GAS-PHASE ACIDITY OF SOME CARBOXYLIC ACIDS CALCULATED BY MNDO

M. Jalali-Heravi* and M. Namazian

Chemistry Department, Shahid Bahonar University of Kerman, Kerman, Islamic Republic of Iran

Abstract

Gas-phase acidities of 15 aliphatic carboxylic acids, $X_nCH_{3-n}COOH$, have been calculated using the MNDO method. Among the substituted groups exist the electron donor alkyl groups and electron acceptor halogens. The average error in acidity is within the experimental uncertainty of the data. Systematic errors have been found for the substituents which form internal hydrogen bondings. A reasonable correlation does exist between the gas-phase acidity and the net atomic charges on the acidic hydrogens in the neutral form and the net atomic charges and ionization potentials of the anions. There is no correlation between the gas-phase acidity and HOMO and bandgaps.

Introduction

Gas-phase acidity studies have become a very important field in recent years since they allow the investigation of intrinsic acidities without the interference of solvent. This conclusion is also supported by the recent gas-phase acidity experiments, which indicate that a wide variety of acids have different relative acidities in gas phase in comparison with the solution phase [1].

Although intrinsic gas-phase acidities can be determined by recent sophisticated experimental methods [2, 3], an important contribution to this field can be expected to be achieved from theoretical calculations. Quantum mechanical methods such as *ab initio* and semiempirical self-consistent field molecular orbital (SCF-MO) theories have been found to be useful in this regard. However, the use of the *ab initio* method is restricted to relatively small systems and requires large computers. On the other hand, for gas-phase acidity calculations one needs to obtain energies for anions. *Ab initio* models have been shown to require the addition of diffuse orbitals in order to obtain reliable energies for anions [4]. This requirement fur-

ther limits the size of a molecule that can be calculated in a reasonable time.

Our aims in this work are: first, to assess the MNDO ability in calculations of gas-phase acidity of aliphatic carboxylic acids, second, to find the correlation of these quantities with structural and electronic parameters such as charge density, O-H bond length, HOMO energies and bandgaps.

Methods

The MNDO calculations were carried out using the MNDO version (QCPE No. 353) [5] running on a UNIVAC 1100 computer at the Oil Ministry computer center. Standard geometries [6] were used for starting calculations. Geometries were fully optimized in internal coordinates by the standard MNDO program based on the Hartree-Fock (HF) method. All optimizations were terminated when the change in energy on successive iteration was less than 0.00001 kcal/mole. For all of the conformations considered, the one with the lowest energy was selected for the correlation analysis.

The gas-phase acidity is defined as the free energy change, $\Delta(\Delta G°)$, for the isodesmic process illustrated in reaction 1.

$$X_nCH_{3-n}COOH+CH_3COO^- \rightarrow X_nCH_{3-n}COO^- +CH_3COOH \qquad (1)$$
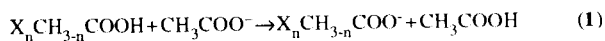
Small entropy changes expected in systems such as isodesmic process 1, thus one may conclude that $\Delta G° \approx \Delta H°$. Therefore, the gas-phase acidities are taken as calculated $\Delta(\Delta H_f)$ for the reaction 1.

Results and Discussion

Acidities of 15 aliphatic carboxylic acids, X_n $CH_{3-n}COOH$, were calculated using the MNDO method and the results are given in Table I along with the experimentally measured values obtained by the PHPMS method [7]. The selection of the carboxylic acids given in Table I is made on the basis of different properties of the substituted groups and the availability of their gas-phase experimental data. It can be seen from Table I that among the substituted groups exist the electron donor alkyl groups and electron acceptor halogens.

The properties shown in Table I include MNDO calculated heats of formation of carboxylic acids, $\Delta H_f°X_n$ $CH_{3-n}COOH$, and the corresponding anions. The regression coefficient (r) and F-ratio are also given in Table I. The overall significance of the regression can be tested with the F-ratio. If the calculated F-ratio exceeds the tabular value of F at the specified level of significance and degrees of freedom, the hypothesis is accepted that the regression parameters are not all equal to zero and that r^2 is signifi-

cantly different from zero.

A plot of calculated gas-phase acidity, $\Delta(\Delta H_f)$, against experimental values, $\Delta(\Delta G)$, is shown in Figure 1. The solid line ($\Delta(\Delta H_f)=1.263$ $\Delta(\Delta G)-1.80$) is a least squares fit of the data. The overall agreement is good with a regression coefficient of 0.9682 and an F value of 194.6, which strongly confirms a linear correlation between the experimental and calculated values.

Examination of the results (Table I) reveals a deviation of about 3 kcal/mole between the MNDO calculated and the experimental gas-phase acidity for OH substituent. Inspection of isodesmic reaction 1 reveals small entropy changes, therefore one may consider the enthalpy changes as Gibbs free energy changes for these type reactions. McMahon and Kebarle [8] have confirmed this argument by reporting an entropy change of 2.0 eu/mole for such reactions. However, this is true when intermolecular hydrogen bonding is not involved.

It can be seen from the following figure that hydrogen bond formation is responsible for large entropy changes in the $HOCH_2COOH$ compound, which have not been considered in our calculation. Calculated
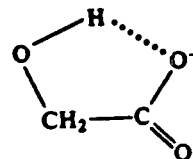

Table I. Comparison of the calculated and experimental gas-phase acidity for some carboxylic acids, $X_nCH_{3-n}COOH$

Substituent X	ΔH_f(acid)	ΔH_f(anion)	$\Delta(\Delta H_f)$ MNDO results	$\Delta(\Delta G)$ EXP. results*
H	-101.04402	-110.11454	0.0	0.0
CH_3	-106.12843	-116.31302	1.1	1.1
CH_3CH_2	-110.81992	-121.55051	1.7	2.0
$CH_3CH_2CH_2$	-115.51970	-126.13924	1.5	2.3
CH_3O	-128.74616	-145.03789	7.2	6.2
C_2H_5O	-133.79053	-149.96074	7.1	6.5
$CH_3CH(Cl)$	-116.05982	-131.09702	6.0	6.7
H_2N	-95.69934	-109.92601	5.2	6.8
F	-143.96155	-162.82433	9.8	9.9
$CH_3CH_2CH(Cl)$	-113.67223	-134.08122	11.3	11.0
OH	-142.59175	-159.90191	8.4	11.5
Cl	-106.01878	-126.11675	11.0	12.5
F_2	-190.08876	-219.60071	20.4	17.7
Cl_2	-107.06287	-136.35915	20.2	19.6
F_3	-237.94885	-280.63423	33.6	24.1
r				0.9682
F-ratio				194.6

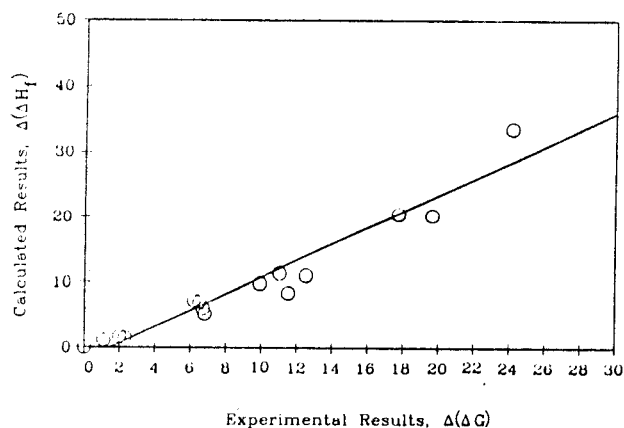* Experimental results are taken from reference 7.

Figure 1. Calculated gas-phase acidities, $\Delta(\Delta H_f)$, against experimental values, $\Delta(\Delta G)$

gas-phase acidity for CF_3COOH shows a significant deviation from the corresponding experimental value. This is due to the large error accompanying the MNDO calculated heats of formation for molecules containing two or more fluorine groups [9]. Therefore, it may not be unreasonable to exclude four points corresponding to the substituents OH, OCH_3, OC_2H_5 and F_3 from the correlation. In this case, the regression coefficient and F-ratio was found to be 0.9767 and 207.3, respectively.

Tables II and III list the MNDO calculated net atomic charges on the acidic hydrogens (qH) and on the acidic (q-O) and carbonyl (q=O) oxygens, respectively. Examination of the results (Tables II and III) reveal that, on the whole, there is a satisfactory correlation between the MNDO calculated gas-phase acidity and the net atomic charges on the acidic hydrogens and acidic and carbonyl oxygens. It should be added that the gas-phase acidities of the carboxylic acids show stronger correlation with the net atomic charges on the acidic hydrogens in comparison with those of the oxygens. Regression coefficient (r) for the net atomic charges of acidic hydrogens is 0.9958, whereas for the acidic and carbonyl oxygens it is 0.9046 and 0.9600, respectively.

Table IV includes the net atomic charges on the acidic (q-O⁻) and carbonyl oxygens (q=O) of the carboxylic acid anions, $X_nCH_{3-n}COO^-$. Sum of the net atomic charges on the acidic and carbonyl oxygens of carboxylic acids, (qO⁻+q=O), and differences of the net atomic charges of the acidic oxygens in the anionic and neutral forms (qO⁻-qO-H), are also given in Table IV. Inspection of these results reveals that there exists a correlation between the gas-phase acidity and the net atomic charges of the oxygens for the anions.

The regression coefficients for the net charges on the acidic oxygens of the anions are higher than those of the corresponding acids. Also, the high correlation (r=0.9889) between the calculated gas-phase acidity and the sum of the net charges on the acidic and carbonyl oxygens of the neutral carboxylic acids should be noted.

Ionization potentials for carboxylic acids and corresponding anions are included in Table V. It can be seen that there is no correlation between the ionization potential of carboxylic acids and the gas-phase acid-

Table II. Correlation between the MNDO calculated gas-phase acidity and net atomic charges on the acidic hydrogens for some carboxylic acids

Substituent X	q(H)	Gas-phase acidity
H	0.2164	0.0
CH_3	0.2159	1.1
CH_3CH_2	0.2158	1.7
$CH_3CH_2CH_2$	0.2159	1.5
$CH_3CH(Cl)$	0.2195	6.0
H_2N	0.2180	5.2
F	0.2226	9.8
$CH_3CH_2CH(Cl)$	0.2226	11.3
Cl	0.2230	11.0
F_2	0.2299	20.4
Cl_2	0.2288	20.2
F_3	0.2373	33.6
r	0.9958	
F-ratio	1183.2	

Table III. Net atomic charges on the acidic and carbonyl oxygens of some carboxylic acids, $X_nCH_{3-n}COOH$

Substituent X	q(-O)	q(=O)	Gas-phase acidity
H	-0.3041	-0.3675	0.0
CH_3	-0.3042	-0.3670	1.1
CH_3CH_2	-0.3042	-0.3669	1.7
$CH_3CH_2CH_2$	-0.3042	-0.3670	1.5
$CH_3CH(Cl)$	-0.2949	-0.3617	6.0
H_2N	-0.2992	-0.3734	5.2
F	-0.2953	-0.3342	9.8
$CH_3CH_2CH(Cl)$	-0.2993	-0.3356	11.3
Cl	-0.2997	-0.3324	11.0
F_2	-0.2926	-0.3029	20.4
Cl_2	-0.2941	-0.3060	20.2
F_3	-0.2669	-0.2862	33.6
r	0.9046	0.9600	
F-ratio	45.0	117.6	

Table IV. Net atomic charges on the acidic and carbonyl oxygens of some carboxylic acid anions, $X_nCH_{3-n}COO^-$

Substituent X	q(-O)	q(=O)	q(-O)+q(=O)[a]	q(-O)-q(O-H)[b]
H	-0.6118	-0.6140	-0.6716	-0.3077
CH_3	-0.6057	-0.6079	-0.6712	-0.3015
CH_3CH_2	-0.6052	-0.6063	-0.6710	-0.3010
$CH_3CH_2CH_2$	-0.6039	-0.6064	-0.6712	-0.2997
$CH_3CH(Cl)$	-0.5828	-0.6052	-0.6567	-0.2878
H_2N	-0.5986	-0.6131	-0.6726	-0.2994
F	-0.5930	-0.5803	-0.6326	-0.2947
$CH_3CH_2CH(Cl)$	-0.5838	-0.5654	-0.6348	-0.2845
Cl	-0.5907	-0.5684	-0.6321	-0.2910
F_2	-0.5707	-0.5431	-0.5955	-0.2781
Cl_2	-0.5691	-0.5290	-0.6000	-0.2750
F_3	-0.5149	-0.5157	-0.5531	-0.2480
r	0.9578	0.9568	0.9889	0.9689
F-ratio	111.2	108.4	441.9	153.2

[a]Sum of the net atomic charges on the acidic and carbonyl oxygens of carboxylic acids, $X_nCH_{3-n}COOH$
[b]Differences of the net atomic charges of the acidic oxygens in the anionic and neutral forms

Table V. Calculated ionization potentials for the neutral and ionic forms of some carboxylic acids

Substituent X	I.P.$(X^nCH_{3-n}COOH)$ (ev)	I.P.$(X_nCH_{3-n}COO^-)$ (ev)	Gas-phase acidity
H	11.5676	3.8418	0.0
CH_3	11.5001	3.9558	1.1
CH_3CH_2	11.4857	3.9830	1.7
$CH_3CH_2CH_2$	11.4761	4.0076	6.0
$CH_3CH(Cl)$	11.6817	4.2706	5.2
H_2N	10.8585	4.0341	5.2
F	11.8048	4.2836	9.8
$CH_3CH_2CH(Cl)$	11.7462	4.5268	11.3
Cl	11.8712	4.4503	11.0
F_2	12.0843	4.7634	20.4
Cl_2	12.1146	4.9706	20.2
F_3	12.7174	5.5068	33.6
r	0.8600	0.9882	
F-ratio	28.4	416.2	

ity, whereas the correlation coefficient for the ionization potential of anions is 0.9882 with an F-ratio of 416.2. This value for F is much higher than corresponding tabular values of this factor and therefore reveals a linear relation between the gas-phase acidity and ionization potential of anionic forms of the carboxylic acids.

Table VI shows the correlation between the O-H bondlength and the gas-phase acidity. A regression coefficient of 0.9194 and F-ratio of 54.6 reveal a reasonable correlation between this structural parameter and the gas-phase acidity.

Regression analysis shows no correlation between the gas-phase acidity and dipole moment, higher oc-

Table VI. Correlation of gas-phase acidity with the O-H bondlength of some carboxylic acids

Substituent X	OH bondlength (A°)	Gas-phase acidity
H	0.9496	0.0
CH_3	0.9494	1.1
CH_3CH_2	0.9494	1.7
$CH_3CH_2CH_2$	0.9497	1.5
$CH_3CH(Cl)$	0.9496	6.0
H_2N	0.9498	9.8
F	0.9497	9.8
$CH_3CH_2CH(Cl)$	0.9497	11.3
Cl	0.9498	11.0
F_2	0.9502	20.4
Cl_2	0.9502	20.2
F_3	0.9516	33.6
r	0.9194	
F-ratio	54.6	

cupied molecular orbital (HOMO) energy and bandgaps (E_{LUMO}-E_{HOMO}) of the carboxylic acids.

Conclusion

One can predict the gas-phase acidity of carboxylic acids by using the MNDO method. The average error in acidity is within the experimental uncertainty of the data. Systematic errors were found for substituents such as OH, OCH_3 and OC_2H_5 which form internal hydrogen bondings.

Gas-phase acidity shows a reasonable correlation with the net atomic charges on the acidic hydrogens and carbonyl oxygens. The latter correlation is stron-

ger for the anionic form of the carboxylic acids than for the corresponding neutral forms. The gas-phase acidity shows correlation with the ionization potentials of the anions. There is no correlation between the gas-phase acidity and the HOMO and the bandgaps.

Acknowledgements

References

1. Brauman, J. I. and Blair, L. K. *J. Am. Chem. Soc.*, **92**, 5986, (1970).
2. Bowers, M. T., Aue, D. H., Webb, H. M. and McIver, Jr. R. T. *Ibid.*, **93**, 4314, (1971); Bartmess, J. E., Scott, J. A. and McIver, Jr. R. T. *Ibid.*, **101**, 6046-6056, (1979).
3. Briggs, J. P., Yamdagni, R. and Kebarle, P. *Ibid.*, **94**, 5128, (1972); Bohme, D. K., Hemsworth, R. S., Rundle, J. W. and Schiff, H. I. *J. Chem. Phys.*, **58**, 3504, (1973); McMahon, T. B. and Kebarle, P. *J. Am. Chem. Soc.*, **99**, 2222, (1977); Kebarle, P. *Ann. Rev. Phys. Chem. Soc.*, **28**, 445, (1977); Cunningham, A. J., Payzant, J. D. and Kebarle, p. *J. Am. Chem. Soc.*, **94**, 7627, (1972).
4. Siggel, M. R., Thomas, T. D. and Seathre, L. J. *J. Am. Chem. Soc.*, **110**, 91, (1988); Carsky, P. and Urban, M. *Lect. Notes Chem.*, **16**, 50, (1980); Kollmar, H. *J. Am. Chem. Soc.*, **100**, 2665, (1978).
5. Dewar, M. J. S. and Thiel, W. *J. Am. Chem. Soc.*, **99**, 4899-4907, (1977).
6. Pople, J. A. and Gordon, M. *Ibid.*, **89**, 4253, (1967).
7. Caldwell, G., Reneboog, R. and Kebarle, P. *Can. J. Chem.*, **67**, 611, (1989).
8. McMahon, T. B. and Kebarle, P. *J. Am. Chem. Soc.*, **98**, 3399, (1976).
9. Dewar, M. J. S. and Rzepa, H. S. *Ibid.*, **100**, 58, (1976).