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ACIDITY AND BASICITY OF THIOCARBOXAMIDES IN THE GAS PHASE

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The gas-phase acidity and basicity of thioacetamide and the basicity of *N,N*-dimethylthioformamide were measured by Fourier transform ion cyclotron resonance (FT-ICR) mass sectrometry under conditions which minimized the extent of their decomposition. Thiocarboxamides are both much stronger acids and stronger bases than carboxamides. The relative stabilities of individual neutral and ionic species were assessed in terms of isodesmic reactions, using the published or estimated enthalpies of formation. The neutral molecules of carboxamides and thiocarboxamides are stabilized by interaction between the C=X and NH_2 functional groups. This interaction is of a similar magnitude in the corresponding protonated forms but it is of greater strength in the deprotonated forms. With regard to the difference between thiocarboxamides and carboxamides, the most significant factor is probably the lone pair–lone pair repulsion operating in the anions.

INTRODUCTION

The importance of thiocarboxamides in pharmacology[1] has prompted us[2,3] and others[4–8] to investigate their physical properties. In addition, thiocarboxamides have been included in some more general studies,[9–11] usually in comparison with carboxamides. Our attention was first focused on the substituent properties of the thiocarboxamide group,[2] which can be expressed in terms of various constants σ[5,9] but these constants in turn depend on the intrinsic characteristics of the functional group itself. Of particular interest are the acidic and basic properties, determining the form in which the molecule is present under a given set of conditions. Thiocarboxamides are both weak acids and weak bases, and have only been investigated in special cases. Their acidity was measured in dimethyl sulphoxide[8] (DMSO) or in 90% aqueous DMSO.[6c] The basicity properties were observed, seldom directly,[7] more often indirectly, from the ^{1}H NMR shifts,[6d] the formation of complexes with Lewis acids,[10] and hydrogen bonding with phenols.[11]

In this paper we report on the acidity and basicity of thiocarboxamides in the gas phase, determined by Fourier transorm ion cyclotron resonance (FT-ICR) mass spectrometry. The few previous measurements[12] of their acidity met with difficulties. In the case of thioacetamide the problem was the low volatility at room temperature and decomposition at higher temperatures.[12a] In the case of *N,N*-dimethylthioformamide the site of acidity remained unknown.[12b] By optimizing the experimental conditions, we were able to obtain quantitative results for the simplest compounds: the acidity and basicity of thioacetamide and basicity of *N,N*-dimethylthioformamide.

EXPERIMENTAL AND RESULTS

The compounds were commercial samples and were used without further purification.

Proton transfer equilibria were monitored by FT-ICR mass spectrometry at a cell temperature of 338 K as described previously for gas-phase acidity and basicity

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measurements.[13] The gauge readings were corrected according to the equation[14a]

$$s_r = 0{\cdot}36\alpha_{ahc} + 0{\cdot}30$$

where s_r is the sensitivity relative to nitrogen and α_{ahc} is the polarizability calculated using atomic hybrid components.[14b]

In a previous study, fairly extensive decomposition of thioacetamide was observed,[12a] which was probably due to there being too high a temperature in the inlet and vacuum chamber of the ICR system. In this work, the decomposition product was identified as acetonitrile by exact mass measurements of the parent and fragment ions and by comparison of the mass spectrum with electron impact ionization with the standard. Using temperatures of 50, 70 and 65 °C for the inlet system, the vacuum chamber and the ICR system, respectively, the partial pressure of acetonitrile was

Table 1. Gas-phase acidity of CH_3CSNH_2 in kJ mol^{-1} according to $CH_3CSNH_2 + Ref^- \rightleftharpoons CH_3CSNH^- + RefH$ (298 K)

RefH	ΔG°_{acid}(RefH)	$\delta\Delta G^\circ_{acid}$[a]	$\Delta G^\circ_{acid}(CH_3CSNH_2)$[b]	$\Delta H^\circ_{acid}(CH_3CSNH_2)$
CH_3COOH	1428·8[c]	−7·3	1421·5	
	1429·7[d]			
	1427·2[e]			
	1428·8[f]			
C_2H_5COOH	1423·8[c]	−5·5	1418·7	
	1424·2[f]			
HCOOH	1415·0[c]	5·0	1420·4	
	1415·9[d]			
	1415·4[f]			
		Mean:	1420·2[g]	1452·6

[a] Measured at 338 K. If we consider only rotational entropy changes, the correction to 298 K is only 0·2 kJ mol^{-1} and not significant.
[b] Calculated choosing ΔG°_{acid}(RefH) values from the reference in footnote f.
[c] Ref. 15.
[d] Ref. 16.
[e] Ref. 17.
[f] Ref. 18.
[g] Preliminary measurements gave $\Delta G^\circ_{acid} \approx 1424$ kJ mol^{-1}.[12] The too high value was due to thermal decomposition.

Table 2. Gas-phase basicities of $HCSN(CH_3)_2$ and CH_3CSNH_2 with some reference compounds according to $BH^+ + Ref \rightleftharpoons B + RefH^+$ (kJ mol^{-1}, 298 K)

B	Ref	*GB*(Ref)[a]	δGB[b]	*GB*(B)[a,b]	*PA*
c-$C_3H_5NH_2$	CH_3NH_2	(860·6)[c]	5·8	866·4 (865·3)	
$C_2H_5NH_2$	*c*-$C_3H_5NH_2$	866·4[d]	5·9	872·3 (871·1)	
Thiazole	*c*-$C_3H_5NH_2$	866·4[d]	0·0	866·4 (859·4)	
$HCSN(CH_3)_2$	CH_3NH_2	(860·6)[c]	11·4	872·0	
	c-$C_3H_5NH_2$	866·4[d]	5·4	871·8	
	Thiazole	866·4	4·9	871·3	
	$C_2H_5NH_2$	872·3	−2·8	869·5	
			Mean:	871·2	903·6
CH_3CSNH_2	CH_3NH_2	(860·6)[c]	−9·3	851·3	
	$HC{\equiv}CCH_2NH_2$	(849·4)	−1·8	847·6	
	$(c\text{-}C_3H_5)_2CO$	(848·5)	6·3[e]	854·8[e]	
			Mean:	849·4	881·8

[a] Selected literature data[19] in parentheses.
[b] This work unless stated otherwise.
[c] Chosen as the anchor point for determining the basicity of all other compounds.
[d] Indirect measurement: Ref. 20, entry 9 in Table I: *c*-$C_3H_5NH_2$ was found to be a stronger base than CH_3NH_2 by 1·38 kcal mol^{-1} (in entry 7 of the same Table the data for cyclopropylamine should be read −2·2 instead of −0·22 kcal mol^{-1}).
[e] This value was not taken into account because of side-reactions.

kept below 20%. The ion gauge readings were then corrected according to the partial pressure determined approximately from the mass spectral data. Owing to the uncertainty in this correction, an uncertainty of roughly ± 1 kJ mol^{-1} arises in the relative value of $\delta\Delta G^\circ$ for the proton transfer.

Table 1 gives the relative acidity of CH_3CSNH_2, $\delta\Delta G^\circ_{acid}$, measured against three reference acids. No temperature correction (from 338 to 298 K) was applied (see footnote a). Absolute values, ΔG°_{acid}, given in Table 1 are based on a selected set of consistent data for the reference acids, taken from the same source (see footnote c). Other data available in the literature are also given to indicate the possible error bar associated with the absolute ΔG°_{acid} values. However, the three consistent values, preferred by us, lie within the range expected from the combined experimental errors. Note that these problems concern only the absolute values, ΔG°_{acid}; the relative values, $\delta\Delta G^\circ_{acid}$, are much more reliable.

Relative basicities, δGB, of CH_3CSNH_2 and $HCSN(CH_3)_2$ are given in Table 2. Four reference bases were used for the latter compound but poor agreement was obtained. Therefore, we redetermined GB's for these reference comounds, ethylamine, cyclopropylamine and thiazole, using the GB value for methylamine as the anchor point (Table 2, lines 1–3). With the corrected values the agreement was much better (Table 2, middle part, last column). When measuring the basicity of CH_3CSNH_2, one of the references used, dicyclopropyl ketone, gave a fast secondary reaction leading to an uncertain δGB. This value was eliminated (see Table 2, footnote e). Nevertheless, the uncertainty of $GB(CH_3CSNH_2)$ is larger than in common measurements, say ± 2 kJ mol^{-1}.

DISCUSSION

In the gas phase, thiocarboxamides are both moderately strong acids and bases. In either case they are situated near to the middle of the respective scale[19,21] of measurable values. Compared with carboxamides (Table 3) they are much stronger acids (by 65 kJ mol^{-1}) and stronger bases (by 19 kJ mol^{-1}), the latter value being equal when determined for thioacetamide or *N,N*-dimethylthioformamide. A more detailed discussion may proceed either in terms of enthalpies or Gibbs energies, but the results are equivalent as far as a comparison with carboxamides is concerned. For practical reasons we shall use ΔG° when comparing to solution measurements, and ΔH° when constructing isodesmic reactions based on the enthalpies of formation, ΔH°_f.

A comparison between the measurements taken in the gas phase and in solution is presented in Table 3. The highly endothermic dissociation process observed in the gas phase is greatly facilitated by solvation and its enthalpy is dramatically reduced. In the case of thioacetamide it is lowered by 1300 kJ mol^{-1} in DMSO and still further in 90% DMSO. Qualitatively the same behaviour is observed for carboxamides. Nevertheless, in terms of Gibbs energy the difference between the two classes (Table 3, last column) is reduced in solution to just two thirds of its original value. When the acidities of various comounds in the gas phase and in DMSO were systematically compared, a group of acids emerged with almost equal relative values: in a plot of ΔG°_{DMSO} vs ΔG°_g these acids were situated near the straight line of unit slope.[24a] These acids are characterized by being large aromatic molecules, giving rise to highly delocalized anions which are poorly solvated. For most other acids, the anions bear a more

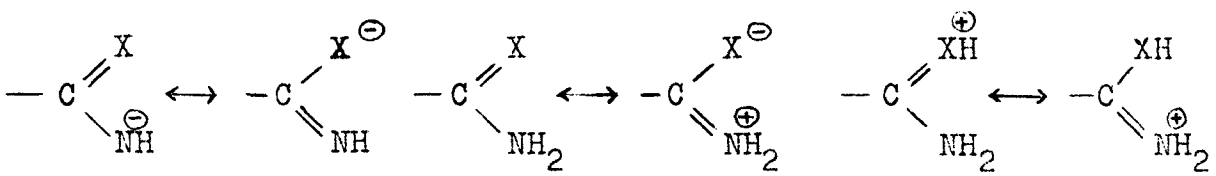
Table 3. Acidity and basicity of simple thiocarboxamides and carboxamides at different conditions (ΔG in kJ mol^{-1}, 298 K)

	X = S	X = O	Δ (thio − oxo)
Acidity:			
CH_3CXNH_2 proton transfer (gas)	1420·2	1485·3[a]	−65·2
CH_3CXNH_2 proton transfer (DMSO)[8]	105·5	145·5	−40·0
$C_6H_5CXNH_2$ proton transfer (DMSO)[8]	96·4	133·2	−36·8
$C_6H_5CXNH_2$ proton transfer (90% DMSO)[7a]	89·1	>95	
Basicity:			
$HCXN(CH_3)_2$ proton transfer (gas)	−871·2	−851·9[b]	−19·3
CH_3CXNH_2 proton transfer (gas)	−849·4	−830·1[b]	−19·3
(thio)caprolactame proton transfer (water)[c]	2·9	−7·4	10·2
$CH_3CXN(CH_3)_2$ H-bonding (CCl_4)[d]	−6·7	−13·0	6·3
$C_6H_5CXN(CH_3)_2$ H-bonding (CCl_4)[d]	−6·3	−11·6	5·3

[a] Ref. 22.
[b] Ref. 19.
[c] Ref. 7, 23.
[d] With 4-FC_6H_4OH, values statistically averaged by means of an empirical equation.[11]

localized charge and are more solvated: in the above-mentioned plot they deviate from the line towards relatively stronger acids in the solution.[24a] If we plot data or acetamide and thioacetamide on such a plot, we observe that the former deviates by a greater amount than the latter. The charge is evidently more delocalized in the case of deprotonated thiocarboxamide, which may be simply due to its larger volume and unrelated to the relative contributions of the resonance formulae **1** and **2**. However, when this concept is extended to other structures, it does not explain why the carboxylate ion should be more solvated and less delocalized than the carboxamide anion.[24a] In our opinion the explanation in terms of charge delocalization and solvation[24] is generally valid but its application to small differences may not be completely satisfactory in all cases.

Few data are available concerning the solution basicity of thiocarboxamides.[7] One example in Table 3 is not a typical structure, but thiocarboxamide is less basic than carboxamide, an opposite trend as observed in the gas phase. Also as hydrogen bond acceptors thiocarboxamides are less efficient than carboxamides (Table 3). Evidently the protonated form of the latter is better solvated in water, probably through the hydrogen bonds to oxygen.

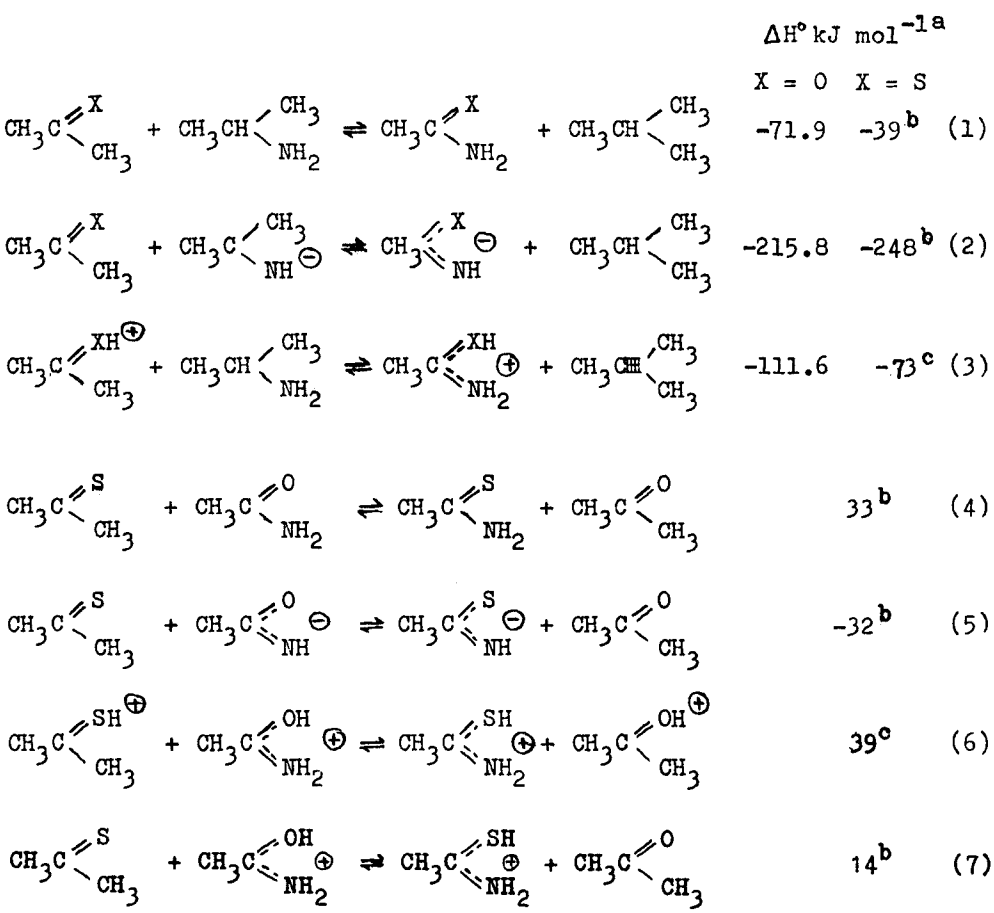


1 **2** **3** **4** **5** **6**

Any previous discussion of the acidity of thiocarboxamides has relied upon using carboxamides as an obvious reference, and apart from a few exceptions was based on the resonance formulae **1** ↔ **2** for the anion and **3** ↔ **4** for the neutral molecule. Bordwell and co-workers considered two explanations for the stronger acidity of thiocarboxamides,[8] later extended to three with a somewhat modified terminology:[24b] (a) the larger S atom is better at accommodating a negative charge,[8] in other words for reducing the lone pair–lone pair repulsion[24a] (polarizability effect[24b]); (b) the weak C=S bond[8] can reduce the weight for structure **1** (or **3**) in favour of **2** (or **4**) (resonance effect[24b]); (c) the greater dipole moment of the C=S bond (compared with the C=O bond) acts by a field effect.[24b] To our knowledge, there is no similar discussion to date concerning the basicity of thiocarboxamides.

The weakness of the above reasoning and generally of the discussions in terms of inductive (field), resonance and polarizability effects[25] is connected with the fact that they do not clearly separate the energy effects in the acid molecule and in the anion. Another drawback may be traced to the interference of individual effects. Thus, effect (a) concerns clearly the anion with the prevailing form **2**. However, effect (b) would be operating both in **3** and **1** with partial compensation. Effect (c) is not easily understandable: in the acid molecule **3** the dipole moment C=X does not interact with any appreciable charge, in the anion (structure near to **2**) there is a charge but no longer the dipole C=X. Note that an alternative theory exists, disputing strongly the importance of resonance in amides,[26] but saying nothing about their deprotonated or protonated forms. A similar theory for carboxylic acids it also highly controversial.[27]

In our opinion, the definitions of resonance[27b,28] and of other effects are ambiguous. Attention should first be focused on the separation of these effects into those operating in the anion and those operating in the neutral acid molecule. This task can be tackled fairly objectively. The isodesmic reaction (1) (Scheme 1, X=O) was constructed in the same way as previously[27b] for carboxylic acids. The reaction enthalpy was calculated from the tabulated enthalpies of formation,[29] and should represent the interaction between the C=O and NH_2 moieties, whatever its origin may be. Equations (2) and (3) were then constructed by means of thermodynamic cycles, introducing the gas-phase acidities and basicities. We conclude that even if the neutral molecule of acetamide is stabilized, its anion is more highly stabilized. A similar conclusion was drawn in the case of carboxylic acids.[27b] For the CH_3CONH^- anion the stabilization energy is so large [equation (2)] that it must be attributed mainly to the resonance **1** ↔ **2** which is predominated by form **2**. On the other hand, the stabilization energy of neutral acetamide, equation (1), may be only partly due to the resonance **3** ↔ **4** when the real structure is close to **3**. The rest of the stabilization energy may be explained by a change of hybridization[26] and by the common interaction of electron-attracting groups as for instance in acetals.[27b] It seems merely fortuitous that an almost equal value to that produced by equation (1) was obtained from a Hückel calculation of the 'resonance energy' of acetamide.[4] Concerning the protonated form, its stabilization energy is much less than that of the anion [equation (3)]. The same trend was



Scheme 1. [a] Calculated from the tabulated values of ΔH_f° (Ref. 29; for thioacetamide, Ref. 4) and from gas-phase acidities and basicities (Refs 19 and 21 and this work), uncertainty estimated to 3 kJ mol^{-1}. [b] Values derived using the estimated ΔH_f° of thioacetone of -2 kJ mol^{-1} (see text); uncertainty may be 6 kJ mol^{-1}. [c] Values derived using the estimate in note b; in addition the estimated *PA* of thioacetone = 848 kJ mol^{-1} (see text); uncertainty of the final value is 10 kJ mol^{-1} (estimated)

observed for the protonated carboxylic acid and carboxylate anion.[27b] In our opinion, the explanation need not be in terms of resonance but simply in terms of electrostatic interaction in structures **2** and **6**: in **2** the C=N dipole is orientated with the positive end towards the negative charge and in **6** the C—O dipole is orientated with its positive end towards the positive charge.

When the above reasoning is extended to thiocarboxamides, it is first necessary to estimate ΔH_f° of thioacetone. The most reliable estimate (-7 kJ mol^{-1}), used in Scheme 1, was obtained from ΔH_f° of thioformaldehyde,[30] formaldehyde and acetone,[29] using a simple additive scheme. In a more sophisticated version of an additive calculation from atom increments[31] a value for =S or C=S was lacking. A system of bond increments[32] is still more sophisticated and its application need not always be unambiguous: we obtained -7 kJ mol^{-1} while -9 kJ mol^{-1} was calculated in Ref. 32. From several *ab initio* calculations[33] we selected a single paper which contained data for all the required compounds[33a] and obtained a value of -2 kJ mol^{-1}. The degree of scattering of all these values gives some idea about their reliability. For equation (3) it was further necessary to estimate the proton affinity of thioacetone. This quantity is not additive but is affected by polarizability effects: one must always compare molecules of similar size.[27a,b] The most promising estimate was based on the compounds CH_3COCH_3 and CH_3COOCH_3, which possess similar proton affinity values.[19] With reference to

CH_3CSOCH_3, we obtained $PA(CH_3CSCH_3) = 848$ kJ mol^{-1}. In any case this value contains the greatest amount of uncertainty of the whole of Scheme 1.

Summarizing the results of Scheme 1, the conclusion is in any case valid that neutral thiocarboxamides are less stabilized than neutral carboxamides, but the opposite is true for their respective deprotonated forms. The difference in acidity between these two classes of compounds is thus given equally by the structure of their anions and by the structure of their acids. In terms of isodesmic reactions this difference is expressed by equations (4) and (5), which are obtained from equations (1) and (2), respectively, by subtracting the values for X = S and X = O. The negative enthalpy of equation (5) is explained unambiguously by the lone pair–lone pair repulsion[8,24a] in the carboxamide anion, formula **2**, which is reduced in thiocarboxamide by the larger size of the sulphur atom. This effect seems to be of primary importance when considering the difference between S and O compounds. On the other hand, an explanation of the positive enthalpy of equation (4) is not evident. The resonance energy[8,24] would predict the opposite and an explanation by C=X bond moments[24b] is not straightforward. The greater dipole moment of C=S is due mainly to the longer bond and not necessarily to a greater charge on the carbon atom: a simple electrostatic calculation would not be reliable. (Note that simple quantum chemical calculations yielded a smaller resonance energy for thioacetamide[4] than for acetamide.[34])

Concerning the protonated form of thiocarboxamides, the negative value for a ΔH° in equation (3) has the same origin as in the case of carboxamides. A comparison of the two classes of compounds is not straightforward since by subtracting equation (3) for X = O from that for X = S we obtain equation (6), which involves different reference compounds to those in equation (4) or (5). Its high positive enthalpy is partly due to the lower stability of the protonated form of acetone. More significant is probably equation (7), which is obtained from both equation (4) and from the gas-phase basicities of acetamide and thioacetamide. Its positive enthalpy indicates that the greater basicity of thiocarboxamides is produced by the lower stability of the neutral molecules, which is only insufficiently compensated for by the lower stability of the protonated forms. A theoretical explanation of this positive enthalpy brings the same problems as in the case of equation (3). Note also that this value has only twice the estimated uncertainty.

We conclude that our approach is capable of separating the observed relative acidities and basicities into those effects operating in the ions and those effects operating in neutral molecules, although some assumptions were fairly crude and led to imprecise values (Scheme 1). On the other hand, any explanation in terms of particular effects (inductive, resonance) would be only tentative. These effects have been defined for special model molecules but can hardly describe the effects between adjoining atoms.[35] In the case of thiocarboxamides and carboxamides it is particularly difficult to formulate any rule capable of predicting the observable quantities, with the possible exception of the above-mentioned principle of lone pair–lone pair repulsion.

As a final note, since the submission of this manuscript a more comprehensive study appeared concerning the basicity of thiocarbonyl compounds generally.[36] Some of the experimental data on thioamides agree reasonably with ours; the interpretation in terms of isodesmic reactions is based on ethylene derivatives as an alternative to our approach.

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