction was determined to be $k_r = 8.40\ (\pm 0.20) \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$. The reverse reaction is expected to protonate sulfur rather than oxygen, as the thiol form has been shown to be energetically favored [38]. Absolute uncertainty in this measurement is ±20%. We determined the gas-phase acidity of thioacetic acid to be $\Delta G_{\mathrm{acid}} = 329.0 \pm 1.5\ \mathrm{kcal\ mol^{-1}}$, where conservative error bars have been assigned.

The general reactivity of the thioacetic acid anion has also been investigated. The anion was allowed to interact with CO_2, COS, N_2O, O_2, and CS_2 in an effort to identify reaction trends. Previous studies have shown that sulfur and oxygen nucleophiles often atom transfer to neutral species to form very stable ions (i.e., CO_3^-) [39–41]. However, for all five neutrals, no reactions were observed. We attribute this result to the stability of the thioacetate anion due to the delocalization of the negative charge.

The results of our calculations, also shown in Table 1, are in good agreement with previous calculations of Remko et al. [12–14], for thioformic and thioacetic acids. Both the *syn* and *anti* conformers of the neutral species were studied; in all cases the *syn* conformers were energetically favored. All calculations are also consistent with our experimental results. This lends support to the calculations performed to determine the gas-phase acidity of thioformic acid, in contradiction to previous estimates [32].

The relationship between thiocarboxylic acids and their carboxylic acid counterparts is shown in Table 2. In all cases, thiocarboxylic acids have been found to be significantly more acidic than their carboxylic acid analogs. This mirrors the trend shown upon substitution of alcohols; for example, the gas-phase acidity of methanethiol, CH_3SH, is 350.6 kcal mol^{-1}, while the gas-phase acidity of methanol, CH_3OH, is 375.1 kcal mol^{-1}. This is also consistent with the only prior thiocarboxylic acid experimental measurement, as shown in Table 2. This result is not surprising since S–H bonds are considerably weaker than O–H bonds [42]. These results provide further evidence that the gas-phase acidity of thioformic acid is accurately reflected by the calculated values and not approximately equal to that of formic acid as previously suggested [32].

Table 1
Experimental and calculated (G3) gas-phase acidities (298 K) of thioacids determined in this work

Thioacid	ΔG_{acid} (experimental, kcal mol^{-1})	ΔG_{acid} (calculated, kcal mol^{-1})	ΔH_{acid} (calculated, kcal mol^{-1})
HC(O)SH	–	325.6[a]	332.9
$CH_3C(O)SH$	329.0 ± 1.5[b]	329.7[c]	336.6
$C_6H_5C(O)SH$	323 ± 5[d]	324.2[e]	331.3

[a] $\Delta S_{\mathrm{acid}} = 24.41\ \mathrm{cal\ mol^{-1}\ K^{-1}}$.

[b] For reaction (8) in the text, $k_f = 1.76\ (\pm 0.06) \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$; $k_r = 8.40\ (\pm 0.20) \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$.

[c] $\Delta S_{\mathrm{acid}} = 23.31\ \mathrm{cal\ mol^{-1}\ K^{-1}}$.

[d] Bracketted between HCl and HBr.

[e] $\Delta S_{\mathrm{acid}} = 23.77\ \mathrm{cal\ mol^{-1}\ K^{-1}}$.

Table 2
Comparison of experimental gas-phase acidities of thiocarboxylic and carboxylic acids at 298 K

Acid	ΔG_{acid} (kcal mol^{-1})
HC(O)SH	–
HC(O)OH	339.2 ± 1.5[a]
$CH_3C(O)SH$	329.0 ± 1.5[f]
$CH_3C(O)OH$	341.1 ± 2.0[b]
$C_6H_5C(O)SH$	323 ± 5[f]
$C_6H_5C(O)OH$	333.0 ± 2.0[c]
$CF_3C(O)SH$	312.5[d]
$CF_3C(O)OH$	317.4 ± 2.0[e]

[a] Ref. [43].

[b] Ref. [44].

[c] Refs. [6,45].

[d] Ref. [5].

[e] Ref. [46].

[f] This work.

5. Conclusion

This work provides the first experimental measurements of the gas-phase acidities of thioacetic acid ($\Delta G_{\mathrm{acid}} = 329.0 \pm 1.5\ \mathrm{kcal\ mol^{-1}}$) and thiobenzoic acid ($\Delta G_{\mathrm{acid}} = 323 \pm 5\ \mathrm{kcal\ mol^{-1}}$). These values are consistent with calculations performed for this study, as well as with past calculations. Additionally, the gas-phase acidity of thioformic acid has been calculated to be $\Delta G_{\mathrm{acid}} = 325.6\ \mathrm{kcal\ mol^{-1}}$, consistent with previous computational studies. These thiocarboxylic acids have been determined to be more acidic than their carboxylic acid counterparts.

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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.2007.02.045.

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