Research Article

Journal of Physical Organic Chemistry

Received: 10 May 2007, Revised: 5 October 2007, Accepted: 9 October 2007,

(www.interscience.wiley.com) DOI 10.1002/poc.1292

Conversion of a weak organic acid to a super acid in the gas phase

Alireza Fattahi[a]* and Elham Tavasoli[a]

The effects of selected metal ions on the gas-phase acidity of weak organic acids have been explored using the DFT and Moller–Plesset Perturbation Theory (MP2) calculations. The three organic acids selected for this study were acetic acid (aliphatic), benzoic acid (aromatic), and glycine (amino acid). The acidities of these compounds are compared with the acidity of their Li^+-, Na^+-, and K^+-complexed species. The results indicate that upon complexation with Li^+, Na^+, and K^+ at 298 K, the gas-phase acidity of acetic acid, for example, varies from 345.3 to 218.8, 230.2, and 240.1 kcal/mol, respectively (i.e., its dissociation becomes much less endothermic). These values indicate that a weak organic acid can be converted to a super acid when it is complexed with an ionic metal. Copyright © 2007 John Wiley & Sons, Ltd.

Supplementary electronic material for this paper is available in Wiley InterScience at http://www.mrw.interscience.wiley.com/suppmat/0894-3230/suppmat/

Keywords: acidity; metal ion affinity; DFT; metal complexation

INTRODUCTION

Gas-phase acidity of organic compounds (Eqn (1)) has been extensively investigated because it eliminates the effects of solvent and thus lets us study the intrinsic factors which influence the acidity of an organic compound.[1,2] These factors include the electronic effects of various groups present in acid. For example, gas-phase acidities of aliphatic acids seem to increase with the size of the alkyl group likely due to the greater polarizabilities of the larger groups. But this order is contrary to that found in solution because the larger anions are less tightly solvated than the smaller anions. On the other hand, the pK values determined in the solution are influenced by the solvent and other conditions of the measurement. The nature of solvent in which the extent or rate of deprotonation is determined has a significant effect on the apparent acidity.[3]

Acidities in the gas phase also provide the data with which one can compare calculations based on high-level molecular orbital theory and thus test the origins of structural effects on the acidity. The large endothermic value of the ΔH for proton dissociation (e.g., ΔH^0_{acid} of Eqn (1)) in the gas phase shows both inherent instability of the conjugate base and also the electrostatic attraction between the oppositely charged conjugate base and proton. Gas-phase acidities vary over a wide range, for instance, from 420 to 350 kcal/mol for hydrocarbons and from 340 to 309 kcal/mol for carboxylic acids.[4] These acidities enhance by withdrawing groups, such as chloro and fluoro groups, that will delocalize negative charge in the conjugate base.[5]

It is well known that Lewis acids play important role as catalysts and include the alkalic-metal cations and divalent ions such as Mg^{2+}, Ca^{2+}, Zn^{2+}, and so on.[6] The catalytic activity of metal ions originates in the formation of a donor–acceptor complex between the cation and the reactant, which must act as a Lewis base.[7] For instance, in many synthetic reactions, Lewis acids are used to enhance the enolization of an aldehyde or ketone as well as to enhance the electrophilicity of the carbonyl carbon.[8]

Ren *et al.* have reported the effect of the Lewis acid BF_3 on the gas-phase acidity of acetaldehyde.[9] They found computationally and experimentally that the acidity of acetaldehyde complexed with BF_3 increases about 50 kcal/mol (Equivalent to 36 pK_a units in solution). The gas-phase acidity of acetaldehyde was found to be 365.8 kcal/mol, while its complex with BF_3 was found to be 316 kcal/mol. This makes the acetaldehyde–BF_3 complex approximately as acidic as HI (314 kcal/mol) in the gas phase.

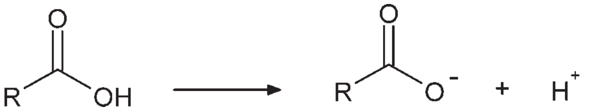
However, to our best of knowledge, a survey of the literature shows no report concerning the effects of metal cations (as Lewis acids) on the acidity of organic acids in the gas phase. The aim of this study is to computationally illustrate to what extent the Lewis acids (such as Li^+, Na^+, and K^+) can increase the acidity of weak organic acids in the gas phase. The acidities of three sample acidic compounds (denoted by RCOOH in Eqn (1)) including acetic acid (aliphatic), benzoic acid (aromatic), and glycine (amino acid) were first calculated based on Eqn (1). Then, using the same computational methods, the acidities of the metal-complexed species of these three sample acids (denoted by $[RCOOHM]^+$, where M^+ includes Li^+, Na^+, or K^+) were also calculated based on Eqn (2). Ultimately, ΔH^0_{acid} (RCOOH) (i.e., the acidity of free acid) has been compared with ΔH^0_{acid} $[RCOOHM]^+$ (i.e., the acidity of metal-complexed acid) based on the following dissociation

---

* Department of Chemistry, Sharif University of Technology, P.O. Box 11365-9516, Tehran, Iran.
E-mail: fattahi@sharif.edu

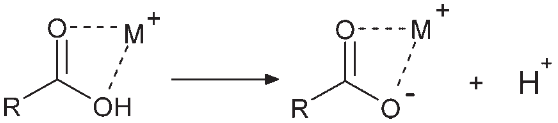
a A. Fattahi, E. Tavasoli
Department of Chemistry, Sharif University of Technology, Tehran, Iran

Eqns (1) and (2):



(1)

Or briefly: RCOOH→$RCOO^- + H^+$ $\Delta H^0_{rxn} = \Delta H^0_{acid}(RCOOH)$



(2)

Or briefly: $[RCOOHM]^+ \rightarrow RCOOM + H^+$ $\Delta H^0_{rxn} = \Delta H^0_{acid}$

COMPUTATIONS

Calculations were carried out using Spartan software.[10] For glycine and its Li^+-, Na^+-, and K^+-complexed species, we used their most stable conformers as reported in the literature. For acetic acid and benzoic acid and their Li^+-, Na^+-, and K^+-complexed species, the conformer search was performed using the 6-31g* basis set and three levels of theory including the Becke three parameter hybrid exchange and Lee–Yang–Parr correlation density functional (B3LYP),[11,12] second-order Moller–Plesset Perturbation Theory (MP2),[13,14] and MPW1PW91.[15] All three methods gave the same geometry for the lowest energy conformer (LEC) of each species. The LEC of each species was then optimized using B3LYP, MP2, and MPW1PW91 and the 6-311++g(d, p) basis set. This basis set was selected for all calculations as it contains both polarized basis set and diffuse functions. Diffuse functions are particularly important for systems where electrons are relatively far from the nucleus including molecules with lone pairs and anions.[16–19] All of the resulting energetic quantities include zero-point energies and have been adjusted to 298.15 K. The computed thermochemical values at 298 and 0 K are respectively given in the text and Supporting Information. Tables and figures given in Supporting Information are denoted by S.

RESULTS AND DISCUSSION

Acidity of free acid

To calculate the acidity of acetic acid, benzoic acid, and glycine, the LECs (or minima) for the acid RCOOH and its conjugate base $RCOO^-$ were first explored. For glycine, the most stable conformer was used, as reported by Hu. et al.[20] In this conformer, the O—H group adopts the *trans* position with respect to the main skeleton which allows intramolecular hydrogen bonding between the C=O and NH_2 groups.

The LECs of these sample acids and their conjugate bases were then optimized by B3LYP, MPW1PW91, and MP2 levels using the basis set 6-311++g(d, p). The representative optimized structures for RCOOH are given in Fig. 1S (in Supporting Information). The absolute energies for RCOOH and $RCOO^-$ are given in Table 1S. Subsequently, based on Eqn (1), the acidity of RCOOH was calculated using

$$\begin{aligned}\Delta H^0_{acid}(RCOOH) &= \Delta U + \Delta(PV) \\ &= U[RCOO^-] + U[H^+] - U[RCOOH] + 2.5RT \qquad (3)\end{aligned}$$

Table 1. Experimental and computed ΔH_{acid} values at 298 K in kcal/mol. The basis set for all calculation levels is 6–311++g**

	Experimental	B3LYP	MPWLPW91	MP2
Acetic acid[a]	348.1 ± 2.2	345.3	347.8	353.4
Benzoic acid[b]	340.2 ± 2.2	338.4	340.2	346.2
Glycine[c]	341.6 ± 2.1	340.1	342.5	349.2

[a] Reference [26].
[b] Reference [27].
[c] Reference [11].

In Eqn (3), U is the calculated absolute energy and $2.5RT$ is the kinetic energy contribution of H^+ at 298 K. $U[H^+] = 0$ because H^+ has no electron. This contribution is zero at 0 K. The computed acidities at 298 and 0 K are given in Table 1 and Table 2S, respectively. The experimental acidity values for the three acids studied herein are also provided in Table 1. As is apparent from this table, the computed acidity values at the B3LYP and MPW1PW91 levels are in good accordance with the experimental values.

Acidity of metal-complexed acid

The acidities of the three metal-complexed acids were calculated based on Eqn (2). The energetically possible conformers of each $[RCOOHM]^+$ and those of its conjugate base RCOOM were first explored. For Li^+-, Na^+-, and K^+-complexed glycine, we used the LECs reported by Russo and co-workers.[16] All three computational levels provided the same geometry for the LECs of $[RCOOHM]^+$ and RCOOM, whereas for $[RCOOHM]^+$ we could not find the LECs by the MP2 method.

The LECs of the $[RCOOHM]^+$ and RCOOM species were then reoptimized using B3LYP, MPW1PW91, and MP2 levels using the basis set 6-311++g(d, p). The representative structures for the LECs of $[RCOOHM]^+$ and RCOOM optimized at the B3LYP level; the energies of the optimized structures are respectively given in Figs. 2S and 3S, and Table 3S. Based on Eqn (2), the acidity of $[RCOOHM]^+$ at 298 K was calculated by using Eqn (4) whose results are given in Table 2. The computed acidity values at 0 K are

Table 2. ΔH_{acid} at 298 K for $[RCOOHM]^+$complexes in kcal/mol. The basis set for all calculation levels is 6–311++g**

	B3LYP	MPWLPW91	MP2
Acetic acid			
Li^+	218.7	220.7	227.0
Na^+	230.2	232.7	239.6
K^+	240.1	240.9	—
Benzoic acid			
Li^+	220.6	221.8	226.3
Na^+	231.0	231.9	238.0
K^+	240.0	241.2	247.2
Glycine			
Li^+	233.7	235.8	240.8
Na^+	239.9	242.2	247.7
K^+	245.2	247.2	253.8

given in Table 4S.

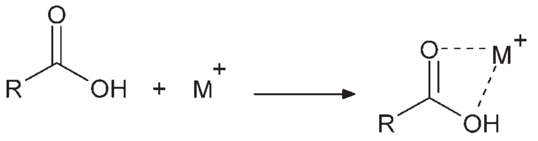
$$\Delta H^0_{\text{acid}}[\text{RCOOHM}]^+ = \Delta U + \Delta(PV)$$
$$= U[\text{RCOOM}] + U[\text{H}^+] - U[\text{RCOOHM}]^+ + 2.5RT \quad (4)$$

A comparison of Tables 1 and 2 demonstrates how drastically the acidity (ΔH^0_{acid}) of acetic acid, benzoic acid, and glycine increases upon complexation with Li^+, Na^+, and K^+. For instance, the B3LYP results given in Tables 1 and 2 indicate that upon complexation with Li^+, Na^+, and K^+ at 298 K, respectively: (a) the acidity of acetic acid has changed from 345.3 to 218.8, 230.2, and 240.1 kcal/mol; (b) the acidity of benzoic acid has changed from 338.4 to 220.6, 231.0, and 240.0 kcal/mol; and (c) the acidity of glycine has changed from 340.1 to 233.7, 239.9, and 245.2 kcal/mol. Thus, the acidity values of a weak organic acid such as acetic acid may be enhanced by more than 100 kcal/mol (i.e., it becomes less endothermic) when it is complexed with Li^+, Na^+, or K^+. It is worth mentioning that these acidity values are even less endothermic than the ΔH^0_{acid} of the most acidic compound (which is considered a super acid) in the gas phase, made recently by Strittmatter et al. with a ΔH^0_{acid} of 252.6 ± 3.1 kcal/mol.[23]

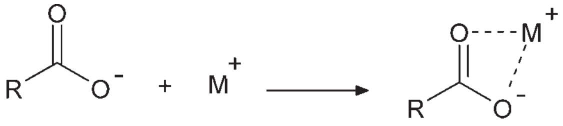
Based on Eqn (2), both the acid RCOOH and its conjugate base RCOO^- can combine with the ionic metal M^+ to make the corresponding complexes $[\text{RCOOHM}]^+$ and RCOOM, respectively. However, as qualitatively expected, the reason the acidity of a metal-complexed weak organic acid is so drastically enhanced is due to the higher metal affinity of the conjugate base RCOO^- compared with that of the acid RCOOH. This is due to higher electrostatic attractions present in RCOOM between M^+ and the negative charge on oxygen (see Eqn (2)). To quantitatively explore this matter, we have calculated the metal ion affinities (MIAs) of the acid RCOOH and its conjugate base RCOO^-, the results of which are given in the following section.

Metal ion affinities of the acid RCOOH and its conjugate base RCOO^-

MIAs for RCOOH and RCOO^- were calculated using the following reactions:



$$-\Delta H^\circ_{rxn} = \text{MIA (RCOOH)} \quad (5)$$



$$-\Delta H^\circ_{rxn} = \text{MIA (RCOO}^-\text{)} \quad (6)$$

In Eqns (5) and (6), the absolute energies of all species except that of M^+ are given in Table 3S. The absolute energies of M^+ were also calculated at B3LYP, MPW1PW91, and MP2 levels using the basis set 6-311++G** whose results are given in Table 5S. The MIAs of RCOOH and RCOOM were calculated by using Eqns (7) and (8), respectively.[16]

$$\text{MIA (RCOOH)} = -\Delta U - \Delta(PV)$$
$$= -U[\text{RCOOHM}]^+ + U[\text{RCOOH}] + U[\text{M}^+] + 2.5RT \quad (7)$$

Table 3. Metal ion affinities (MIAs) of RCOOH and RCOO^- in kcal/mol at 298 K. The basis set for all calculation levels is 6-311++g**

	B3LYP	MPW1PW91	MP2
Acetic acid			
Li^+	43.9	43.1	45.2
Na^+	30.1	29.5	31.5
K^+	21.8	20.6	—
Acetate			
Li^+	169.1	170.3	171.6
Na^+	145.2	144.6	145.3
K^+	127.0	127.5	—
Benzoic acid			
Li^+	47.0	45.7	45.4
Na^+	32.5	31.5	30.6
K^+	23.6	23.1	21.5
Benzoate			
Li^+	164.8	164.1	165.3
Na^+	139.8	138.8	138.8
K^+	121.9	122.0	120.5
Glycine			
Li^+	59.7	57.9	62.7
Na^+	39.1	39.6	43.1
K^+	28.6	27.9	30.8
Glycine (anion)			
Li^+	165.6	165.3	167.6
Na^+	140.9	140.17	141.1
K^+	122.9	123.3	122.6

$$\text{MIA (RCOO}^-\text{)} = -\Delta U - \Delta(PV)$$
$$= -U[\text{RCOOM}] + U[\text{RCOO}^-] + U[\text{M}^+] + 2.5RT \quad (8)$$

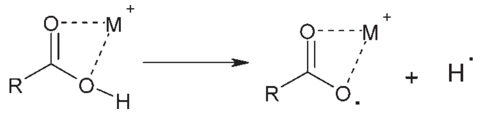
In Eqns (7) and (8), U is the computed absolute energy and $2.5RT$ is the kinetic energy contribution of M^+ at 298 K. The MIAs of RCOOH and RCOO^- were calculated for each acid at B3LYP, MPW1PW91, and MP2 levels using the basis set 6-311++g(d, p). These computed MIAs at 298 and 0 K are given in Table 3 and Table 6S, respectively.

As shown in Table 3, for all three acids, the MIA of the conjugate base RCOO^- is much higher than that of the acid RCOOH. Moreover, for all acids examined herein, the MIAs of both RCOOH and RCOO^- decrease from Li^+ to K^+. For example, as given in Table 3, the Li^+, Na^+, and K^+ affinities for acetic acid are respectively 43.8, 30.1, and 21.8 kcal/mol at B3LYP/6-311++g(d, p). The Li^+, Na^+, and K^+ affinities for the acetate anion are respectively 169.1, 145.2, 127.0 kcal/mol at B3LYP/6-311++g(d, p). These trends in the MIAs of RCOOH and $RCOO^-$ are in accordance with the hard–soft acid–base concept.[21] The better matched the donor and acceptor, the stronger the complexation. For instance, for the Li^+-acetate complex, the hard–hard electrostatic interactions between Li^+ and O^- result in stronger metal complexation, as compared with the Na^+-acetate and K^+-acetate complexes.

It is also interesting to mention that several linear correlations between various calculated thermochemical values and the atomic numbers (Z) of the metal ions of Li^+, Na^+, and K^+ were found. For instance, using the data given in Table 3, we obtained the linear plots shown in Figs. 4S–9S. Such a linear correlation between measured MIA and Z for the metal complexes of many biomolecules with Li^+, Na^+, K^+ could be found using the data given in literature.[22]

The homolytic O—H bond dissociation energy (BDE) of $[RCOOHM]^+$

As discussed above, the acidity of a weak acid is drastically enhanced upon metal complexation. Another interesting feature could be the effect of the ionic metal complexation of a weak acid on O—H BDE. We have calculated the O—H BDE for a metal-complexed acid based on the following homolytic bond dissociation reaction:



(9)

or briefly

$$RCOOHM^+ \rightarrow RCOOM^{\bullet+} + H^\bullet \quad \Delta H^0_{rxn} = BDE$$

The O—H BDEs for various metal-complexed acids can be calculated using the following equation[24]:

$$\begin{aligned} &BDE(O-H \text{ of } RCOOHM^+) \\ &= \Delta H^0_{acid}(RCOOHM^+) - IP(H^\bullet) + EA(RCOOM^{\bullet+}) \end{aligned} \quad (10)$$

Eqn (10) is derived from the following thermodynamic cycle:

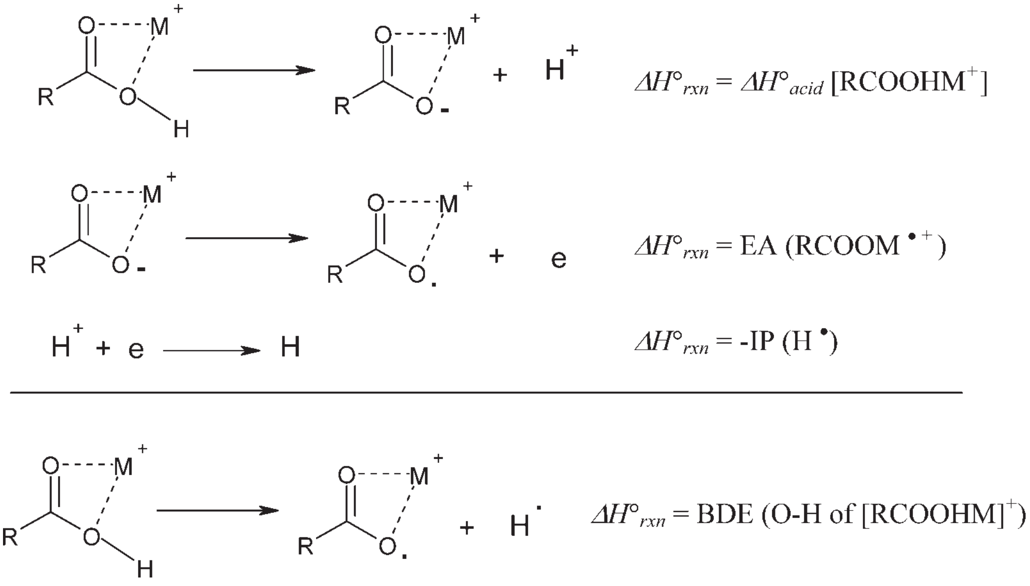
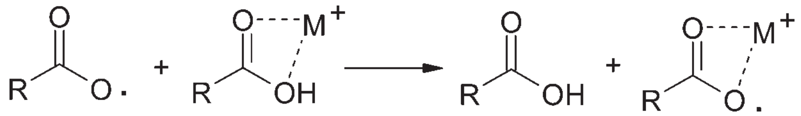


Table 4. B3LYP/6-311++g** O–H bond dissociation energies (BDE), electron affinities (EA), and ΔH_{acid} in kcal/mol

	EA	BDE	ΔH_{acid}
Acetic acid	73.0	104.7	345.3
Li^+	208.5	113.6	218.8
Na^+	192.5	109.1	230.2
K^+	181.3	107.9	240.1
Benzoic acid	80.2	104.9	338.4
Li^+	199.1	106.1	220.6
Na^+	188.4	105.8	231.0
K^+	178.9	105.3	240.0
Glycine	—	—	340.1
Li^+	186.0	106.0	233.7
Na^+	172.9	99.2	239.9
K^+	162.8	94.5	245.2

In this thermodynamic cycle, ΔH^0_{acid} ($RCOOHM^+$) was already calculated and given in Table 2 and $IP(H^\bullet) = 313.58$ kcal/mol. The only parameter to be calculated is EA ($RCOOM^{\bullet+}$), which is the electron affinity of the radical cation $RCOOM^{\bullet+}$. This value has been calculated using the computed absolute energies of RCOOM and $RCOOM^{\bullet+}$ (Table 3S). The calculated EA ($RCOOM^{\bullet+}$), ΔH^0_{acid} $[RCOOHM]^+$, and the O—H BDE of $[RCOOHM]^+$ (obtained from Eqn (10)) are given in Table 4. As shown in Table 4, upon Li^+, Na^+, and K^+ complexation, the O—H BDEs of acetic acid and glycine change remarkably. The OH BDE for benzoic acid, however, does not vary considerably upon complexation with these three metal ions. To get an insight into origin of these trends in the calculated OH BDEs of $[RCOOHM]^+$, we have also calculated ΔH^0_{rxn} for the following isodesmic reaction 11. This ΔH^0_{rxn} value (designated by ΔH^0_{rad}) indicates to what extent the metal ion affects the OH BDE of the acid:



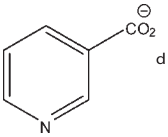
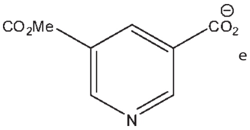
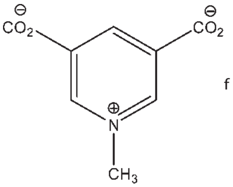
$$\Delta H^\circ_{rxn} = \Delta H^\circ_{rad} \qquad (11)$$

The absolute energies of each species in Eqn (11) (Table 3S) were used to calculate the ΔH^0_{rad} values for acetic acid and benzoic acid where M^+ is Li^+, Na^+, or K^+. These resulting values at 298 and 0 K are given in Table 5 and Table 7S, respectively. As seen in Table 5, ΔH^0_{rad} values for acetic acid are 8.9, 4.4, and 3.2 kcal/mol when M^+ is Li^+, Na^+, or K^+, respectively. On the other hand, the small ΔH^0_{rad} values for benzoic acid indicate that Eqn (11) for benzoic acid is almost thermoneutral and thus its OH BDE does not greatly vary upon its complexation with Li^+, Na^+, or K^+. This suggests that the phenyl group, as a mild electron-donating group, can compensate some of the electron deficiency of

Table 5. B3LYP/6311++g** ΔH_{rad} at 298 K in kcal/mol

	M^+	$RCOO^\bullet + RCOOHM^+ \rightarrow RCOOH + RCOOM^{\bullet +}$
Acetic acid	Li^+	8.9
	Na^+	4.4
	K^+	3.2
Benzoic acid	Li^+	1.2
	Na^+	0.9
	K^+	0.4

Table 6. B3LYP/6-311++g** theoretical and experimental values for ΔH_{acid}, electron affinities (EA), and O–H bond dissociation energies (BDE) in kcal/mol

	ΔH_{acid}		EA		BDE	
	Exp	Calc	Exp	Calc	Exp	Calc
HCO_2^- [a]	345.3 ± 2.2		80.3 ± 0.3		112.4 ± 2.2	
$CH_3CO_2^-$ [b]	348.1 ± 2.2	345.3	77.3 ± 1.8	73.0	111.8 ± 1.8	104.7
$C_6H_5CO_2^-$ [c]	340.2 ± 2.2	338.3	85.3 ± 2.3	80.2	111.9 ± 3.2	104.9
 [d]	333.4 ± 2.8		91.1 ± 2.3		110.9 ± 3.6	
 [e]	328.4 ± 5.2		96.2 ± 1.6		111.0 ± 5.4	
 [f]	309.9 ± 5.0		111.8 ± 1.2		108.1 ± 5.1	
$CH_3CO_2^-Li^+$		218.8		208.5		113.6
$CH_3CO_2^-Na^+$		230.2		192.5		109.2
$CH_3CO_2^-K^+$		240.1		181.3		107.9
$C_6H_5CO_2^-Li^+$		220.6		199.1		106.1
$C_6H_5CO_2^-Na^+$		231.0		188.4		105.8
$C_6H_5CO_2^-K^+$		240.0		178.9		105.3
$NH_2CH_2CO_2^-Li^+$		233.7		186.0		106.0
$NH_2CH_2CO_2^-Na^+$		239.9		172.9		99.2
$NH_2CH_2CO_2^-K^+$		245.2		162.8		94.5

[a] Reference [25].
[b] Reference [26].
[c] Reference [27].
[d] Reference [28].
[e] Reference [29].
[f] Reference [30].

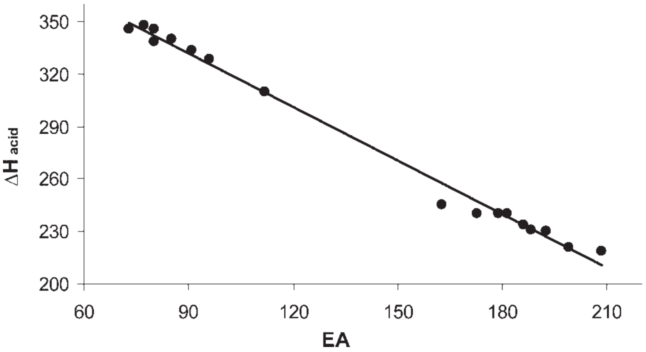


Figure 1. B3LYP/6-311++g** proton affinity *versus* electron affinity (EA) of corresponding radical [$\Delta H_{\mathrm{acid}} = (-1.0261 \times \mathrm{EA}) + 424.46$, $R^2 = 0.99$]

—COO radical produced upon its metal complexation. This observation is also in accordance with the charge distribution (Table 8S) on the oxygen and hydrogen atoms in acetic acid and benzoic acid and their metal complexes. As seen in Table 8S, the polarity of OH bond in acetic acid changes significantly upon its metal complexation and thus its OH BDE is altered. However, for benzoic acid, the polarity of OH bond does not vary notably upon metal complexation and thus its OH BDE is almost unaffected.

We have recently reported[24] that for several classes of compounds (such as alcohols, carboxylic acids, amines, etc.) a linear correlation exists between the acidity $\Delta H^{0}_{\mathrm{acid}}$ and the EA in Eqn (12). This linear correlation can greatly facilitate the measurement of each unknown term in Eqn (12) because it reduces the number of unknowns from 3 to 2.

$$\mathrm{BDE(RCOOH)} = \Delta H^{0}_{\mathrm{acid}}(\mathrm{RCOOH}) - \mathrm{IP}(\mathrm{H}^{\bullet}) + \mathrm{EA}(\mathrm{R}^{\bullet}) \qquad (12)$$

In this work we found that a linear correlation also exists between $\Delta H^{0}_{\mathrm{acid}}$ $[\mathrm{RCOOHM}]^{+}$ and EA ($\mathrm{RCOOM}^{\bullet+}$) in Eqn (10) for the three metal-complexed acids studied herein. The corresponding plots and their linear equations are given in Figs. 10S–12S. Thus, for a metal-complexed acid, these plots and their linear equations simplify determination of the OH bond energies as well as electron affinities and $\Delta H^{0}_{\mathrm{acid}}$. More importantly, by combining the computed results for $\Delta H^{0}_{\mathrm{acid}}$ $[\mathrm{RCOOHM}]^{+}$ and EA ($\mathrm{RCOOM}^{\bullet+}$) with the experimental values of $\Delta H^{0}_{\mathrm{acid}}$ (RCOOH) and EA ($\mathrm{R}^{\bullet}$) of some other carboxylic acids (given in Table 6), we also obtained a linear plot shown in Fig. 1. This indicates that the linear correlation between $\Delta H^{0}_{\mathrm{acid}}$ (RCOOH) and EA ($\mathrm{R}^{\bullet}$) of a weak organic acid is sustained even when it is complexed with the metal ions Li^{+}, Na^{+}, and K^{+}.

CONCLUSION

The results of this study indicate that, upon metal complexation, the gas-phase acidity of the studied weak organic acid drastically increases to the extent that it converts the weak acids of interest to a super acid. For instance, $\Delta H^{0}_{\mathrm{acid}}$ of H_2SO_4 (known as a super acid in the gas phase) is 299.0 kcal/mol.[31,32] However, the acidities of all three weak acids examined herein are considerably enhanced (they become less endothermic, on average, by almost 110 kcal/mol) when the acid is complexed with the metal ions Li^{+}, Na^{+}, and K^{+}. The homolytic OH BDE of the examined organic acid may also vary upon metal complexation. The other interesting result of this study concerns the existence of linear plots for various thermochemical parameters discussed herein. These include the linear correlations of MIA *versus* the atomic number (Z) of the metal ion and of $\Delta H^{0}_{\mathrm{acid}}$ $[\mathrm{RCOOHM}]^{+}$ *versus* EA ($\mathrm{RCOOM}^{\bullet+}$).

SUPPORTING INFORMATION

Computed absolute energies, computed thermochemical values at 0 K, charge distribution, structures of B3LYP LECs, plots for MIA *versus* atomic number (Z) of metal, and plots for B3LYP/6-311++g** proton affinity *versus* EA.

Acknowledgements

We wish to thank Professor Steven R. Kass for helpful discussions. A. F. thanks Nicholas Calandra for his assistance in revising the manuscript. Support from Sharif University of Technology is gratefully acknowledged.

REFERENCES

[1] F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry, 4th edn, Kluwer Academic/Plenum Publishers, New York,* **2000**.
[2] E. V. Anslyn, D. A. Dougherty, *Modern Physical Organic Chemistry*, University Science Books, Sausalito, **2006**.
[3] T. Brink, J. S. Murray, P. Politzer, *J. Org. Chem.* **1991**, *56*, 5012–5015.
[4] S. G. Lias, J. E. Bartmess, Gas-Phase ion thermochemistry, in *NIST Chemistry WebBook* (Eds: P. J. Linstrom, W. G. Mallard), NIST Standard Reference Database No. 69, National Institute of Standards and Technology, Gaithersburg, MD, (http://webbook.nist.gov), **2006**, and references therein.
[5] J. I. Brauman, L. K. Blair, *J. Am. Chem. Soc.* **1971**, *93*, 4315–4316.
[6] D. A. Pena, B. S. Uphade, E. P. Reddy, P. G. Smirniotis, *J. Phys. Chem. B* **2004**, *108*, 9927–9936.
[7] J. W. J. Kennedy, D. G. Hall, *J. Am. Chem. Soc.* **2002**, *124*, 11586–11587.
[8] S. Kamijo, Y. Yamamoto, *J. Org. Chem.* **2003**, *68*, 4764–4771.
[9] J. Ren, C. J. Cramer, R. R. Squires, *J. Am. Chem. Soc.* **1999**, *121*, 2633–2634.
[10] Spartan 04; Wavefunction, Inc., Irvine, CA.
[11] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[12] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
[13] W. J. Hehre, L. Radom, P. V. R. Schleyer, J. A. Pople, *In Ab initio Molecular Orbital Theory*, John Wiley and Sons, New York, **1986**.
[14] C. Moller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618–622.
[15] C. Adamo, V. Barone, *J. Chem. Phys.* **1998**, *108*, 664–675.
[16] T. Marino, N. Russo, M. Toscano, *J. Inorg. Biochem.* **2000**, *79*, 179–185.
[17] S. Hoyau, G. Ohanessian, *Chem. Eur. J.* **1998**, *4*, 1561–1569.
[18] J. Bertran, L. Rodriguez-Santiago, M. Sodupe, *J. Phys. Chem. B* **1999**, *103*, 2310–2317.
[19] T. Marino, T. Mineva, N. Russo, E. Sicilia, M. Toscazo, in *Metal-Ligand Interaction in Chemistry, Physics and Biology* (Eds: N. Russo, D. R. Salahub), Kluwer Academic Publishers, Dordrecht, **2000**.
[20] C. H. Hu, M. Shen, H. F. Schaefer, III, *J. Am. Chem. Soc.* **1993**, *115*, 2923–2929.
[21] A. A. Garcia, D. H. Kim, D. R. Miles, *Ind. Eng. Chem. Res.* **1996**, *35*, 1097–1106.
[22] B. A. Cerda, C. Wesdemiotis, *J. Am. Chem. Soc.* **1996**, *118*, 11884–11892.
[23] E. F. Strittmatter, R. L. Wong, E. R. Williams, *J. Am. Chem. Soc.* **2000**, *122*, 1247–1248.
[24] A. Fattahi, S. R. Kass, *J. Org. Chem.* **2004**, *69*, 9176–9183.
[25] L. S. Wang, C. F. Ding, X. B. Wang, J. B. Nicholas, *Phys. Rev. Lett.* **1998**, *81*, 2667–2670.
[26] E. H. Kim, S. E. Bradforth, D. W. Arnold, R. B. Metz, D. M. Neumark, *J. Chem. Phys.* **1995**, *103*, 7801–7814.

[27] X. B. Wang, J. B. Nicholas, L. S. Wang, *J. Chem. Phys.* **2000**, *113*, 653–661.
[28] X. B. Wang, J. E. Dacres, X. Yang, K. M. Broadus, L. Lis, L. S. Wang, S. R. Kass, *J. Am. Chem. Soc.* **2003**, *125*, 296–304.
[29] X. B. Wang, K. M. Broadus, L. S. Wang, S. R. Kass, *J. Am. Chem. Soc.* **2000**, *122*, 8305–8306.
[30] K. M. Broadus, S. R. Kass, *J. Am. Chem. Soc.* **2000**, *122*, 9014–9018.
[31] A. A. Viggiano, M. J. Henchman, F. Dale, C. A. Deakyne, J. F. Paulson, *J. Am. Chem. Soc.* **1992**, *114*, 4299–4306.
[32] X. B. Wang, J. B. Nicholas, L. S. Wang, *J. Phys. Chem. A* **2000**, *104*, 504–508.