

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231657092>

A Comparative Study of the Gas-Phase Acidities of Aliphatic Alcohols and Carboxylic Acids from Generalized Valence Bond and Generalized Multistructural Calculations

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · SEPTEMBER 1996

Impact Factor: 2.78 · DOI: 10.1021/jp961120p

CITATIONS

19

READS

26

2 AUTHORS, INCLUDING:



Marco Nascimento

Federal University of Rio de Janeiro

143 PUBLICATIONS 1,928 CITATIONS

SEE PROFILE

A Comparative Study of the Gas-Phase Acidities of Aliphatic Alcohols and Carboxylic Acids from Generalized Valence Bond and Generalized Multistructural Calculations

Joaquim Delphino da Motta Neto and Marco Antonio Chaer Nascimento*

Instituto de Química, Departamento de Físico-Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, CT bloco A sala 412, Rio de Janeiro, RJ 21949-900 Brazil

Received: April 17, 1996; In Final Form: June 11, 1996[⊗]

It is well-known that carboxylic acids and phenols are stronger acids than the corresponding aliphatic alcohols. The often accepted explanation is that carboxylate and phenoxy anions are stabilized by resonance. However, from a theoretical point of view, the inductive and resonance effects for these compounds have not yet been well quantified. Making use of generalized multistructural (GMS) wave functions, we computed the gas-phase acidities of methanol, ethanol, formic acid, and acetic acid. It is shown that, in the absence of resonance, acetic acid is slightly more acidic than ethanol and that the difference in acidity between formic acid and methanol is only half of the experimental value. Assuming that, in the absence of resonance, the difference in acidities can be attributed mainly to the inductive effect of the carbonyl group, it can be shown that resonance is the dominant effect in determining the greater acidity of the carboxylic acids relative to the corresponding aliphatic alcohols.

1. Introduction

Carboxylic acids and phenols are relatively stronger acids than alcohols both in gas phase and in solution. The difference in the gas-phase acidities is usually attributed to a low energy content of the carboxylate anions, which would be stabilized by the resonance effect. This generally accepted interpretation can be found in any contemporary textbook.^{1,2}

Siggel and Thomas^{3,6} have challenged this view, attributing the large acidity of carboxylic acids to an unusual high energy content of the undissociated acid molecules. This conclusion was based on ab-initio calculations as well as comparison with experimental gas-phase acidities. Those authors claim that the decisive factor for the higher acidity of acids would be the inductive effect due to the carbonyl group. Exner,⁷ using simple thermodynamic considerations, confirmed the classical view which favors the idea of stabilization of anions by resonance. However, Siggel and Thomas⁸ refuted Exner's analysis on the basis that the use of isodesmic reactions would not provide information that could separate the contributions of inductive and resonance effects.

On the other hand, Dewar et al.⁹ comparing the theoretical acidities of the vinylogues of formic acid concluded that resonance, rather than inductive effects, was responsible for the enhanced acidities of the acids relative to the corresponding alcohols. More recently, Bordwell and Satish,¹⁰ comparing the equilibrium acidities in DMSO, for benzoic acid, tropolone, and the enol of 1,3-cyclohexadione, also concluded that resonance in the carboxylate-like ions was the major effect making carboxylic acids more acidic than alcohols. Very recently Hiberty and Byrman,¹¹ in a series of calculations aimed not at the determination of acidities but at the examination of the relative importance of inductive and resonance effects, concluded that they contribute with equal importance to the acidity of carboxylic acids, although the calculations would only provide lower bounds for the delocalization effects.

Several calculations of Brønsted acidities and proton affinities have been reported. Chandrasekar, Andrade, and Schleyer¹² carried out calculations at the Hartree–Fock (HF) level. This

was the first calculation to use diffuse functions although their importance for correctly describing anions was already known.^{13,14} Ewig and van Wazer¹⁵ studied the hydrolysis of simple formates and related reactions at the MP2/4-31*G level. Gao, Gardner, and Jorgensen¹⁶ published an extensive study, at Hartree–Fock level, which included geometry optimization with 6-31G* basis and correlation treatment, including just valence orbitals, at the MP2 level. Siggel, Thomas, and Saethre⁵ calculated gas-phase acidities for methane and formic acid at the MP4/6-31++G level and for several other compounds at lower levels (HF with 3-21+G and 6-311+G basis sets). All calculations quoted above provide gas-phase acidity values that systematically differ from experimental values. Nevertheless, the results show good linear correlation with experimental data.^{17,18}

In spite of many calculations, for a large number of different systems, from a theoretical point of view there are still uncertainties concerning the relative importance of inductive and resonance effects to the acidity of those compounds. Since the difference in the O–H bond strengths, in acids and alcohols, is much smaller than the observed differences in acidities, it is reasonable to assume that those will be determined mainly by the electron affinities of the species RO and RCOO, and therefore stabilization by resonance may play an important role. In this work we present an alternative approach to this problem. To estimate the relative contributions of inductive and resonance effects, we used the recently proposed generalized multistructural (GMS) wave function^{19–25} which has proven to be quite successful when applied to a diversity of problems which required a localized description of the system. In a previous publication²² we advanced some results for the gas-phase acidity of formic acid as one of the examples illustrating the usage of GMS wave functions. In this publication we present a detailed description of the calculations performed for the pairs methanol–formic acid and ethanol–acetic acid. It is shown that resonance is the dominant effect determining that carboxylic acids are stronger acids, in gas phase, than the corresponding aliphatic alcohols.

2. Computational Details

Only a brief description of the GMS wave function will be presented here. A full discussion of the theory, with a detailed

* To whom correspondence should be addressed. E-mail: chaer@chaer.iq.ufrj.br.

[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1996.

description of all the computational aspects involved in obtaining the solution of this kind of wave function, can be found elsewhere.²²

A GMS wave function can be defined as

$$\Psi_{\text{GMS}} = \sum_{l=1}^{N_{\text{struct}}} \sum_{i=1}^{N_{\text{sef}}} c_i^l \varphi_i^l \quad (1)$$

where φ_i^l represents the i th spin-eigenfunction (N_{sef}) of the l th bonding structure (N_{struct}) and the c_i^l its weight in expansion (1). In principle, there are no restrictions whatsoever on the form of the wave function φ_i^l . Each of the φ_i^l 's can be individually optimized at the HF or multiconfigurational (generalized valence-bond method, GVB, complete-active-space self-consistent-field method, CASSCF, etc.) level, followed or not by a configuration interaction (CI) treatment, or else can be taken simply as a VB-type function. In this last case the Ψ_{GMS} is obviously identical to the VB function of the molecule.

Each one of the φ_i^l is represented in a basis of orthogonal orbitals $\{\phi_a^l\}$, properly optimized for the l th structure. Although the orbitals of a given structure are taken to be orthogonal to each other,

$$\langle \phi_a^l | \phi_b^l \rangle = \delta_{a,b} \quad (2)$$

no such restriction exists for the orbitals belonging to different structures **I** and **II**,

$$\langle \phi_a^{\text{I}} | \phi_b^{\text{II}} \rangle = \mathbf{S}_{a,b}^{\text{II}} \quad (3)$$

However, when using GVB wave functions, the GVB orbitals describing a given structure are not necessarily orthogonal.

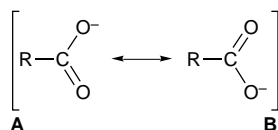
The coefficients c_i^l are obtained variationally by solving the equations

$$\langle \delta \Psi_{\text{GMS}} | \mathbf{H} - E | \Psi_{\text{GMS}} \rangle = 0 \quad (4)$$

$$(\mathbf{H} - \mathbf{S}\mathbf{E})\mathbf{C} = 0 \quad (5)$$

where \mathbf{H} and \mathbf{S} are interaction supermatrices containing the diagonal (same structure) and the interstructural matrix elements. The matrix elements involving orbitals belonging to different structures are computed using a biorthogonalization procedure. In principle, the $\{\varphi_i^l\}$ can either be optimized separately or in the presence of each other. Optimizing them separately is computationally simpler, and in applications dealing with localized structures it seems that, as long as they are well localized (i.e., the overlap between their wave functions is small), there is no need to optimize them in the presence of each other.

The main advantage of the GMS wave function is that it easily incorporates the important correlation effects while retaining the simple picture provided by chemical structures. Besides, since the orbitals are optimized for each particular structure, there is no need to incorporate some unphysical structures normally present in the standard VB expansions.¹⁹ With the GMS wave function one can compute the resonance stabilization of the carboxylate ions by direct computation of the matrix element²⁰ between the two resonant structures:



In order to obtain appropriate localized structures, the geometry of all the studied species was optimized at GVB(PP) level of calculation²⁶ using a threshold of 10^{-5} hartree for the energy gradient, correlating all the bonding electron pairs. In the case of anions, the electron pair resulting from the heterolytic dissociation of the neutral molecule was also correlated. For the neutral species the calculations were performed with the 6-31G** basis set while for the anions the 6-31G**+ basis was used.²⁷⁻²⁹ The influence of the diffuse functions in the description of the neutral species was tested and found to be negligible (<4 mhartrees) for both methanol and formic acid. Similarly, calculations for the methoxide ion showed an even smaller (<0.4 mhartree) contribution of the diffuse functions on the hydrogen atoms. Besides the energy criterion, we also tested the influence of the latter diffuse functions on the geometry and atomic charges for methanol, methoxide ion, and formic acid. Their effect on both geometry and charges was found negligible. For the carboxylate anions special care was taken to avoid delocalization, as much as possible, in order to assure that the resulting wave function could be associated with the classical resonant structures. Starting from HF wave functions, the orbitals were localized using the Boys procedure.³⁰ A GVB wave function was then computed setting the Hamiltonian off-diagonal π elements between the oxygen atoms equal to zero.³¹ After convergence was attained, those matrix elements were turned on, and a new GVB wave function was computed. At the end of each geometry optimization cycle the orbitals related to the carbonyl group were examined, and whenever some delocalization character started to build in, the Boys³⁰ localization was again used. Using this procedure, we achieved a much better localization than in our previous calculation.²²

In addition, using the optimized GVB wave functions, CI calculations were performed in order to take into account the interaction among electrons on different GVB pairs (interpair correlations) and also that part of the intrapair dynamical correlation energy not present in the GVB(PP) wave function.

For the CI calculations we considered a variational space formed by 30 orbitals, including the GVB pairs (GVB space) plus the virtual orbitals from the self-consistent calculations performed for each one of the molecules. The core orbitals (1s) of the heavy atoms were kept frozen in all calculations. For each molecule the calculations were performed allowing a full-CI in the GVB space plus single and double (SD) excitations from the occupied orbitals to the respective virtual spaces.

The GMS wave functions for the carboxylate anions were constructed using eq 1 and structures **A** and **B**, both represented at the GVB and GVB+CI levels of calculation. It was found that neglecting all the configurations which contribute an energy lowering³² $< 10^{-5}$ hartree would not affect either the GMS wave function energy or the matrix element between structures **A** and **B** for the formate ion. Therefore, this cutoff was also adopted for the acetate GMS wave function.

Vibrational frequencies were calculated using numerical derivatives (second derivatives) of analytic gradient of the energy and used, unscaled, to compute the zero-point energy (ZPE) corrections. It is usual to scale vibrational frequencies obtained from HF wave functions by a factor of ~ 0.9 , as recommended by Pople and co-workers. However, there are not enough calculations of vibrational frequencies using GVB-type wave functions to justify the use of that factor or any other. Atomic charges were computed using electrostatic potential fitting (EPF).^{33,34}

At this point it would be instructive to outline the differences between the VB-type calculations of Hiberty and Byrman¹¹ and the present ones, based on the GMS approach. In their

TABLE 1: Energy (hartrees) of the Optimized Geometries at the GVB Level

species	basis set		
	6-31G**	6-31G**+	6-31G**++
CH ₃ OH	-115.134 366		-115.138 154
CH ₃ O ⁻		-114.482 860	-114.483 153
HCOOH	-188.864 494		-188.868 419
HCOO ⁻ (C _s)		-188.223 145	
HCOO ⁻ (C _{2v} ^a)		-188.236 047	
C ₂ H ₅ OH	-154.222 522		
C ₂ H ₅ O ⁻		-153.574 415	
CH ₃ COOH	-227.957 794		
CH ₃ COO ⁻		-227.307 643	

^a See text for discussion.**TABLE 2: Configuration Interaction Results Using the Optimized Geometries at the GVB Level and 6-31G** Basis for the Neutral Species and 6-31G**+ for the Anions**

species	energy (hartrees)	species	energy (hartrees)
CH ₃ OH	-115.377 472	C ₂ H ₅ OH	-154.559 827
CH ₃ O ⁻	-114.756 912	C ₂ H ₅ O ⁻	-153.944 935
HCOOH	-189.230 177	CH ₃ COOH	-228.417 161
HCOO ⁻	-188.637 984	CH ₃ COO ⁻	-227.816 642

calculations Hiberty and Byrman used only one set of orbitals to represent all the structures while in the GMS approach each structure has its own set of specific orbitals. In the present calculations the σ orbitals are localized and correlation effects within the σ space and also among the σ and π electrons were taken into account, while in Hiberty and Byrman's calculations the σ orbitals remained fully delocalized and uncorrelated. The resonance contribution was calculated by those authors as the difference in energy between the π -localized and π -fully delocalized states, while we computed the matrix element between the two carboxylate hybrid structures. Finally, those authors localized the π orbital in the oxygen atom (atomic character) while we localized it in the C=O bond.

3. Results and Discussion

Table 1 shows the energy of the optimized structures, using different basis sets and levels of calculation. Table 2 shows the results of the CI calculations. The optimized geometries are available as Supporting Information in order to avoid excessive use of tables and/or figures. Most of these molecules have had their geometries optimized at either the Hartree–Fock³⁵ (HF) or CASSCF¹¹ levels of calculation. The optimized GVB structures do not differ appreciably from the ones obtained in the previous calculations and show the same trends observed when comparing the geometries of the anions with the ones of the respective parent acids. However, the origin of the changes in geometry deserves some comments before we proceed to the calculations of the relative acidities. For all the studied molecules, there is a shortening in the C–O bond and an increase in the adjacent C=O bond length of the anions relative to the same bonds in the respective parent acids. Besides that, the OCH bond angles in the alkoxide ions and the OCO bond angles in the carboxylate ions also increase relative to these angles in the parent acids. Wiberg³⁵ tried to explain those geometrical differences for the alkoxide ions in terms of changes in electronegativity at the oxygen atom and Bader's³⁶ theory of atoms in molecules. He refuted any explanation in terms of hyperconjugation based on the high energy of the σ^* orbitals which would be involved in the process. On the other hand, Hiberty and Byrman¹¹ showed that those geometrical changes also occur, at almost the same extent, in "localized states" for which charge delocalization is partially precluded. The latter

authors¹¹ attributed the geometrical changes to hyperconjugation between the free lone pair on the oxygen atom (resulting from the breaking of the O–H bond) and the carbon atom, in detriment of σ hyperconjugation in the adjacent C=O bond. However, differences in bond lengths of the order of ~ 0.1 Å are observed, twice as much as it would be expected to be accounted for by hyperconjugation.³⁷ Besides, the orbital containing the free lone pair in the anions becomes more diffuse than the O–H bond orbital in the parent acids, making hyperconjugation less effective. A much simpler explanation for the origin of those geometrical changes can be given by observing the changes in the oxygen lone pair and O–H bond orbitals when going from the acid form to the parent anion. Irrespective of the molecule, when the O–H bond is broken, both oxygen orbitals, containing lone pairs, rotate counterclockwise around the oxygen center. As a result of this rotation, the orthogonality (imposed in order to satisfy the Pauli principle) and electron repulsion effects, between the free σ pair and the C–O bond electrons, are considerably reduced. The latter bond is stabilized and may become shorter. For the alkoxide anion, as that bond is shortened, the interaction between the electrons in the C–O and C–H bond increases and forces the OCH bond angle and C–H bond lengths to increase. This same sort of description, when applied to the carboxylate anions, explains why the C–O bond length is reduced and the C=O bond length and OCO bond angle increase.

The Brønsted acidity of a compound can be defined as the variation on the Gibbs free energy (ΔG^0_T) for the reaction



However, because the entropic term (mainly due to the H^+) cancels out in a comparison of relative acidities, one may take ΔH^0_T as a measure of compound acidity. This is also a convenient definition for the purpose of comparison to experimental enthalpies. From the results in Tables 1 and 2 one can compute ΔE^0_{eq} , i.e., the variation in internal energy, at zero temperature and at the equilibrium positions of RH and R^- . In order to convert ΔE^0_{eq} to values comparable to experiments, we used eq 6

$$\Delta H^0_T = \Delta E^0_{\text{eq}} + \Delta(\text{PV}) + \Delta(\text{ZPE}) + \Delta E^v_T + \Delta E^r_T + \Delta E^t_T \quad (6)$$

where $\Delta(\text{PV})$ is the contribution which converts internal energy to enthalpy and $\Delta(\text{ZPE})$ is the variation in zero-point vibration energies. ΔE^v_T , ΔE^r_T , and ΔE^t_T are terms which correct for the changes in vibrational, rotational, and translational energies, respectively, when the system is brought from zero degrees to temperature T .

For the pressures normally used in the measurements of gas-phase acidities, it is reasonable to consider reagents and products as ideal gases, and therefore

$$\Delta(\text{PV}) = RT\Delta n = RT \quad (7)$$

for all reactions, since $\Delta n = 1$. The corrections due to translation and rotation can be treated classically, using the equipartition theorem. Thus, considering that in the final state we have always two species (RO^- and H^+) present and one in the initial state, and also that the proton has only translational degrees of freedom, we can write

$$\Delta E^t_T = (3/2)RT \quad \text{and} \quad \Delta E^r_T = 0 \quad (8)$$

In units of RT , room temperature corresponds to an energy of 201.63 cm^{-1} . None of the studied species present normal

TABLE 3: Calculated Acidities in the Absence of Resonance, at the GVB and GVB+CI Levels (All Values in eV)

species	ΔE_{eq}^0		$\Sigma(\text{corrections})$	ΔH_{298}^0	
	GVB	GVB+CI		GVB	GVB+CI
CH ₃ OH	17.73	16.88	-0.360	17.37	16.52
HCOOH	17.45	16.11	-0.318	17.13	15.79
C ₂ H ₅ OH	17.45	16.73	-0.356	17.09	16.37
CH ₃ COOH	17.69	16.34	-0.311	17.38	16.03

vibrational modes of such low energy that could be excited when bringing the system from zero degrees to room temperature. Therefore, the population of the vibrational states should not change to a significant extent and

$$\Delta E_T^v = 0 \quad (9)$$

Finally, the $\Delta(\text{ZPE})$ correction is computed, in the harmonic approximation, as

$$\Delta(\text{ZPE}) = \Delta\left(\sum_i (1/2)h\nu_i\right) \quad (10)$$

with the normal-mode frequencies (ν_i) calculated as described in the previous section.

Once the corrections defined in eq 6 are computed, the acidities can be determined using the results in Tables 1 and 2. These are straightforward calculations for the alcohols, inasmuch as the alkoxides can be well represented by a single chemical structure. For the carboxylic acids one still has to take into account the contribution of resonance. However, it would be instructive at this point to compare the acidities of alcohols and the carboxylic acids using only one localized structure to represent the carboxylate ions. Before doing that, it is worth mentioning that an attempt was made to provoke charge delocalization on the carboxylate ions, by forcing a local C_{2v} on the COO^- group, during the GVB optimization process and relaxing the PP spin coupling in order to allow conjugation between the carbon and the two oxygen atoms. Although the C—O bond lengths turned out to be practically identical (1.246 Å), the two oxygen atoms remained nonequivalent as far as atomic charges are concerned (-0.903 for the hydroxyl and -0.844 for the carbonyl oxygen). Thus, the difference in energy between the C_{2v} and C_s structures (see Table 1) could not be used to estimate the delocalization contribution as prescribed by Kollmar³⁸ or Behren et al.³⁹ Alternatively, one could try to obtain a delocalized description by treating the π electrons at the HF level, what would be equivalent to solving for a GVB-(3/PP) wave function in the case of the formate ion. However, this latter description would not be appropriate for comparison with the localized structures whose wave functions were obtained at a higher level of calculation.

Table 3 shows the acidities, in the absence of resonance, computed at the GVB and GVB+CI levels of calculation. Interesting enough, in the absence of resonance, ethanol is the strongest acid at the GVB level while at the GVB+CI level acetic acid is slightly more acidic than ethanol and formic acid is only half more acidic than methanol when compared to experimental results. At this point it is important to realize that inductive effects are being taken into account in all calculations. In fact, since we are using localized orbitals, one should expect the carbonyl group dipole moment, in the carboxylic acids, to be larger than in the delocalized description and so its inductive effect.

In order to compute the resonance contribution to the acidity of the carboxylic acids, we constructed GMS wave functions for the carboxylate ions as

$$\Psi_{\text{GMS}} = c_A \Psi_A + c_B \Psi_B$$

where Ψ_A and Ψ_B represent structures **A** and **B**, at either the GVB⁴⁰ or GVB+CI level of calculation. The energy of the resonant state is given by

$$E = H_{AA} + (H_{AB} - S_{AB}H_{AA})/(1 + S_{AB})$$

where H_{AA} ($=H_{BB}$) is the energy of wave function Ψ_A , H_{AB} the Hamiltonian matrix element between Ψ_A and Ψ_B , and S_{AB} the overlap between the wave functions, $\langle \Psi_A | \Psi_B \rangle$. The resonance energy, as given by the GMS wave function, will be equal to $E - H_{AA}$.

Before presenting and discussing the results of the GMS calculations, some comments relative to the definition of resonance energy are in order. By comparing the energy of the GMS wave function, at the GVB(PP) level, with the one of a localized structure (**A** or **B**), we imply that the GVB wave function is a nonresonating reference state. However, the localization in the π space is not totally complete, and therefore the GVB wave function does include some resonance. Thus, the energy lowering provided by the GMS wave function, when compared to the GVB one, should be taken as a lower bound on the true resonance energy. Moreover, the resonance energy concept is intimately related to the idea of chemical structure and derives from the fact that some compounds cannot be represented by a single valence bond structure. Therefore, in order to quantify the resonance effect, one should make use of wave functions which could be interpreted in terms of orbitals associated with the bonds which define the chemical structure. In other words, one should make use of single-particle wave functions. The GVB(PP) wave function, due to its restrictive form, is a multiconfigurational wave function which retains the single-particle picture and therefore serves our purposes. However, in order to obtain a better geometry for a particular structure, one needs to go beyond the single-particle description, to incorporate the missing correlation effects. But, on doing so, we lose the simple picture provided by the orbitals, and no longer can we view the wave functions as quantum-mechanical translations of the bonding structures. Nevertheless, one can still interpret the energy difference between the GMS (GVB+CI) and the GVB+CI wave function derived from one of the localized structures as the contribution to the resonance energy due to correlation effects.

Table 4 shows the relevant parameters to compute the resonance energy, using the GMS wave function and structures **A** and **B** represented at both GVB and GVB+CI levels. The inclusion of correlation considerably reduces the overlap between the structures for both carboxylate ions and also affects the value of the H_{AB} matrix element. Table 5 shows the final acidity values, computed at the GVB+CI and GMS(GVB+CI) levels, including all the corrections to ΔE_{eq}^0 , compared to experiments and other theoretical results, at 298 K. From Table 5 it is clear that once resonance effects are taken into account, we obtain acidities, for the carboxylic acids, comparable to the experimental values, with the same degree of accuracy as for the alcohols. Therefore, resonance is an important factor determining the acidity of carboxylic acids in the gas phase. The relative importance of resonance and the inductive effect of the carbonyl group can be estimated if one assumes that, in the absence of resonance, the inductive effect of the carbonyl group on the carboxylic acids would be mainly responsible for the stronger acidity of these compounds relative to the alcohols. Using the values shown in Tables 3 and 5, we compute the difference in acidity between all pairs (alcohol-acid) in the presence, $(\Delta A)_{\text{th}}$, and in the absence, $(\Delta A)_{\text{ind}}$, of resonance. The

TABLE 4: Resonance Energies (hartrees) at the GVB and GVB+CI Levels of Calculation

	CH ₃ O ⁻		CH ₃ COO ⁻	
	GVB	GVB+CI	GVB	GVB+CI
H _{ab}	-152.047 038	-122.718 527	-198.498 317	-160.931 330
S _{ab}	0.807 6	0.650 3	0.873 1	0.706 2
resonance	-0.021 037	-0.028 629	-0.019 227	-0.027 674

TABLE 5: Final Acidities at the GVB and GVB+CI Levels of Calculation

	CH ₃ OH	HCOOH	C ₂ H ₅ OH	CH ₃ COOH
ΔE^0_{eq}	0.6206	0.5922	0.6149	0.6005
corrections (eV)				
ΔE_T	0.038	0.038	0.038	0.038
ΔE^*_{T}	0.0	0.0	0.0	0.0
ΔE^*_{T}	0.0	0.0	0.0	0.0
$\Delta(\text{PV})$	0.025	0.025	0.025	0.025
$\Delta(\text{ZPE})$	-0.423	-0.381	-0.419	-0.374
resonance	0.0	-0.779	0.0	-0.753
ΔH^0_{298} (this work)				
(kcal/mol)	381.11	346.26	377.62	352.13
(eV)	16.52	15.02	16.37	15.27
(hartree)	0.6073	0.5520	0.6018	0.5612
ΔH^0_{298} (ref 5)				
(kcal/mol)	383.26	343.14	380.03	343.60
(eV)	16.62	14.88	16.48	14.90
(hartree)	0.6108	0.5468	0.6056	0.5476
ΔH^0_{298} (expt ¹⁷)				
(kcal/mol)	379.14	345.19	376.13	348.46
(eV)	16.44	14.97	16.30	15.11
(hartree)	0.6042	0.5501	0.5994	0.5553

TABLE 6: Relative Contributions of Resonance and Inductive Effects for the Acidity of Carboxylic Acids (eV)

pairs	(ΔA) _{th}	(ΔA) _{ind}	(ΔA) _{res}	(ΔA) _{exp}
methanol-formic acid	1.50	0.73	0.77	1.47
methanol-acetic acid	1.25	0.49	0.76	1.33
ethanol-formic acid	1.35	0.58	0.77	1.33
ethanol-acetic acid	1.10	0.34	0.76	1.19

difference between those two values, (ΔA)_{res}, was taken as the resonance contribution to the difference in acidity for that given pair. Since the resonance contribution to the acidity of alcohols is negligible, (ΔA)_{res} can be viewed as the resonance contribution to the acidity of the carboxylic acid of the pair. Table 6 shows the results of this analysis together with the differences in experimental acidities, (ΔA)_{exp}, for the sake of comparison. The resonance contribution to the acidity of the carboxylic acids is the same irrespective of the pair we choose for comparison. This is consistent with the fact that, for the carboxylate ions (R-COO⁻) under study, the resonance effect is basically associated with the -COO⁻ group and independent of the nature of the radical -R (R = H or -CH₃). On the other hand, the contribution of the inductive effects varies with the nature of -R, and in principle, we cannot separate the (-I) enhancing effect of the carbonyl group from the (+I) weakening effect of the -CH₃ group. Thus, the most reasonable estimate of the inductive effect of the carbonyl group should be provided by the (ΔA)_{ind} of the pair (methanol-acetic acid) for which the -R group is the same. In spite of the difficulties in separating the different inductive effects, the larger values of (ΔA)_{ind} observed for the pairs containing formic acid are consistent with the fact that for acetic acid the carbonyl (-I) effect is to some extent reduced by the (+I) effect of the -CH₃ group, the overall effect being larger for the formic acid. From Table 6 one can see that the resonance contribution is dominant for all pairs, although from the results for the pair methanol-formic acid it looks like the inductive and resonance contributions to the acidity of formic acid are practically the same. The results for formic acid are in agreement with the Hiberty and Byrman

analysis.¹¹ However, it is important to emphasize that the calculated resonance energies represent only lower bounds to the true contribution. Thus, from the results in Tables 5 and 6, we can say that resonance is not only important but the dominant effect responsible for the greater acidity, in the gas phase, of the carboxylic acids relative to the corresponding aliphatic alcohols.

4. Conclusions

The gas-phase acidities of methanol, ethanol, formic, and acetic acids were computed using the GVB+CI wave functions and the GMS wave function to calculate the resonance stabilization of the carboxylate ions. From the results of these calculations it was shown that, in the absence of resonance, acetic acid is slightly more acidic than ethanol and that the difference in acidities between formic acid and methanol is only half of the experimental value. Assuming that, in the absence of resonance, the difference in acidities can be attributed mainly to the inductive effect of the carbonyl group, we concluded that resonance is not only an important factor but the dominant effect responsible for the greater acidity exhibited by the carboxylic acids, in the gas phase, when compared to the acidity of the corresponding aliphatic alcohols.

Acknowledgment. M.A.C.N. acknowledges CNPq and Finep for financial support. J.D.M.N. thanks CNPq and FAPERJ for a scholarship.

Supporting Information Available: Available: Listing of optimized geometries at the GVB level and 6-31G** basis for the neutral species and 6-31G**+ for the anions (10 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) Wheland, G. W. *Resonance in Organic Chemistry*; John Wiley & Sons: New York, 1955.
- (2) Pauling, L. *Nature of the Chemical Bond*, 2nd ed.; Cornell University Press: Ithaca, NY, 1960.
- (3) Siggel, M. R. F.; Thomas, D. T. *J. Am. Chem. Soc.* **1986**, *108*, 4360.
- (4) Siggel, M. R. F.; Thomas, D. T.; Streitwieser, A. *J. Mol. Struct. (THEOCHEM)* **1988**, *165*, 309.
- (5) Siggel, M. R. F.; Thomas, D. T.; Saethre, L. J. *J. Am. Chem. Soc.* **1988**, *110*, 91.
- (6) Siggel, M. R. F.; Streitwieser, A.; Thomas, D. T. *J. Am. Chem. Soc.* **1988**, *110*, 8022.
- (7) Exner, O. *J. Org. Chem.* **1988**, *53*, 1810.
- (8) Thomas, D. T.; Carroll, T. X.; Siggel, M. R. F. *J. Org. Chem.* **1988**, *53*, 1812.
- (9) Dewar, M. J. S.; Krull, K. L. *J. Chem. Soc., Chem. Commun.* **1990**, 344.
- (10) Bordwell, F. G.; Satish, A. V. *J. Am. Chem. Soc.* **1994**, *116*, 8885.
- (11) Hiberty, P. C.; Byrman, C. P. *J. Am. Chem. Soc.* **1995**, *117*, 9875.
- (12) Chandrasekar, J.; Andrade, J. C.; Schleyer, P. V. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609.
- (13) Dunning, T. H.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer III, H., Ed.; Plenum: New York, 1977; Vol. 3, p 1.
- (14) Kollmar, H. *J. Am. Chem. Soc.* **1978**, *100*, 2665.
- (15) Ewing, C. S.; van Wazer, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 4774.
- (16) Gao, J.; Garner, D. S.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1988**, *110*, 4784.
- (17) Bartmess, J. E.; McGiver, R. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2.
- (18) Taft, R. W.; Koppel, I. A.; Topsom, R. D.; Anvia, F. J. *J. Am. Chem. Soc.* **1990**, *112*, 2047.
- (19) Floriano, W. B.; Blaszkowski, S. R.; Nascimento, M. A. C. *J. Mol. Struct. (THEOCHEM)* **1995**, *335*, 51.
- (20) Miranda, M. P.; Bielschowsky, C. E.; Nascimento, M. A. C. *J. Phys. B* **1995**, *28*, L15.

- (21) Hollauer, E.; Nascimento, M. A. C. *Chem. Phys.* **1993**, *177*, 79.
(22) Hollauer, E.; Nascimento, M. A. C. *J. Chem. Phys.* **1993**, *99*, 1207.
(23) Bielscowsky, C. E.; Nascimento, M. A. C.; Hollauer, E. *Phys. Rev. A* **1992**, *45*, 7942.
(24) Hollauer, E.; Nascimento, M. A. C. *Chem. Phys. Lett.* **1991**, *184*, 470.
(25) Nascimento, M. A. C. In *Collision Processes of Ion, Positron, Electron and Photon Beams with Matter*; Silveira, E., Ed.; World Scientific: River Edge, NJ, 1992; p 247.
(26) Bobrowicz, F. B.; Goddard III, W. A. In *Modern Theoretical Chemistry*; Schaefer III, H., Ed.; Plenum: New York, 1977; Vol. 3, p 79.
(27) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2567.
(28) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
(29) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
(30) Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296.
(31) Kitaura, K.; Morokuma, K. *Int. J. Quantum Chem.* **1976**, *10*, 325.
(32) The energy lowering of a configuration is defined as the difference in energy when a configuration is deleted from the full configurational list without reoptimizing the coefficients of the remaining configurations.
(33) (a) Chirlian, L. E.; Francl, M. M. *J. Comput. Chem.* **1987**, *8*, 894.
(b) Woods, R. J.; Khalil, M.; Pell, W.; Moffit, S. H.; Smith, W. H. *J. Comput. Chem.* **1990**, *11*, 297.
(34) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.
(35) Wiberg, K. B. *J. Am. Chem. Soc.* **1990**, *112*, 3379.
(36) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *9*, 18.
(37) Coulson, C. A. *Valence*, 2nd ed.; Oxford University Press: New York, 1961.
(38) Kollmar, H. *J. Am. Chem. Soc.* **1971**, *101*, 4832.
(39) Behrens, S.; Koster, A. M.; Jug, K. *J. Org. Chem.* **1994**, *59*, 2546.
(40) With this particular choice, the GMS wave function becomes equivalent to the RGVb wave function. See: Voter, A.; Goddard III, W. A. *Chem. Phys.* **1981**, *57*, 253.

JP961120P