

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/265100145>

Behavior of Carboxylic Acids Upon Complexation with Beryllium Compounds

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · JULY 2014

Impact Factor: 2.69 · DOI: 10.1021/jp504405r

CITATIONS

2

READS

62

4 AUTHORS:



[Kateryna Mykolayivna Lemishko](#)

Universidad Autónoma de Madrid

2 PUBLICATIONS 2 CITATIONS

[SEE PROFILE](#)



[M. Merced Montero-Campillo](#)

Universidad Autónoma de Madrid

29 PUBLICATIONS 148 CITATIONS

[SEE PROFILE](#)



[Otilia Mó](#)

Universidad Autónoma de Madrid

403 PUBLICATIONS 6,379 CITATIONS

[SEE PROFILE](#)



[Manuel Yanez](#)

Universidad Autónoma de Madrid

271 PUBLICATIONS 3,747 CITATIONS

[SEE PROFILE](#)

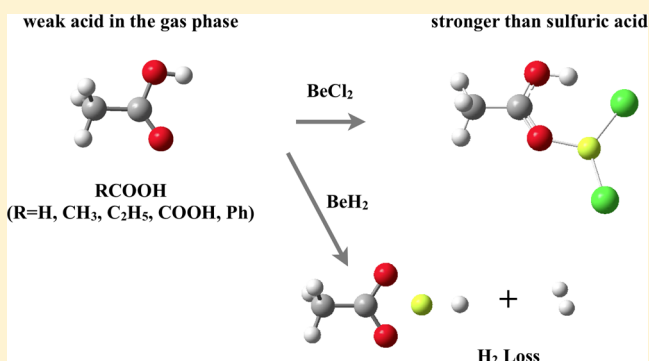
Behavior of Carboxylic Acids upon Complexation with Beryllium Compounds

Kateryna Mykolayivna-Lemishko, M. Merced Montero-Campillo,* Otilia Mó, and Manuel Yáñez

Departamento de Química, Facultad de Ciencias, Módulo 13 Universidad Autónoma de Madrid Campus de Excelencia UAM-CSIC, Cantoblanco, 28049 Madrid, Spain

S Supporting Information

ABSTRACT: A significant acidity enhancement and changes on aromaticity were previously observed in squaric acid and its derivatives when beryllium bonds are present in those systems. In order to know if these changes on the chemical properties could be considered a general behavior of carboxylic acids upon complexation with beryllium compounds, complexes between a set of representative carboxylic acids RCOOH (formic acid, acetic acid, propanoic acid, benzoic acid, and oxalic acid) and beryllium compounds BeX₂ (X = H, F, Cl) were studied by means of density functional theory calculations. Complexes that contain a dihydrogen bond or a OH...X interaction are the most stable in comparison with other possible BeX₂ complexation patterns in which no other weak interactions are involved apart from the beryllium bond. Formic, acetic, propanoic, benzoic, and oxalic acid complexes with BeX₂ are much stronger acids than their related free forms. The analysis of the topology of the electron density helps to clarify the reasons behind this acidity enhancement. Importantly, when the halogen atom is replaced by hydrogen in the beryllium compound, the dihydrogen bond complex spontaneously generates a new neutral complex [RCOO:BeH] in which a hydrogen molecule is lost. This seems to be a trend for carboxylic acids on complexing BeX₂ compounds.



INTRODUCTION

During the last years the attention of many researchers working on chemistry, biology, physics, medicine and material science has been focused on noncovalent interactions.^{1–3} It is well-known that noncovalent interactions play a main role in the formation of biomolecular assemblies, such as proteins or DNA. Their study is crucial for the development of new supramolecular materials. Typically, a wide range of noncovalent interactions between closed shell systems engage a certain amount of charge transfer between an electron donating moiety and an electron accepting one, such as hydrogen bonds,^{4–6} halogen bonds,^{7–11} or beryllium bonds.^{12–16} In the case of X–H...Y hydrogen bonds, the X–H group acts as a Lewis acid accepting electronic charge from the lone pair of Y acting as a Lewis base. In a similar way, due to the presence of available vacant orbitals in beryllium atom, beryllium compounds can act as a Lewis acid as well, and therefore a charge transfer process between an electron donating group and beryllium atom gives place to the so-called beryllium bond, a non covalent interaction in which our group is particularly interested in.

A Lewis acid–Lewis base interaction can cause significant changes on the physicochemical properties of the substances involved in the interaction, the intrinsic acidity of a substance being one of those properties. It has been recently shown that the acidity of several organic and inorganic compounds may be changed by noncovalent interactions with boranes and

alanes.^{17–19} When beryllium bonds are involved, similar, although stronger, changes on acidity are observed.²⁰ We very recently investigated the intrinsic acidity of squaric acid and its chalcogen containing derivatives, its aromaticity and its self-assembly capacity, properties that significantly change when beryllium bonds are present.^{21,22} More importantly, our group showed that squaric acid and its derivatives release H₂ when bound to beryllium dihydride.²¹ This fact is relevant enough for its potential consequences in hydrogen storage materials to deserve further investigation. In particular it would be important to establish if this reaction always takes place (or not) in carboxylic acids complexed with beryllium compounds. Therefore, the aim of the present work is to investigate in a series of complexes between prototype carboxylic acids (formic, acetic, propanoic, benzoic, and oxalic acids) and BeX₂ compounds (where X = H, F, Cl) three different aspects: acidity, aromaticity (only for benzoic acid), and H₂ release.

COMPUTATIONAL DETAILS

Geometries of all complexes were fully optimized and their corresponding harmonic vibrational frequencies calculated using Gaussian 09 software²³ with B3LYP hybrid density

Received: May 5, 2014

Revised: July 9, 2014

Published: July 10, 2014

functional,^{24,25} which have been proved to provide very similar acidity predictions to those obtained with G4 composite method in similar complexes.²¹ Additionally, DFT structures were compared with second order Möller-Plesset (MP2) calculations in order to check possible dispersion effects, obtaining analogous results in all cases. Several Pople double and triple- ζ basis sets 6-31+G(d), 6-311G, 6-311G(d), 6-311+G(d), 6-311+G(d,p), and 6-311+G(3df,2p) were used to select the one that minimizes average errors on comparing theoretical and experimental proton dissociation free energies. As a result of this assessment, 6-311+G(3df,2p) was selected for the calculation of the beryllium complexes. Intrinsic reaction coordinate (IRC)^{26,27} technique was used at the same level of theory to ensure that reactants and products were connected through a given transition state. In order to check whether static correlation effects are significant for the complexes investigated here, we evaluated the T1 diagnostic at CCSD(T)/6-311+G(3df,2p) level of theory for the most stable acetic acid complexes with BeH₂ and BeF₂. The values obtained (0.015) clearly indicate that these complexes can be considered single-reference systems.

Atoms in molecules quantum theory (QTAIM)^{28,29} and the electron localization function (ELF)^{30,31} were used to study RCOOH:BeX₂ complexes. QTAIM calculations were carried out with AIMALL software³² to obtain the corresponding molecular graphs. A molecular graph is the collection of bond paths linking the nuclei of bonded atoms at a given equilibrium geometry. A bond path contains a bond critical point (BCP), a (3;−1) saddle point in which the electron density is minimum with respect to the maximum density path connecting two nuclear attractors, but maximum with respect to other directions. The ELF is a tool that permits to study the electron density of a chemical system by dividing the space into regions (basins) with the highest probability of locating electron pairs. ELF aims to describe chemical bonding by recovering the traditional “Lewis picture” of molecules, in which a chemical bond is formed by two atoms whose orbitals overlap and share electron pairs. NBO (natural bond orbital) and LMO-EDA (localized molecular orbital-energy decomposition analysis) calculations were performed for some particular structures.^{33–35}

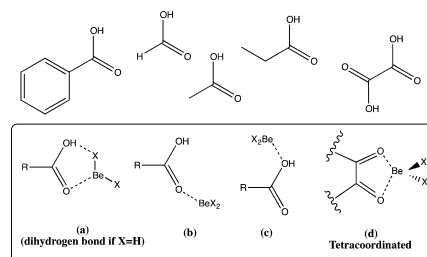
Several approaches can be used to determine quantitatively aromaticity in a molecule. To quantify aromaticity of benzoic acid complexes with beryllium dihydride, nucleus independent chemical shift (NICS) technique was chosen. NICS values were calculated using the continuous set of gauge transformations method (CSGT).^{36–38} An external magnetic field applied to an aromatic system induces a ring current and, hence, an internal magnetic field as response. The shielding tensor σ links those two fields, which can be obtained directly from the current density. The isotropic magnetic shielding is 1/3 of a trace of the shielding tensor, and NICS is the negative of this value. NICS changes depend on the distance to the molecular plane. According to that, a scan of NICS along the axis perpendicular to the plane of benzene ring in the interval [−1 Å;1 Å] was considered, in order to capture a better and less arbitrary measure of the π electron delocalization than NICS(1).³⁹ Aromatic compounds exhibit very negative NICS values.

RESULTS AND DISCUSSION

Carboxylic acids can form several stable complexes with beryllium compounds, depending on the available basic sites in the molecule. Our set is composed of an aromatic acid (benzoic acid), small acids of linear alkyl chain (formic,

ethanoic and propanoic acids), and a diacid molecule (oxalic acid). Scheme 1 resumes the bonding patterns of these acids with beryllium compounds. These complexes are analogous to those previously found for squaric acid.^{21,22}

Scheme 1. Bonding Patterns of BeX₂ (X = H, F, Cl) in Carboxylic Acids



Bonding patterns labeled as (a), (b), and (c) in Scheme 1 are shared by all acids in our set, and also by squaric acid. Conversely, form (d) was only found in oxalic acid but not in squaric acid. These complexes are shown in Figure S1 in the Supporting Information along with their energies collected in Table S1. Bonding pattern (a) is the most stable one in all cases.

We previously showed how squaric acid and its derivatives can vary their acidity properties when BeF₂ is attached to the molecule. In order to know how general this trend is, that is, if beryllium compounds affect in a similar way the acidity properties of carboxylic acids, we first compared theoretical and experimental values for free acids, and then evaluated the acidity in the presence of BeX₂ compounds. Table 1 contains

Table 1. Calculated ($\Delta G_{\text{acid}}^\circ$ 298 K, kJ mol^{−1}) and Experimental Acidities Regarding the Gas-Phase Process RH → H⁺ + R[−] for Noncomplexed Acids

acid	$\Delta G_{\text{acid}}^\circ$ (exp) ^a	$\Delta G_{\text{acid}}^\circ$ (calc) ^b
formic	1415 ± 8.4	1400.2
acetic	1427 ± 8.4	1421.4
propanoic	1424 ± 8.4	1413.9
benzoic	1394 ± 8.4	1388.8
oxalic	1327 ± 8.4	1330.5

^a $\Delta G_{\text{acid}}^\circ$ (exp) from refs 40–42. ^b $\Delta G_{\text{acid}}^\circ$ at 298 K was calculated at B3LYP/6-311+G(3df,2p) level of theory.

the results obtained for free acids in the gas-phase at B3LYP/6-311+G(3df,2p) level of theory (see Computational Details). Looking at the deviation from the experimental value, relative errors are found to be very small in all cases (0.3%–0.7%), with the only exception of formic acid, which is slightly larger (1.0%). Also importantly, the acidity trends, in terms of free energies, are very well reproduced, and in agreement with the experimental outcomes, oxalic acid is predicted as the stronger of the whole series and acetic as the weakest. Additional information about these results can be found on Table S2, in which we show the effect of the basis set in these values.

When complexes with BeF₂ or BeCl₂ are formed, acidity properties dramatically change, as reflected in Table 2. On passing from the free acid to the complex, the free energy of the deprotonation reaction decreases significantly, from 105.4 kJ mol^{−1} for the benzoic acid:BeF₂ complex, to 177.1 kJ mol^{−1} for the acetic acid:BeCl₂ complex. This indicates that substitution

Table 2. Gas-Phase Acidities $\Delta G_{\text{acid}}^\circ$ at 298 K in kJ mol^{-1} Regarding the Gas-Phase Process $[\text{RCOOH} \cdots \text{BeX}_2] \rightarrow \text{H}^+ + [\text{RCOO}^- \cdots \text{BeX}_2]$ for Complexed Acids^{a,b}

acid	$\Delta G_{\text{acid}}^\circ$, BeF_2	$\Delta(\Delta G_{\text{acid}}^\circ)$	$\Delta G_{\text{acid}}^\circ$, BeCl_2	$\Delta(\Delta G_{\text{acid}}^\circ)$
formic	1279.1	121.1	1234.1	166.1
acetic	1290.7	130.7	1244.3	177.1
propanoic	1293.1	120.8	1249.9	164.0
benzoic	1283.4	105.4	1241.4	147.4
oxalic	1222.0	108.5	1188.6	141.9

^a $\Delta G_{\text{acid}}^\circ$ at 298 K was calculated at B3LYP/6-311+G(3df,2p) level of theory. ^bAll acidities are referred to complexes with bonding pattern (a), the most stable ones.

of F atom by Cl reinforces the beryllium bond effect. Also interestingly, the largest acidity enhancement $\Delta(\Delta G_{\text{acid}}^\circ)$ is found for the acetic, which is the weakest acid, whereas the smallest is found for oxalic acid which is the strongest. This is consistent with the fact that, as illustrated by the molecular graphs of both complexes (see Figure 1), the beryllium bond in

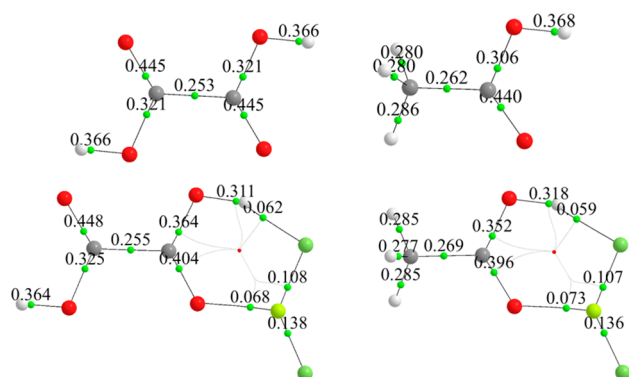


Figure 1. Molecular graphs for the strongest and weakest acids of the set, oxalic and acetic acids, and their complexes with BeF_2 , along with their density values at bond critical points (green dots). Electron densities are in atomic units.

the acetic acid: BeCl_2 cluster is stronger than that in the oxalic acid: BeCl_2 complex. This is not surprising if one takes into account that the fact that acetic acid is a weaker proton donor than oxalic, makes it a stronger electron donor. But, what is really significant is that the consequences of beryllium bond formation are so remarkable that acetic acid changes from being the weakest gas-phase acid of this series to be stronger than sulfuric acid ($\Delta G_{\text{acid}}^\circ$ H_2SO_4 ($1265.0 \pm 23.0 \text{ kJ mol}^{-1}$)),⁴⁰ whereas oxalic acid becomes stronger than perchloric acid ($1200 \pm 50 \text{ kJ mol}^{-1}$). This spectacular change on the acidity properties is triggered by the redistribution of the charge that the formation of the beryllium bond is able to induce, as it will be soon analyzed through the analysis of the topology of the electron density with Atoms in Molecules (AIM) theory.

As mentioned before, molecular graphs of oxalic acid and acetic acid and their complexes with beryllium difluoride are shown in Figure 1. These acids are the most and less acidic of the series, respectively. The density at the BCPs of the O–H bond in both carboxylic groups has values of 0.366 and 0.368 au, respectively. If we move to their complexes with BeF_2 , there is a huge change in the BCPs densities of the O–H bonds: oxalic acid passes from 0.366 to 0.311 au, whereas acetic acid passes from 0.368 to 0.318 au. This weakening agrees with the acidity enhancement observed in the Gibbs energy values of the

deprotonation process. That severe decrease is related to the formation of two noncovalent interactions in the system: an O–H \cdots F hydrogen bond and the C=O \cdots Be beryllium bond, both stronger than the usual hydrogen bond interactions. Additionally, we checked the laplacian of the electron density at both O–H \cdots F and C=O \cdots Be bonds, $\nabla^2\rho$, which sign is related to covalent bonding (negative values) or typical closed-shell bonding as ionic bonds, hydrogen bonds or van der Waals interactions (positive values). Both interactions present large positive values (acetic acid complex: +0.169 (HB), +0.440 (BB); oxalic acid complex: +0.171 (HB), +0.411 (BB)). Beryllium–oxygen interaction can be considered as a strong noncovalent interaction, which is the result of significant charge donations.¹² In our case, these charge donations involve the C–O bonding orbital, the carbonyl oxygen lone-pairs and the empty p orbitals of beryllium, as well as the σ_{BeX}^* antibonding orbitals. In fact, the NBO analysis describes these complexes as an unique molecular unit with a very polar Be–O bonding orbital (see Table S3 of the Supporting Information). The LMO-EDA analysis (see Table S4 of the Supporting Information) shows that the total interaction energy is clearly dominated by electrostatic and polarization contributions, the former being the largest. This is not surprising taking into account that in the beryllium bonds involved in the complexes investigated, a positively charged Be atom is directly interacting with a negatively charged carboxylic oxygen atom. The large weight of the polarization is in agreement with the charge transfers found in the NBO analysis, whereas dispersion has little effect.

The acidity enhancement is not only revealed by density values in BCPs. Other analysis are able to reflect the charge density redistribution in the complexes, as for example the ELF, which not only gives a Lewis picture of the system but also the populations of the disynaptic basins involved in the deprotonation process. Let us take free formic acid and its complexes with BeF_2 and BeCl_2 . As shown in Tables 1 and 2, on passing from free formic acid to the complexes, a significant acidity enhancement, $\Delta(\Delta G_{\text{acid}}^\circ) = 121.1$ and $166.1 \text{ kJ mol}^{-1}$ upon complexation with BeF_2 and BeCl_2 , respectively, is observed, being the formic: BeCl_2 complex the most acidic of these three species. The ELF representation of the complexes (see Figure 2) evidence a huge decrease of the volume of O–H disynaptic basins of formic acid upon complexation in comparison to the volumes of corresponding disynaptic basin of the free formic acid; the O–H basin of the free acid appears to be a 50% larger than the corresponding basin of the complexes (basin volumes HCOOH : 49.23; $\text{HCOOH}:\text{BeF}_2$: 24.04; $\text{HCOOH}:\text{BeCl}_2$: 24.58). Also, the population of the

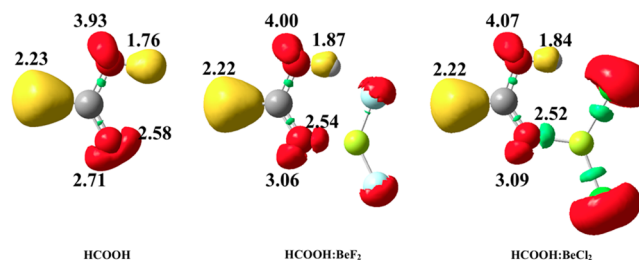


Figure 2. Three-dimensional electron localization function (ELF = 0.85) for HCOOH , $\text{HCOOH}:\text{BeF}_2$, and $\text{HCOOH}:\text{BeCl}_2$. Basins color code: yellow, disynaptic hydrogen-containing basin; green, disynaptic basin; red: lone pair monosynaptic basin. Population is shown in a.u.

disynaptic acidic hydrogen basin changes from 1.76 to 1.87 and 1.84, due to the presence of the $\text{OH}\cdots\text{F}$ and $\text{OH}\cdots\text{Cl}$ interactions. Also, lone pairs from oxygen in free formic acid (2.71 e^- and 2.58 e^- each) split into two well separated basins in BeF_2 and BeCl_2 complexes: the beryllium bond in the case of BeF_2 is too polarized and the electrons remain with oxygen (2.54 e^-), whereas for BeCl_2 complex beryllium bond is characterized by a disynaptic basin (2.52 e^-), although still very polarized and close to oxygen atom.

Let us now briefly analyze the influence of substituents in the benzoic moiety in collaboration with the noncovalent interactions present in the system. Table 3 shows the effect

Table 3. Gas-Phase Acidities $\Delta G_{\text{acid}}^\circ$ at 298 K in kJ mol^{-1} at B3LYP/6-311+G(3df,2p) Level of Benzoic Acid– BeF_2 Complexes (a) with Cl and NO_2 Substituents on Different Positions^a

acid	$\Delta G_{\text{acid}}^\circ$, BeF_2	$\Delta(\Delta G_{\text{acid}}^\circ)$
$\text{C}_6\text{H}_5\text{COOH}-\text{BeF}_2$	1283.4	105.4
o-Cl	1265.6	123.2
m-Cl	1278.9	109.9
p-Cl	1268.6	120.2
o- NO_2	1249.2	139.6
m- NO_2	1256.8	132.0
p- NO_2	1254.5	134.3

^a $\Delta(\Delta G_{\text{acid}}^\circ)$ value takes as reference free benzoic acid.

of substituents in the ring on the acidity for $\text{C}_6\text{H}_5\text{COOH}-\text{BeF}_2$ complexes. A deactivating substituent as $-\text{Cl}$ slightly increases the acidity of the complex, but this effect is very small in meta positions and more significant in ortho and para positions. Instead, a very deactivating substituent as $-\text{NO}_2$ has a similar effect in the acidity of the $\text{C}_6\text{H}_5\text{COOH}-\text{BeF}_2$ complex in all ortho, meta and para cases, although again larger in ortho and para positions.

Molecular graphs of some selected complexes of benzoic acid with BeF_2 and o-Cl, m-Cl, and o- NO_2 substituents in the ring are represented and compared in Figure 3. As shown in Table 3, the m-Cl complex is less acidic than the o-Cl one. They have the same density value on their O–H BCP bonds, although they present some differences: $\text{OH}\cdots\text{F}$ bond and beryllium bond are stronger in the o-Cl complex, and a halogen bond exists between Cl and O in the o-Cl complex that is not present in the m-Cl complex. The nitro complexes are more acidic than the chloro ones. We show the o- NO_2 complex in Figure 3, the most acidic of them. Here the O–H BCP density is 0.02 smaller than in the Cl containing complexes, but also additional van der Waals interactions appear, in this case between oxygen atoms.

Hydrogen Loss. It was previously observed in squaric acid complexes that on passing from beryllium fluoride to beryllium hydride a hydrogen molecule is lost, the process being highly exergonic.²¹ Taking into account the consequences of this in hydrogen storage, we found important to determine if this was a particular case or a general behavior in carboxylic acids. For all the considered acids of the set, a hydrogen molecule loss was observed, the resulting equilibrium structures shown in Figure 4.

In all cases, when BeF_2 is replaced by BeH_2 , the structures resulting from the release of a hydrogen molecule are much more stable than structures for the corresponding complexes with dihydrogen bond (structure (a) in Scheme 1). Moreover, for formic and oxalic acids in contact with beryllium dihydride no dihydrogen bond complex is observed, this form being metastable in the potential energy surface. Dihydrogen bond structures (a) are stable for benzoic, acetic and propanoic acids at B3LYP/6-311+G(3df,2p) level of theory, but with negligible electronic energy barriers with respect to their corresponding transition states in the hydrogen loss reaction (1.4, 0.8, and 2.0 kJ mol^{-1}). Looking at free energy values, the reaction becomes spontaneous in all cases. The resulting products are 108.4, 108.0, and 111.2 kJ mol^{-1} , respectively lower in terms of Gibbs

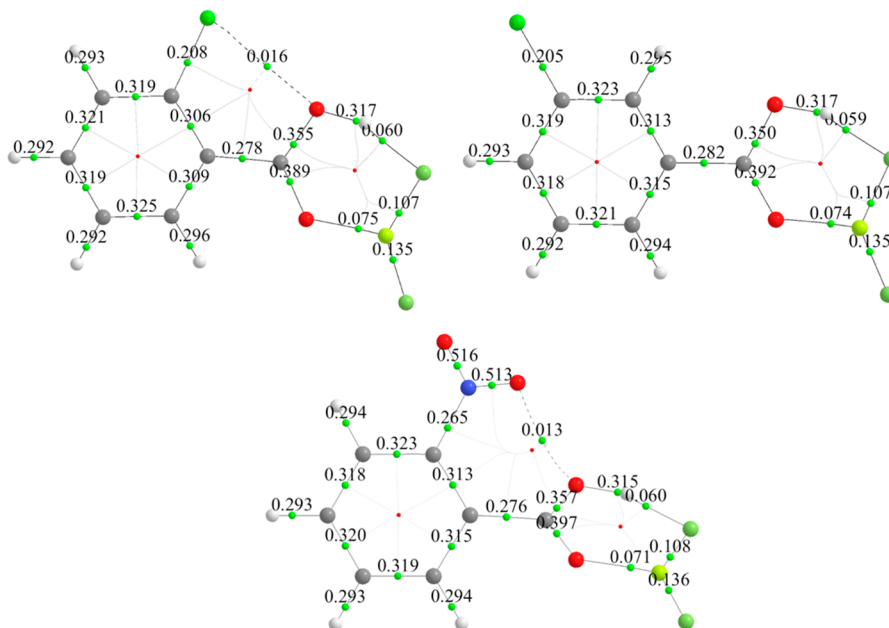


Figure 3. Molecular graphs for o-Cl– $\text{C}_6\text{H}_5\text{COOH}-\text{BeF}_2$, m-Cl– $\text{C}_6\text{H}_5\text{COOH}-\text{BeF}_2$, and o- NO_2 – $\text{C}_6\text{H}_5\text{COOH}-\text{BeF}_2$, along with their density values at bond critical points (green dots).

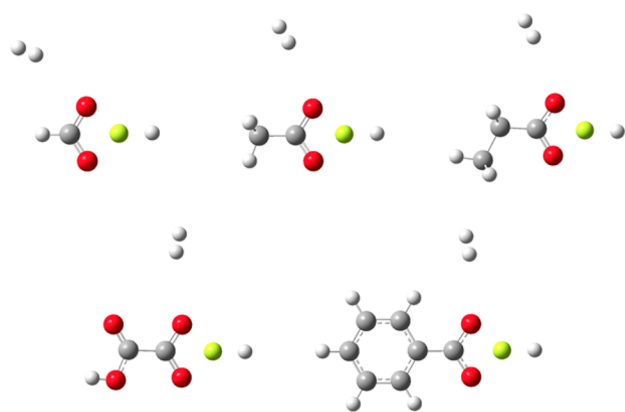


Figure 4. Formic, acetic, propanoic, oxalic and benzoic acids complexes with BeH_2 release H_2 at B3LYP/6-311+G(3df,2p) level of theory.

energy than their corresponding dihydrogen bond structures $\text{RCOOH}:\text{BeH}_2$.

In these new complexes, shown in Figure 4, the $-\text{BeH}$ moiety acts as a bidentate ligand after the hydrogen molecule is lost. The reaction paths corresponding to the H_2 loss were studied by means of IRC technique for benzoic, acetic, and propanoic cases (see Figure 5 and Figure S2).

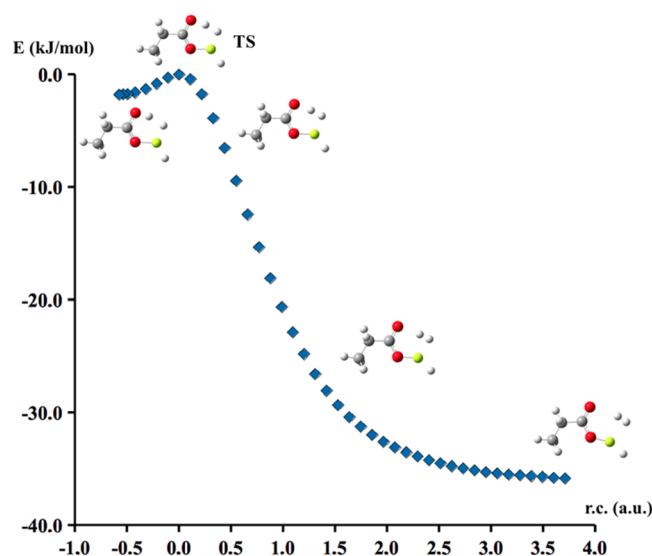


Figure 5. IRC path for propanoic acid complex $\text{C}_3\text{H}_5\text{COOH}:\text{BeH}_2$ hydrogen loss at B3LYP/6-311+G(3df,2p) level of theory.

Aromaticity. Benzene molecule is the most emblematic aromatic molecule, and its derivative benzoic acid is also an aromatic system. As far as the formation of beryllium bonds affects the properties of the system, something that we already studied in the topological analysis, we found interesting to see how the aromaticity of benzoic acid changes due to the presence of noncovalent interactions such as dihydrogen bonds and beryllium bonds. NICS is probably the most standard technique to quantify aromaticity (see Computational Details), related to the magnetic properties of the system. Very negative values of NICS are associated with aromaticity, the usual values in benzene ring of NICS(1) around -12 ppm depending on the method and basis set. NICS values for benzoic acid with different substituents have been already studied.⁴⁴ As the

maximum NICS that better captures the π delocalization depends on the ring size and the substituents, we decided to perform a longitudinal NICS instead of choosing only NICS(1), which is obviously also included in this calculation.

Figure 6 represents the obtained values along an axis perpendicular to the ring plane in a $(-1 \text{ \AA}, +1 \text{ \AA})$ interval of

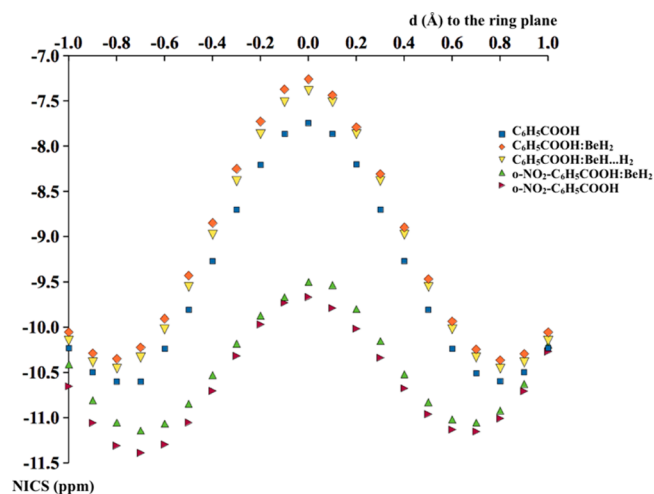


Figure 6. NICS along an axis perpendicular to the benzene ring plane that crosses the geometrical center of the ring at B3LYP/6-311+G(3df,2p) level of theory for $\text{C}_6\text{H}_5\text{COOH}$, $\text{C}_6\text{H}_5\text{COOH}:\text{BeH}_2$, $\text{C}_6\text{H}_5\text{COOH}:\text{BeH}\cdots\text{H}_2$, $o\text{-NO}_2\text{-C}_6\text{H}_5\text{COOH}$, and $o\text{-NO}_2\text{-C}_6\text{H}_5\text{COOH}:\text{BeH}_2$.

distances, for free benzoic acid $\text{C}_6\text{H}_5\text{COOH}$, the $\text{C}_6\text{H}_5\text{COOH}:\text{BeH}_2$ (a) complex and the product formed in the H_2 loss process, $\text{C}_6\text{H}_5\text{COO}:\text{BeH}\cdots\text{H}_2$. The $o\text{-NO}_2\text{-C}_6\text{H}_5\text{COOH}:\text{BeH}_2$ complex has been also included, to explore the effects of electron withdrawing substituents. Free benzoic acid (blue squares) presents slightly more negative NICS values than its complex with BeH_2 (orange diamonds) and the ring produced in the H_2 loss process (yellow triangles), the maximum value being -10.6 ppm around 0.8 \AA , compared to -10.4 and -10.5 ppm. These findings are in contrast with the behavior of squaric acid, which is a $2\pi e^-$ system, and whose aromaticity increases on going from the free form to the beryllium difluoride complexes.²¹ The aforementioned results also indicate that the NICS becomes slightly more negative when H_2 is released, but the difference is so small that aromaticity cannot be considered a driven force in the H_2 loss process. In other words, the induced magnetic field due to the delocalized πe^- is not seriously affected by the reaction, as not one but two beryllium bonds are still present in the system, that reinforce a little bit this delocalized current. Substitution by a nitro group at the ortho position with respect to the acidic function leads to a significant increase in aromaticity (green triangles), but once again the formation of the beryllium bond (purple triangles) has a very small effect on this property.

CONCLUSIONS

Formic, acetic, propanoic, oxalic, and benzoic acids on complexing beryllium halides or beryllium hydrides experience a remarkable enhancing on their acidity properties with respect to their free forms. The formation of beryllium bonds in these systems increases the free energy of the proton dissociation reaction in at least a hundred kJ mol^{-1} at B3LYP/6-311+G(3df,2p) level of theory, changing weak acids in very

strong acids in the gas-phase. On replacing BeF_2 by BeH_2 , a hydrogen molecule loss is observed, as in the case of squaric acid. This process is almost barrierless at 298 K in terms of electronic energy and highly exergonic when looking at Gibbs energies. Therefore, it can be concluded that RCOOH compounds in the presence of beryllium dihydride are susceptible of losing molecular hydrogen, R– being cyclobutene, benzene, carboxyl, methyl, ethyl, or hydrogen, a fact that suggests a general trend.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional figures and tables of data for the compounds studied. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mm.montero@uam.es.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work has been partially supported by the Ministerio de Economía y Competitividad (Project No. CTQ2012-35513-C02-01), by the CMST COST Action CM1204, by the Project MADRISOLAR2, ref.: S2009PPQ/1533 of the Comunidad Autónoma de Madrid, and by Consolider on Molecular Nanoscience CSC2007-00010. K.M.L. thanks the European Union for her Erasmus Mundus grant. Computational time at Centro de Computación Científica (CCC) of Universidad Autónoma de Madrid is also acknowledged.

■ REFERENCES

- (1) Hobza, P.; Müller-Dethlefs, K. *Non-covalent interactions: Theory and Experiment*; RSC: London, U.K., 2009.
- (2) Raeburn, J.; Zamith Cardoso, A.; Adams, D. J. The Importance of the self-assembly process to control mechanical properties of low molecular weight hydrogels. *Chem. Soc. Rev.* **2013**, 42 (12), 5143–5156.
- (3) Georgakilas, V.; Otyepka, M.; Bourlinos, A. B.; Chandra, V.; Kim, N.; Kemp, K. C.; Hobza, P.; Zboril, R.; Kim, K. S. Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications. *Chem. Rev.* **2012**, 112 (11), 6156–6214.
- (4) Pimentel, G. C.; McClelland, A. L. *The Hydrogen Bond*; W. H. Freeman and Co.: San Francisco, CA, 1960.
- (5) Kollman, P. A.; Allen, L. C. Theory of the hydrogen bond. *Chem. Rev.* **1972**, 72, 283–303.
- (6) Grabowski, S. J. *Hydrogen Bonding: New Insights*; Springer: Heidelberg, Germany, 2006; Vol. 3.
- (7) Meryer, F.; Dubois, P. Halogen bonding at work: recent applications in synthetic chemistry and materials science. *CrystEngComm* **2013**, 15 (16), 3058–3071.
- (8) Cooke, S. A.; Cottig, G.; Evans, C. M.; Holloway, J. H.; Kisiel, Z.; Legon, A. C.; Thumwood, J. M. A. Pre-reactive complexes in mixtures of water vapour with halogens: Characterisation of $\text{H}_2\text{O}\cdots\text{CIF}$ and $\text{H}_2\text{O}\cdots\text{F}_2$ by a combination of rotational spectroscopy and ab initio calculations. *Chem.—Eur. J.* **2001**, 7, 2295–2305.
- (9) Karpfen, A. The intermolecular interaction in the charge-transfer complexes between amines and halogens: A theoretical characterization of the trends in halogen bonding. *Theor. Chem. Acc.* **2003**, 110 (1), 1–9.
- (10) Pennington, W. T.; Hanks, T. W.; Arman, H. D. *Halogen Bonding with Dihalogens and Interhalogens*; Metrangolo, P., Resnati, G., Eds.; Springer-Verlag: Berlin, Germany, 2008; Vol. 126.
- (11) Alkorta, I.; Blanco, F.; Elguero, J. A computational study of the cooperativity in clusters of interhalogen derivatives. *Struct. Chem.* **2009**, 20, 63–71.
- (12) Yáñez, M.; Sanz, P.; Mó, O.; Alkorta, I.; Elguero, J. Beryllium Bonds, Do They Exist? *J. Chem. Theory Comput.* **2009**, 5, 2763–2771.
- (13) Eskandari, K. Characteristics of beryllium bonds; a QTAIM study. *J. Mol. Mod.* **2012**, 18, 3481–3487.
- (14) Martín-Sómer, A.; Lamsabhi, A. M.; Mó, O.; Yáñez, M. The importance of deformation on the strength of beryllium bonds. *Comput. Theor. Chem.* **2012**, 998, 74–79.
- (15) Mó, O.; Yáñez, M.; Alkorta, I.; Elguero, J. Modulating the strength of hydrogen bonds through beryllium bonds. *J. Chem. Theory Comput.* **2012**, 8, 2293–2300.
- (16) Albrecht, L.; Boyd, R. J.; Mó, O.; Yáñez, M. Cooperativity between hydrogen bonds and beryllium bonds in $(\text{H}_2\text{O})_n\text{BeX}_2$ ($n=1-3$, $X=\text{H}, \text{F}$) complexes. A new perspective. *Phys. Chem. Chem. Phys.* **2012**, 14, 14540–14547.
- (17) Hurtado, M.; Yáñez, M.; Herrero, R.; Guerrero, A.; Dávalos, J. Z.; Abboud, J.-L. M.; Khater, B.; Guillemin, J. C. The ever-surprising chemistry of boron: enhanced acidity of prosphine-boranes. *Chem.—Eur. J.* **2009**, 15, 4622–4629.
- (18) Martín-Sómer, A.; Lamsabhi, A.; Mó, O.; Yáñez, M. Unexpected acidity enhancement triggered by AlH_3 association to phosphines. *J. Phys. Chem. A* **2012**, 116, 6950–6954.
- (19) Martín-Sómer, A.; Lamsabhi, A.; Yáñez, M.; Dávalos, J. Z.; Gonzalez, J.; Ramos, R.; Guillemin, J. C. Can a amine be a stronger acid than a carboxylic acid? The surprisingly high acidity of amine-borane complexes. *Chem.—Eur. J.* **2012**, 18, 15699–15705.
- (20) Yáñez, M.; Mó, O.; Alkorta, I.; Elguero, J. Can conventional bases and unsaturated hydrocarbons be converted into gas-phase superacids that are stronger than most of the known oxyacids? The role of beryllium bonds. *Chem.—Eur. J.* **2013**, 19, 11637–11643.
- (21) Montero-Campillo, M. M.; Lamsabhi, A.; Mó, O.; Yáñez, M. Spontaneous H_2 loss through the interaction of squaric acid derivatives and BeH_2 . *Chem.—Eur. J.* **2014**, 20, 1–9.
- (22) Montero-Campillo, M. M.; Lamsabhi, A.; Mó, O.; Yáñez, M. Modulating weak intermolecular interactions through the formation of beryllium bonds. The complexes between squaric acid and BeH_2 . *J. Mol. Mod.* **2013**, 19, 2759–2766.
- (23) Frisch, M. J. et al. *Gaussian 09*, Revision C.01; Gaussian, Inc.: Wallingford, CT, 2009.
- (24) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, 98, 5648–5652.
- (25) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, 37, 785–789.
- (26) Fukui, K. The path of chemical reactions. The IRC approach. *Acc. Chem. Res.* **1981**, 14, 363–68.
- (27) Hratchian, H. P.; Schlegel, H. B. *Theory and Applications of Computational Chemistry: The First 40 Years*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G., Eds.; Elsevier: Amsterdam, Netherlands, 2005.
- (28) Bader, R. F. W.; *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, U.K., 1990.
- (29) Matta, C. F.; Boyd, R. J., Eds.; *The Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design*; Wiley-VCH: Weinheim, Germany, 2007.
- (30) Becke, A. D.; Edgecombe, K. E. A simple measure of electron localization in atomic and molecular orbital systems. *J. Chem. Phys.* **1990**, 92 (9), 5397–5403.
- (31) Savin, A.; Nesper, R.; Wengert, S.; Fälsler, T. F. ELF: The Electron Localization Function. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 1808–1832.
- (32) Keith, T. A. *AIMAll*, version 13.11.04; TK Gristmill Software, Overland Parks, KS, 2013.
- (33) Reed, A. E.; Curtiss, L. A.; Weinhold, F. Intermolecular interactions from a Natural Bond Orbital, donor-acceptor viewpoint. *Chem. Rev.* **1988**, 88, 899–926.

- (34) Su, P.; Li, H. J. Energy Decomposition Analysis of covalent bonds and intermolecular interactions. *Chem. Phys.* **2009**, *131*, 014102–014015.
- (35) Chen, Y.; Li, H. J. *Phys. Chem. A* **2010**, *114*, 11719–11724.
- (36) Schleyer, P. V.; Maerker, C.; Dransfeld, A.; Jiao, H. J.; Hommes, N. Nucleus Independent Chemical Shifts: A simple and efficient aromaticity probe. *J. Am. Chem. Soc.* **1996**, *118*, 6317–6318.
- (37) Keith, T. A.; Bader, R. F. W. Calculation of magnetic response properties using atoms in molecules. *ChemPhysLett.* **1992**, *194*, 1–8.
- (38) Keith, T. A.; Bader, R. F. W. Calculation of magnetic response properties using a continuous set of gauge transformations. *ChemPhysLett.* **1993**, *210*, 223–231.
- (39) Montero-Campillo, M. M.; Rodríguez-Otero, J.; Cabaleiro-Lago, E. M. Ab initio and DFT study of the aromaticity of some fulvalenes derived from MCPB. *J. Mol. Model.* **2007**, *13*, 919–926.
- (40) Caldwell, G.; Renneboog, R.; Kebarle, P. Gas phase acidities of aliphatic carboxylic acids, based on measurements of proton transfer equilibria. *Can. J. Chem.* **1989**, *67*, 611–618.
- (41) Taft, R. W.; Topsom, R. D. The nature and analysis of substituent effects. *Prog. Phys. Org. Chem.* **1987**, *16*, 1.
- (42) Kumar, M. R.; Prabhakar, S.; Nagaveni, V.; Vairamani, M. Estimation of gas-phase acidities of a series of dicarboxylic acids by the kinetic method. *Rapid Commun. Mass Spectrom.* **2005**, *19*, 1053–1057.
- (43) Wang, X. B.; Nicholas, J. B.; Wang, L. S. Photoelectron spectroscopy and theoretical calculations of SO₄⁻ and HSO₄⁻: confirmation of high electron affinities of SO₄ and HSO₄. *J. Phys. Chem. A* **2000**, *104*, 504–508.
- (44) Krygowski, T. M.; Stępień, B. T.; Cyrański, M. K. How the substituent effect influences π -electron delocalization in the ring of reactants in the reaction defining the Hammett Substituent Constant and σ_p . *Int. J. Mol. Sci.* **2005**, *6*, 45–51.