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Acidity of hydroxamic acids and amides

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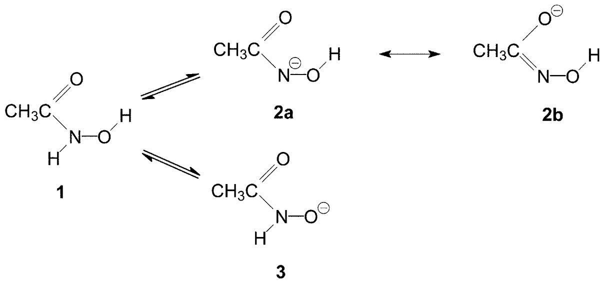
The relatively strong acidity of hydroxamic acids was analyzed by means of isodesmic reactions in which this acid or its anion is formed from simpler precursors. Acidity of amides was analyzed in the same way. Energies of all compounds involved in the reactions were calculated at the B3LYP/AUG-cc-pVTZ//B3LYP/6-311+G(d,p) level; at this level a good agreement was reached with the sparse experimental data. Interpretation of the results was the same as in the recent discussion of the acidity of carboxylic acids, and the conclusions were similar: both amides and hydroxamic acids are stabilized with respect to simpler reference molecules of amines or *N*-alkylhydroxylamines, respectively. However, their anions are stabilized still more and are responsible for the acidity. This effect is stronger in hydroxamic acids or amides than in carboxylic acids. The problem of whether it is due to resonance depends on the definition of this term. Semiquantitative comparison suggests that resonance in hydroxamic acids is more important than in amides and still more than in carboxylic acids. The stronger acidity of hydroxamic acids compared to amides is due to the destabilizing inductive effect of the hydroxyl group in the acid molecule, not to any effect in the anion.

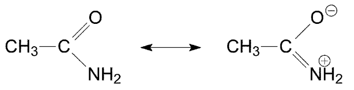
Introduction

Among many structural problems in the chemistry of hydroxamic acids (*N*-hydroxyamides),[1] their acidity has received particular attention since two structures of the anion are possible.[2–4] For instance, acetohydroxamic acid **1** yields the N-anion **2** and O-anion **3** in equilibrium. Summarizing the experimental results revealed that this equilibrium depends strongly both on the structure of hydroxamic acid and on reaction conditions:[4] while the N-anion overweighs in the gas phase[2d] and in nonpolar solvents,[2c] in water the O-anion may be populated in a comparable amount[2a,4] or even prevail.[2e] The N-acidity is strengthened by electron attracting substituents; hence for instance 4-nitrobenzohydroxamic acid behaves only as an N-acid.[2b] Recently, the problem was attacked by calculations at various levels:[2e,5] N-anions were always preferred in isolated molecules. Older literature described hydroxamic acids as O-acids without actual proof.[6]



In this communication we are interested in the N-anion and its unusual stability, *i.e.* in the cause of relatively strong N-acidity of hydroxamic acids. They are strong acids, particularly when compared with amides;[2d,3] in most cases they are stronger as N-acids than as O-acids. A qualitative *ad hoc* explanation was suggested, based on comparison with related compounds, that the hydroxyl group modifies the resonance **2a** ↔ **2b** in favour of **2a**, making it more significant than the resonance in the anions of amides.[3] Resonance in the anion **2** is analogous to the resonance in carboxylate anion, which has recently been the object of broad controversy.[7–9] The common classic opinion is that the acidity of carboxylic acids as compared to alcohols (eqn. (1), Table 1) is due to resonance in the anion. This view was more recently challenged and the main effect attributed to the high electrostatic potential in the acid molecule.[7] Our approach to this problem[9] was based on the precondition that two questions must be distinguished sharply, *viz.* a) whether the increased acidity is to be attributed merely to the energy of the acid or of the anion, and b) whether it is due to resonance. The first question was answered unambiguously[9] in terms of isodesmic[10] reactions; for instance the reaction energies Δ_2E and Δ_3E of eqns. (2) and (3) describe the stabilization energy in the molecule of acetic acid and in its anion, respectively. Evidently, acetic acid is a stronger acid than methanol because its anion is more stable and in spite of the fact that the acid molecule is also stabilized. The second question is more problematic and the answer depends on how resonance is defined and how a reference model is constructed devoid of any resonance. Nevertheless, some estimates agreed that resonance is responsible for about one third of the enhanced acidity of carboxylic acids relative to alcohols.[8d–f,9b]

Before applying the above principle to hydroxamic acids, comparison with amides seems appropriate: the pertinent isodesmic reactions have the form of eqns. (4)–(6). Resonance in amides, **4a** ↔ **4b**, was discussed in terms similar to those used in the case of carboxylic acids; attention was focused merely on the structure of the uncharged molecule.[11]The isodesmic reactions for hydroxamic acids have then the form of eqns. (7)–(9); the hydroxylamine group NHOH is taken as an entity. The effect of the hydroxyl group on acidity can be obtained subsequently from the difference compared to amides.



In this communication, we extended the approach used for carboxylic acids[9] to amides and hydroxamic acids; in the case of hydroxamic acids we were dealing only with their N-acidity. Reaction energies Δ_4E – Δ_9E of the isodesmic reactions,

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Table 1 Isodesmic reactions revealing the stabilization energy in carboxylic acids, amides and hydroxamic acids (energies in kJ mol^{-1})[a]

Eqn.		ΔE calc.	
(1)	$CH_3COOH + CH_3O^- \rightleftharpoons \mathbf{CH_3COO^-} + CH_3OH$	−142.6	
(2)	$CH_3OH + CH_3CHO \rightleftharpoons \mathbf{CH_3COOH} + CH_4$		−135.4[b]
(3)	$CH_3O^- + CH_3CHO \rightleftharpoons \mathbf{CH_3COO^-} + CH_4$		−278.0
(4)	$CH_3CONH_2 + CH_3NH^- \rightleftharpoons \mathbf{CH_3CONH^-} + CH_3NH_2$	−172.7	
(5)	$CH_3NH_2 + CH_3CHO \rightleftharpoons \mathbf{CH_3CONH_2} + CH_4$		−119.4[c]
(6)	$CH_3NH^- + CH_3CHO \rightleftharpoons \mathbf{CH_3CONH^-} + CH_4$		−292.2
(7)	$\mathbf{CH_3CONHOH} + CH_3N^-OH \rightleftharpoons \mathbf{CH_3CON^-OH} + CH_3NHOH$	−193.4	
(8)	$CH_3NHOH + CH_3CHO \rightleftharpoons \mathbf{CH_3CONHOH} + CH_4$		−102.4
(9)	$CH_3N^-OH + CH_3CHO \rightleftharpoons \mathbf{CH_3CON^-OH} + CH_4$		−295.8
(10)	$CH_3CONHOH + CH_3CONH^- \rightleftharpoons \mathbf{CH_3CON^-OH} + CH_3CONH_2$	−67.9	
(11)	$CH_3CONH_2 + CH_3NHOH \rightleftharpoons \mathbf{CH_3CONHOH} + CH_3NH_2$		+17.0
(12)	$CH_3CONH^- + CH_3N^-OH \rightleftharpoons \mathbf{CH_3CON^-OH} + CH_3NH^-$		−3.6

[a] Calculated at the B3LYP/AUG-cc-pVTZ//B3LYP/6-311+G(d,p) level. For the sake of clarity, the crucial compound in each reaction for which the interaction is estimated is printed in bold. [b] Experimental $\Delta H°(298) = -140$ kJ mol^{-1}; obtained as the sum of experimental gas-phase enthalpies of formation, ref. 13. [c] Experimental $\Delta H°(298) = -125$ kJ mol^{-1}, ref. 13.

Table 2 DFT Energies and some geometrical parameters of compounds involved in eqns. (1)–(6)

Compound	Conformation	*E*(DFT)[a]/a. u.	*E*(DFT)[b]/a. u.	ΔE[a]/kJ mol^{-1}	C=O/Å	C–N/Å	C–O/Å
$CH_3CONHOH$	*Z,sp* **1a**	−284.4724790	−284.4995171	0	1.226	1.365	
	E,ac **1b**	−284.4702633		5.8	1.215	1.393	
CH_3CON^-OH	*Z*	−283.9123433	−283.9374790	0	1.279	1.317	
	E	−283.8981731		37.2			
CH_3NHOH	*ac* **5a**	−171.0871613	−171.1029088	0		1.460	
	sc **5b**	−171.0805877		17.3		1.464	
CH_3N^-OH		−170.4494727	−170.4671996			1.412	
CH_3CONH_2		−209.2883302[c]	−209.3060678		1.217	1.370	
CH_3CONH^-	*Z* **6a**	−208.7004628	−208.718363	0	1.269	1.322	
	E **6b**	−208.6914281		23.7			
CH_3NH_2		−95.8938400[c]	−95.2494663			1.465	
CH_3NH^-		−95.2376682	−95.9029609			1.435	
CH_3COOH		−229.1647182[c]	−229.1857162		1.205		1.359
CH_3COO^-		−228.6023227	−228.6217908		1.256		1.256
CH_3OH		−115.7649436[c]	−115.7765427				1.423
CH_3O^-		−115.1459146	−115.1582881				1.335
CH_3CHO		−153.8821476[c]	−153.8960173		1.206		
CH_4		−40.5339278[c]	−40.5384024				

[a] Level B3LYP/6-311+G(d,p). [b] Level B3LYP/AUG-cc-pVTZ//B3LYP/6-311+G(d,p). [c] The energies were already reported, ref. 15.

Table 3 Comparison of calculated and experimental reaction energies of isodesmic reactions (kJ mol^{-1})

	Eqn. (1)	Eqn. (4)	Eqn. (10)
B3LYP/6-311+G(d,p)	−148.7	−179.3	−73.3
B3LYP/6-311++G(3df,3pd)//B3LYP/6-311+G(d,p)	−144.4	−172.5	−71.3
B3LYP/AUG-cc-pVTZ//B3LYP/6-311+G(d,p)	−142.6	−172.7	−67.9
Experimental $\Delta G°(298)$	−141.8[a]	−170.3[b]	−66.5[c]
Experimental $\Delta G°_{aq}(298)$[d]	−62	~−130	−33

[a] Relative experimental gas-phase acidities, ref. 14; the more recent values were selected. [b] Refs. 14 and 2*d*. [c] Ref. 2*d*. [d] Rough estimate on the basis of the available p*K* values (ref. 6*b*) and empirical correlations (ref. 21).

eqns. (4)–(9), were calculated within the framework of the density functional theory (DFT).[12] For an accurate comparison, we recalculated also these energies for carboxylic acids [Δ_1E – Δ_3E, pertinent to eqns. (1)–(3)], obtained previously either with a different theoretical model[9b] or on an experimental basis.[9a] We preferred throughout the values calculated uniformly on the basis of data from Table 2 to some experimental enthalpies of formation[13] or Gibbs energies of ionization,[2d,14] which would be available only for few compounds. We started with the level B3LYP/6-311+G(d,p) which was recently found sufficient for somewhat larger molecules with a greater distance between the interacting groups.[15,16] On the basis of comparison to some experimental gas-phase acidities (Table 3), we chose ultimately the level B3LYP/AUG-cc-pVTZ//B3LYP/6-311+G(d,p).

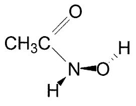
Results and discussion

Calculations

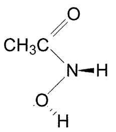
The DFT calculations were performed according to the original proposal[12] using the standard program.[17] No symmetry conditions were presumed. All energy-optimized structures were checked by vibrational analysis and represented energy minima. The energies and some geometric parameters are listed in Table 2. In the case of compounds which can exist in several conformations, all possibilities were examined (Table 2 and footnotes).

Conformations

Possible conformations were investigated at the B3LYP/6-311+G(d,p) level. The conformation of acetohydroxamic acid deserves particular attention. Analysis of solution dipole moments[18] assumed an intramolecular hydrogen bond and hence a near-to-planar *Z*,*sp*-conformation as in the formula **1**. The hydrogen bond is also compatible with the IR spectra;[19] however, most of these proofs were obtained on aromatic hydroxamic acids.[18,19b] Results of calculations[2e,5,20] for formohydroxamic acid, mostly at various MP2 levels, were somewhat inconsistent, sometimes rather sensitive to the theoretical model used.[5d] Nevertheless, a structure similar to **1** was predicted in all cases, either planar (**1**)[2e,5d,20] or with the OH hydrogen slightly out of the plane (**1a**);[5a,c] sometimes they should exist in equilibrium with an *E*-conformation,[5a,20] or with tautomeric forms.[5a,d] Some of the assumed conformers[2e,5c] seem doubtful, particularly as they can hardly coexist in equilibrium. For acetohydroxamic acid, the planar form **1** was predicted only as a minor conformer,[2e] again together with an improbable form. Our calculations yielded the almost planar *Z*,*sp* conformation **1a**, with a slightly puckered five-membered ring, and only the N–H bond strongly out of plane. The previously supposed[2e,5c,18,19] intramolecular H-bond is indicated by the distance O. . .H of 2.00 Å. The minor *E*,*ac* conformer **1b** has an energy higher by 5.8 kJ mol^{-1} and accounts for an energy correction of only +0.5 kJ mol^{-1}. For further conclusions, the exact conformation is immaterial.

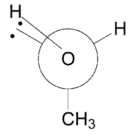


1a

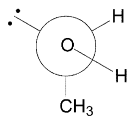


1b

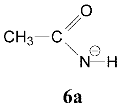
For *N*-methylhydroxylamine three staggered conformations on the N–O bond are possible but only *sc* (**5b**) was found as a minor form. The prevailing conformer is *ac* (**5a**) with the hydrogen and the lone electron pair almost in an eclipsed position. A corresponding conformation was found also for the anion CH_3N^-OH. The anion of acetamide exists in two conformations, **6a** and **6b**, of which the former strongly prevails. Energies of the isodesmic reactions (Table 1) were calculated with the assumed equilibrium of conformers (at 298 K, taking ΔG as equal to ΔE), even when some of them were negligibly populated.



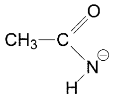
5a



5b



6a



6b

Relation to the experimental values

Comparison with some experimental values was important for choosing a suitable theoretical model. The B3LYP/6-311+G(d,p) level, well-tried in previous work,[15,16] need not be sufficient for smaller molecules, particularly for the anions, and for reactions which are not homodesmotic.[10b] From our set of isodesmic reactions, the reaction energies Δ_1E and Δ_4E can be compared with the experimental gas-phase acidities;[14] particularly important for this purpose may be eqn. (10) for which the acidities were measured in one laboratory.[2d] The comparison (Table 3) reveals that the level B3LYP/AUG-cc-pVTZ//B3LYP/6-311+G(d,p) is good: for eqn. (10) the deviation does not exceed the experimental error of 1.2 kJ mol^{-1}. (It was given[2d] as 0.8 kJ mol^{-1} for one molecule.) In the case of eqns. (1) and (4), the worse agreement may be caused by the experimental values since they were taken from different sources.[14]

Hence we recalculated all the energy values at the above level. They are given in Table 2, column 3, the isodesmic reaction energies in Table 1. The level chosen influences mainly the energies of anions, much less the energies of neutral species.

Another experimental proof could be comparison of the reaction energies Δ_2E and Δ_5E with the pertinent enthalpies $\Delta_2H°(298)$ and $\Delta_5H°(298)$ obtained as sums of the available experimental enthalpies of combustion[13] $\Delta_fH°$ (Table 1, footnotes *b* and *c*). The agreement is reasonable considering the uncertainty in the experimental $\Delta_fH°$. Previous analysis[15] revealed that for molecules of this size the calculated ΔE(DFT) are more dependable than experimental ΔH°.

Further conclusions will be based on the calculated DFT energies, which are of uniform reliability and in accord with the available experimental data in the gas phase. The acidities in water parallel these values only in the qualitative sense, although the solvent attenuation is relatively small (Table 3, last line).

Interaction energies in the neutral molecules and in the anions

The interaction energies $\Delta_1E – \Delta_9E$ (Table 1) can be summarized and interpreted in a uniform way: all neutral molecules involved are strongly stabilized with respect to the unconjugated models, their anions are stabilized still more. Consequently all the compounds examined appear as relatively strong acids. All stabilization energies are great and exceed many times any possible error of the model. Stabilization of the neutral molecule decreases in the series carboxylic acids > amides > hydroxamic acids; anions of amides and hydroxamic acids are stabilized equally and more than carboxylate anions. This finding is only partly in agreement with the classical rules of resonance.

The central problem for the acidity of hydroxamic acid is the difference towards amides, *i.e.* the substituent effect of the OH group. Previously it was assumed that this effect is operating mainly in the anion. When its stability is influenced both by resonance with the CO group and by the inductive effect of OH, the two effects together should be stronger than additive.[3] This idea can be tested on isolated molecules by means of isodesmic reactions, separately for the acid molecule and for the anion, eqns. (11) and (12). If the two effects were additive, the reaction energies, $\Delta_{11}E$ and $\Delta_{12}E$ would be zero and the acidity of hydroxamic acids would not be exceptional taking into account the inductive effect of hydroxyl. Table 1 reveals that this is true for the anion but the acid molecule is destabilized by almost 20 kJ mol^{-1}. When the acidity is strengthened from one side by the inductive effect of OH and from the other side by conjugation with CO, these two effects are not additive but strengthen each other. However, this effect does not take place in the anion as anticipated[3] but in the uncharged molecule of the acid.

Effect of resonance

As mentioned in the Introduction, this question is not unambiguous; it would need a model defining exactly what is the reference molecule without resonance. In the case of carboxylic acids, we used reference to alcohols substituted with

Table 4 Attempted semiquantitative separation of substituent inductive and resonance effects on the ionization of carboxylic acids, amides and hydroxamic acids (kJ mol^{-1})

Compound	R anion	−R acid[a]	I anion[b]	−I acid[a,b]	Acidity	% of resonance
CH_3COOH	−180	+146	−98	−11	−143	24
CH_3CONH_2	−194	+130	−98	−11	−173	37
$CH_3CONHOH$	−198	+113	−98	−11	−193	44

[a] These values are given with an inversed sign corresponding to their contribution to the acidity. [b] These values include possible polarizability effects and are based on the correlation analysis of experimental data for substituted alcohols, ref. 9*b*.

unconjugated substituents. The contribution of resonance to the acidity enhancement was estimated[9b] to be 28% (for formic acid – methanol). This agrees reasonably with other empirical estimates[8f] (20% or 37% for acetic acid – *t*-butanol) and fairly with an approach based on VB structures without resonance[8d] (48%). The differences between these figures give an idea about their reliability and show also the dependence on the particular compound. The relatively small contribution of resonance may be understood when bisection into effects in the anion and in the acid molecule is carried out[9b] (Table 4, first line): the inductive effect acts in the same sense while the effects of resonance partly cancel. The calculation can be tentatively extended to amides and hydroxamic acids, assuming that the inductive effect is equal in all cases (Table 4). The result is that the contribution of resonance decreases in the sequence carboxylic acids > amides > hydroxamic acids. In the anions, the differences are smaller and the resonance is weaker in the carboxylate anion. Note that the contribution of the inductive (or "electrostatic"[8f]) effect was also estimated from the electronegativities of C and O;[8f] in this approach also the inductive effect was taken as equal in the three classes of compounds. (For the pair acetic acid – *t*-butanol, one gets[8f] −76 kJ mol^{-1} compared to our −109; the difference agrees roughly with the different acidity of *t*-butanol and methanol.[14])

The above calculations are essentially based on the well-known approach formulated most exactly by Taft:[22] inductive effects are estimated on a system without conjugation and a deviation observed in a conjugated system is ascribed to "resonance" without giving this term any particular physical meaning. Another problem is whether resonance is well reproduced by any structural formula, particularly by the common structures like **2b** and **4b**. It was pointed out that **4b** is an insufficient description since the C–N bond is shortened but the C=O bond is not lengthened.[11] Similar objections arose from an analysis of experimental dipole moments:[23] the charge transfer does not proceed from N to O but merely from N to C. In the case of esters, the charge transfer was too small for a reliable determination, nevertheless a similar direction was found.[24]

Our geometrical parameters (Table 2) confirm this statement in a qualitative sense. The C=O bond is only a little lengthened in acetamide and in acetohydroxamic acids (compared to methylamine and *N*-methylhydroxylamine, respectively) and unchanged in acetic acid (compared to methanol). In the anions, the changes are more evident: the C=O bond is lengthened and the C–N or C–O bonds are shortened. The changes are always greatest in hydroxamic acids and smallest in carboxylic acids. This succession is in agreement with the classic rules of resonance: structures with a negative charge on a more electronegative atom (in the anions) or with a positive charge on a less electronegative atom are more important for strengthening the resonance. However, the resonance energies in Table 4 do not accord with these rules: formula **4b** with a positive charge on N should be more important than the corresponding formula for carboxylic acids with a charge on O but the ratio of resonance energies is reversed. One can conclude only that resonance formulae like **2b** or **4b** describe only some features of the structure.

Conclusions

We do not want to overestimate the accuracy of our results and the reliability of our model; in particular the relative effects of resonance are rough estimates dependent both on the basic approximation and on the theoretical model. Nevertheless, the following statements formulated merely qualitatively are in our opinion dependable. The acidity of both amides and hydroxamic acids is caused by low energy of the anions and not by a high energy of the acid molecules, as in carboxylic acids; differences between the three classes of compounds are relatively small. However, the stronger acidity of hydroxamic acids compared to amides is due to the higher energy of the hydroxamic acid molecule, not to the energy of anions. The acidity may be attributed to "resonance" defined as a substituent effect of the acetyl group exceeding that in unconjugated molecules (say in alcohols or amines). Then resonance is responsible for about one quarter of the enhanced acidity of carboxylic acids, one third in the case of amides and one half in the case of hydroxamic acids.

Acknowledgements

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