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Ab initio calculations of pK_a values of some organic acids in aqueous solution

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Abstract

The acidity of different classes of organic compounds in aqueous solution has been calculated. The calculations are carried out at the SCF level with inclusion of entropic and thermochemical correction to yield free energies of dissociations.

The polarized continuum model is used to describe the solvent. The model furnishes pK_a values in relatively good agreement with experimental data. Scaling different parts of solvation energies provides a significant improvement in results and signifies the importance of balance of individual contributions from electrostatic, cavity, dispersion and repulsion interactions.

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Keywords: pK_a ; Carboxylic acids; Alcohols; Solvation energy; Polarized continuum model; Ab initio calculations

1. Introduction

Proton transfer reactions constitute an important class of chemical reactions and have been studied extensively over a long period of time [1]. These studies in a gas phase and solution phase provides information on inherent substituent effects and solute–solvent interactions. The study of acidities in the gas phase allows assessment of effects in the absence of the perturbing influence of a solvent or counter ions [2–4]. The acidity of compounds in solution phase is also of interest since many reactions occur practically and experimentally in solution phase. Many biological systems use proton-transfer reactions to perform communication between the extracellular and intra-

cellular media and the rate of these reactions depends on the degree of dissociation of the species [5].

Quantum mechanical calculations in both ab initio and semi-empirical levels of theory, have been extensively employed to the study of acidities in the gas phase and the results have been compared with the experimental values. It is now known that the calculated gas-phase acidities using a high level theory such as GAUSSIAN-2 (G2) are reliable [6]. In cases where theoretical acidities showed deviation from experimental values, the experimental estimates were generally found to be associated with large uncertainties [6]. Despite the gas-phase acidities, the calculations of acidities in solution phase are still deficient. This deficiency is due to the lack of a complete and precise model of solvation. Even recent models of solvation such as polarizable continuum model (PCM) [7] ignore some parts of solute–solvent interactions [8].

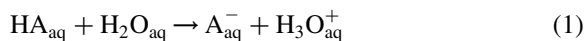
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In the present study, the acidities of some carboxylic acids and alcohols in the aqueous phase have been calculated and the results have been found to be improved compared with the previous reports [5,8,9].

2. Methods and theoretical considerations

A compound is defined as Brönsted acid in aqueous solution if it dissociates as follows:



The equilibrium constant is related to the change of standard Gibbs energy; therefore, there is a simple relation between the change of standard Gibbs energy and $\text{p}K_{\text{a}}$

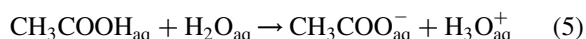
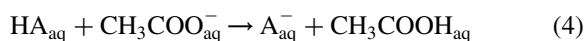
$$\Delta G_1^\circ = -2.303 RT \log(K_{\text{a}}/[\text{H}_2\text{O}]) \quad (2)$$

or following Nascimento [8,9], a simpler form of Eq. (2) can be used:

$$\Delta G_1^\circ (\text{kcal/mol}) = 1.36 \text{p}K_{\text{a}} + 2.36 \quad (3)$$

where ΔG_1° is the standard change of the Gibbs energy related to the process taking place in water at 298.15 K.

In order to calculate the ΔG_1° , we have used an isodesmic reaction (4) and the dissociation of acetic acid (Eq. (5)) as a reference molecule.



Gibbs energy of reaction (1), ΔG_1° , can be written as a sum of the Gibbs energy of reaction (4), ΔG_2° , and the Gibbs energy of reaction (5), ΔG_3° .

$$\Delta G_1^\circ = \Delta G_2^\circ + \Delta G_3^\circ \quad (6)$$

Fig. 1 shows a thermodynamical cycle proposed to calculate the ΔG_2° . From this cycle, ΔG_2° is given by the following expression

$$\Delta G_2^\circ = \Delta G_{2,\text{gas}}^\circ + \Delta G_{2,\text{sol}}^\circ \quad (7)$$

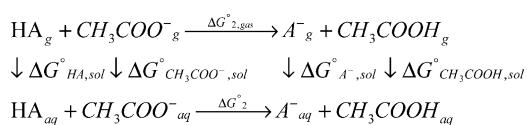


Fig. 1. The thermodynamic cycle proposed to convert $\Delta G_{2,\text{gas}}^\circ$ to ΔG_2° .

in which $\Delta G_{2,\text{sol}}^\circ$ is defined as follow:

$$\Delta G_{2,\text{sol}}^\circ = \Delta G_{\text{A}^-,\text{sol}}^\circ + \Delta G_{\text{CH}_3\text{COOH},\text{sol}}^\circ - \Delta G_{\text{HA},\text{sol}}^\circ - \Delta G_{\text{CH}_3\text{COO}^-,\text{sol}}^\circ \quad (8)$$

The gas phase contribution to the Gibbs energy can be determined from ab initio calculations. Solvation energies have been calculated using PCM [7,10–15]. The ab initio calculations have been performed at the level of Hartree–Fock. The zero-point energies and thermal corrections together with entropies have been used to convert the internal energies to the Gibbs energies at 298.15 K. A medium-size basis set, 6-31(d,p), has been chosen by considering the size of studied molecules. Higher level of theory was not justified because of hardware limitations and the significant length of time of computations. GAUSSIAN98 [16] have been employed for all ab initio calculations.

3. Results and discussion

First, we chose a limited number of alcohols and carboxylic acids which are shown in Table 1. These molecules have been recently studied by Nascimento and his group [8,9]. The list of acids consists of mainly aliphatic alcohols, aliphatic and halogenated carboxylic acids. The experimental $\text{p}K_{\text{a}}$ values are in the wide range of 2.66–17.1.

Table 1
The aliphatic alcohols, aliphatic and halogenated carboxylic acids studied in this work

No.	Compound	$\text{p}K_{\text{a}}^{\text{a}}$
1	MeOH	15.50
2	EtOH	15.90
3	<i>n</i> -PrOH	16.10
4	<i>i</i> -PrOH	17.10
5	HCOOH	3.75
6	CH ₃ COOH	4.76
7	CH ₃ CH ₂ COOH	4.87
8	CH ₃ (CH ₂) ₂ COOH	4.82
9	(CH ₃) ₃ CCOOH	5.05
10	FCH ₂ COOH	2.66
11	ClCH ₂ COOH	2.86
12	BrCH ₂ COOH	2.86

^a Refs. [8,9].

Table 2

Gibbs free energy of each molecule and its anion in the gas phase together with Gibbs energy changes of reaction (1), $\Delta G_{1,\text{gas}}^\circ$ in the gas phase

Compound ^a	$\Delta G_{\text{gas,acid}}^\circ$ ^b	$\Delta G_{\text{gas,anion}}^\circ$ ^c	$\Delta G_{1(\text{gas})}^\circ$ ^d	$\Delta G_{1,\text{exp}}^\circ$ ^e	%error ^f
1	−115.01426	−114.37369	372.6	372.6	0.0
2	−154.02977	−153.39352	369.9	369.5	0.1
3	−193.03948	−192.40519	368.7	368.1	0.2
4	−193.04472	−192.41175	367.8	367.5	0.1
5	−188.75750	−188.18563	339.6	338.3	0.4
6	−227.78051	−227.20557	341.5	341.5	0.0
7	−266.78858	−266.21719	339.3	340.4	−0.3
8	−305.79807	−305.22773	338.6	339.5	−0.3
9	−344.80659	−344.23819	337.4	337.6	−0.1
10	−326.62806	−326.06714	332.7	331.6	0.3
11	−686.68312	−686.12971	328	329	−0.3
12	−2797.09363	−2796.54112	327.4	328.2	−0.2

^a See Table 1 for the list of compounds.^{b,c} Gibbs free energies in atomic units, Hartree (1 Hartree = 627.5095 kcal/mol [7]).^d Gibbs free energies of reaction (1) in kcal/mol.^e The experimental values are taken from Refs. [8,9].^f Relative error.

Table 2 shows the calculated Gibbs energy of each molecule and its anion in the gas phase together with Gibbs energy changes of reaction (1), $\Delta G_{1,\text{gas}}^\circ$. Comparison between calculated energies and experimental values shows that only small deviations exist with a maximum of 0.3%.

The solvation energy of each molecule and its anion calculated using PCM model are shown in Table 3 as

well as four components of solvation energies from the electrostatic interaction, cavity term, dispersion and repulsion energies. Examination of the calculated values shows that electrostatic interactions between anions and solvent are much greater than interaction of neutral molecules and solvent (seven to ten times). Dispersion and repulsion energies of anions are also greater than acids because of the extra net charge on

Table 3

Solvation energy and its four components (electrostatic interaction, cavity term, dispersion and repulsion energies) of each molecule and its corresponding anion calculated using PCM model (All values are in kcal/mol)

Compound ^a	$\Delta G_{\text{ele}}^\circ$		$\Delta G_{\text{cav}}^\circ$		$\Delta G_{\text{dis}}^\circ$		$\Delta G_{\text{rep}}^\circ$		$\Delta G_{\text{solv}}^\circ$	
	Acid	Anion	Acid	Anion	Acid	Anion	Acid	Anion	Acid	Anion
1	−5.68	−89.56	6.86	5.54	−8.24	−9.19	1.87	3.54	−5.19	−89.68
2	−5.57	−86.91	8.89	8.06	−11.33	−11.90	2.66	3.99	−5.35	−86.76
3	−5.47	−85.71	11.44	10.65	−13.30	−13.79	2.80	3.97	−4.54	−84.88
4	−5.46	−83.61	11.06	10.54	−13.62	−13.76	3.02	3.84	−4.99	−82.99
5	−8.45	−76.29	7.54	6.66	−8.27	−8.12	1.79	2.08	−7.39	−75.67
6	−8.36	−77.22	9.92	9.11	−10.91	−10.91	2.16	2.50	−7.19	−76.52
7	−8.49	−75.78	11.84	11.11	−13.71	−13.78	2.87	3.15	−7.49	−75.29
8	−8.30	−75.22	14.41	13.69	−15.60	−15.72	2.97	3.30	−6.52	−73.95
9	−7.86	−71.99	15.77	15.12	−17.37	−17.42	3.23	3.46	−6.22	−70.83
10	−10.23	−74.53	10.72	9.98	−11.95	−12.01	2.47	2.78	−9.09	−73.78
11	−11.54	−70.85	12.25	11.60	−13.40	−13.41	2.79	3.05	−9.90	−69.61
12	−10.64	−69.61	12.86	12.14	−13.99	−14.18	2.83	3.12	−8.94	−68.53

^a See Table 1 for the list of compounds.

Table 4

Solvation energies calculated using D-PCM, C-PCM and IEF-PCM (All values are in kcal/mol)

Compound ^a	$\Delta G_{\text{sol,acid}}^{\circ}$			$\Delta G_{\text{sol,anion}}^{\circ}$		
	PCM	CPCM	IEFPCM	PCM	CPCM	IEFPCM
1	−5.15	−5.19	−5.14	−91.51	−89.68	−87.17
2	−5.20	−5.35	−5.3	−88.41	−86.76	−84.78
3	−4.34	−4.54	−4.48	−88.08	−84.88	−83.11
4	−4.87	−4.99	−4.94	−85.3	−82.99	−81.34
5	−7.31	−7.39	−7.33	−76.18	−75.67	−74.79
6	−7.27	−7.19	−7.13	−76.92	−76.52	−75.70
7	−7.50	−7.49	−7.43	−76.17	−75.29	−74.32
8	−6.40	−6.52	−6.46	−74.94	−73.95	−72.74
9	−6.25	−6.22	−6.13	−72.13	−70.83	−70.89
10	−9.05	−9.09	−8.99	−74.31	−73.78	−72.93
11	−9.83	−9.9	−9.81	−70.23	−69.61	−68.79
12	−8.97	−8.94	−8.87	−69.01	−68.53	−67.83

^a See Table 1 for the list of compounds.

anions. Cavity energies of acids are slightly greater than anions because of the extra hydrogen atom. Overall, the calculated solvation energies of anions are of significant and play an important role in total solvation energy of reaction (4). Different solvation

Table 5

The pK_a values calculated in this work using different PCM models

Compound	pK_a				
	PCM	CPCM	IEFPCM	Prev. ^a	Exp. ^b
1	15.50	15.50	15.50	20.14	15.50
2	15.83	15.78	15.39	18.84	15.90
3	14.53	15.66	15.11	19.37	16.10
4	16.36	16.77	16.14	20.56	17.10
5	3.94	4.14	4.19	2.92	3.75
6	4.76	4.76	4.76	4.32	4.76
7	3.84	4.25	4.36	4.76	4.87
8	3.45	4.03	4.32	4.59	4.82
9	4.51	5.21	4.54	5.42	5.05
10	1.52	1.7	1.69	1.14	2.66
11	1.63	1.9	1.88	1.57	2.86
12	1.48	1.57	1.48	0.63	2.86
r.m.s. ^c	1.0	0.6	0.8	2.3	–

The values are compared with those obtained from the theoretical calculations previously reported, as well as with the experimental values.

^a Taken from Refs. [8,9].^b Taken from Refs. [8,9].

^c Root-mean-square of errors. The experimental values of 8.86 and 23.44 kcal/mol are used for ΔG_3° for the case of acetic acid and methanol as reference molecules (Ref. [5]).

Table 6

A wider range of carboxylic acids studied in this work

No.	Compound	$pK_{a,\text{exp}}^a$
1	HCOOH	3.75
2	CH ₃ COOH	4.76
3	CH ₃ CH ₂ COOH	4.87
4	CH ₃ (CH ₂) ₂ COOH	4.82
5	(CH ₃) ₃ CCOOH	5.05
6	FCH ₂ COOH	2.66
7	ClCH ₂ COOH	2.81
8	BrCH ₂ COOH	2.86
9	CH ₃ CHClCOOH	2.80
10	CH ₂ ClCH ₂ COOH	4.10
11	Cl ₂ CHCOOH	1.30
12	NCCH ₂ COOH	2.44
13	O ₂ NCH ₂ COOH	1.32
14	CH ₃ CHOHCOOH	3.87
15	CH ₂ =CHCOOH	4.26
16	F ₃ CCOOH	0.23
17	HOCH ₂ COOH	3.83
18	CH ₃ OCH ₂ COOH	3.54
19	CH ₂ =CHCH ₂ COOH	4.35
20	HC=CCH ₂ COOH	3.32
21	ClCH ₂ CH ₂ CH ₂ COOH	4.52
22	C ₆ H ₅ COOH	4.20
23	<i>o</i> -ClC ₆ H ₄ COOH	2.88
24	<i>p</i> -ClC ₆ H ₄ COOH	3.99
25	<i>p</i> -CH ₃ C ₆ H ₄ COOH	4.36
26	<i>p</i> -NO ₂ C ₆ H ₄ COOH	3.41
27	C ₆ H ₅ CH ₂ COOH	4.31
28	<i>m</i> -ClC ₆ H ₄ COOH	3.83

^a The experimental values are taken from Ref. [5].

algorithms have been employed in order to calculate solvation energies. These models have been Dielectric-PCM (D-PCM) [10], Conductor-PCM (C-PCM) [13] and Integral Equation Formalism-PCM (IEF-PCM) [11]. These methods are different in their modeling of the cavity created in solvent in order to place the solute molecules. The isodensity surface, which is employed in the recent version of PCM methods, is a natural shape for the cavity and it corresponds to the reactive shape of molecules. Table 4 shows the solvation energies calculated using these methods. All energies are almost the same for the neutral molecules. However, anions result in different values because of

the importance of electrostatic interaction between solute and solvent and the cavity term.

The pK_a values calculated in this work are shown in Table 5 where they are compared with those obtained from the theoretical calculations previously reported, as well as with the experimental values. The studied molecules are alcohols and carboxylic acids and have been chosen to be consistent with previous studies [8,9]. Among different version of PCM methods, C-PCM presents better results with a standard error of 0.6. We now analyse the pK_a of different compounds. Significant improvement over previous results can be seen for the acids studied here.

Table 7

The standard Gibbs free energies calculated at the Hartree level of theory using 6-31(d,p) basis set and solvation energies obtained by CPCM model

No.	$\Delta G_{\text{acid,gas}}^{\text{a}}$	$\Delta G_{\text{anion,gas}}^{\text{b}}$	$\Delta G_{\text{sol,acid}}^{\text{c}}$	$\Delta G_{\text{sol,anion}}^{\text{d}}$	ΔG_1^{e}
1	−188.75750	−188.18563	−7.39	−75.67	7.95
2	−227.78051	−227.20557	−7.19	−76.52	8.83
3	−266.78858	−266.21719	−7.49	−75.29	8.13
4	−305.79807	−305.22773	−6.52	−73.95	7.85
5	−344.80659	−344.23819	−6.22	−70.83	9.45
6	−326.62806	−326.06714	−9.09	−73.78	4.67
7	−686.68312	−686.12971	−9.90	−69.61	4.95
8	−2797.0936	−2796.5411	−8.94	−68.53	4.5
9	−725.69661	−725.14147	−7.90	−68.50	5.14
10	−725.69824	−725.14506	−8.91	−67.67	5.75
11	−1145.5762	−1145.0411	−8.49	−63.01	−1.37
12	−319.50546	−318.96364	−12.94	−68.81	1.51
13	−431.23775	−430.70206	−15.64	−68.5	0.67
14	−341.64458	−341.08724	−10.20	−69.26	8.05
15	−265.62037	−265.04914	−6.22	−73.16	8.89
16	−524.36517	−523.83215	−6.73	−64.14	−5.55
17	−302.62414	−302.0719	−11.97	−71.14	4.73
18	−341.61958	−341.05048	−10.89	−79.16	6.22
19	−304.62283	−304.05823	−7.37	−71.58	7.46
20	−303.43651	−302.87657	−8.42	−72.62	4.55
21	−764.70856	−764.14966	−9.59	−71.14	6.55
22	−418.24806	−417.68371	−6.90	−70.09	8.33
23	−877.14370	−876.58562	−6.66	−67.23	7.02
24	−877.15774	−876.60274	−6.59	−65.02	7.22
25	−457.26148	−456.69551	−6.71	−70.39	8.86
26	−621.71476	−621.17235	−8.78	−61.32	5.21
27	−457.24170	−456.68169	−8.83	−69.78	7.84
28	−877.15694	−876.60256	−6.43	−65.17	6.52

^a Energies are in atomic units, Hartree (1 Hartree = 627.5095 kcal/mol [7]).

^b Energies are in atomic units, Hartree (1 Hartree = 627.5095 kcal/mol [7]).

^c Values are in kcal/mol.

^d Values are in kcal/mol.

^e Values are in kcal/mol.

If the pK_a value for iso-propanol is compared with the one obtained by the previous studies [8], it can be seen that the result is improved by two pK_a units. This trend is more or less the same with other alcohols and carboxylic acids as well. The root-mean-square errors are also presented in Table 5.

The next step is to examine the presented model by calculating the pK_a of a wide range of carboxylic acids. Table 6 shows a list of the studied acids in which a variety of substituted acids such as alkyl, alkenyl, halogen, cyano, nitro, ortho and para halogenated phenyl, can be seen. The list consist a wide range of acids and the pK_a values are in the range of 0.23 for F_3CCOOH to 5.05 for $(CH_3)_3CCOOH$. The Gibbs free energy of each molecule is calculated at the Hartree–Fock level of theory using the 6-31(d,p) basis set. The standard free energies of solvation of the acids and anions are calculated using C-PCM. The results are presented in Table 7. Inspection of calculated pK_a reveals that in most cases the pK_a values are reasonably close to the experimental values. For example, the calculated pK_a is 4.39 for phenol whereas the experimental pK_a is reported to be 4.20. In some cases, large deviations are observed so that some negative values can be seen. These deviations are mainly because of solvation energies and they are for polar substituent such as hydroxyl, nitro and cyano groups. The root-mean-square error is 1.79 including those giving high deviations.

Since the main source of deviation comes from the solvation energies and the gas-phase energies should be also considered if a small basis set is used, we have tried to modify the contribution of different parts of ΔG^0 . A stepwise multi-linear regression is carried out and the following relation is obtained:

$$pK_a = (4.770 \pm 0.066) + (0.304 \pm 0.012) \Delta G_{\text{gas}} + (0.286 \pm 0.018) \Delta G_{\text{elec.}} + (4.520 \pm 0.640) \Delta G_{\text{rep.}} \quad (9)$$

with a standard error of 0.396 and correlation coefficient of 0.953. ΔG_{gas} is the Gibbs energy of reaction (1) in the gas phase and ΔG_{elec} is contribution of electrostatic interaction in solvation free energy and ΔG_{rep} presents repulsion energy between solute and solvent. The F - and P -value are 65.86 and 0.000, respectively, which confirm the validity of regression

results. In this analysis, 24 acids are considered and four acids have been randomly chosen as the prediction set. The gas free energy and all components of solvation energies are considered in the regression. Among the components, only electrostatic and repulsion energies are determined to play significant roles. Table 8 presents the calculated values of pK_a obtained by Eqs. (3) and (9) and the experimental values as well. Much improvement can be seen and the standard error decreased from 1.76 to 0.37.

Table 8
The calculated pK_a together with experimental values

Compound ^a	$pK_{a,\text{calc.}}^b$	$pK_{a,\text{calc.}}^c$	$pK_{a,\text{exp}}$
1	4.11	4.18	3.75
2	4.76	4.77	4.76
3	4.24	4.18	4.87
4	4.04	4.29	4.82
5	5.21	4.20	5.05
6	1.70	2.94	2.66
7	1.90	2.49	2.81
8	1.57	2.53	2.86
9	2.04	2.44	2.80
11	−2.74	0.36	1.30
13	−1.24	0.63	1.32
14	4.18	3.77	3.87
16	−5.82	−1.15	0.23
17	1.74	2.69	3.83
18	2.84	3.56	3.54
19	3.75	4.14	4.35
20	1.61	2.82	3.32
21	3.08	4.02	4.52
23	3.43	3.08	2.88
24	3.57	3.18	3.99
25	4.78	4.11	4.36
26	2.10	2.11	3.41
27	4.03	4.06	4.31
28	3.06	3.34	3.83
<i>Prediction set:</i>			
10	2.49	3.50	4.10
12	−0.63	2.11	2.44
15	4.80	4.56	4.26
22	4.39	4.31	4.20
r.m.s. ^d	1.79	0.37	
r^e	0.92	0.95	

^a See Table 6.

^b The calculated pK_a obtained by Eq. (3).

^c The calculated pK_a obtained by Eq. (9).

^d The root-mean-square of deviations of calculated pK_a from experimental values.

^e The correlation coefficient of calculated pK_a with the experimental values.

4. Conclusions

The pK_a values obtained using the proposed thermodynamic cycle and at the Hartree–Fock level of theory with a medium-size basis set, are improved with respect to previous calculations and are in better agreement with experimental results, for the majority of the studied acids.

The main source of deviation comes from solvation energies, so the calculated pK_a values for compounds with high electrical dipole moment dramatically deviated from experimental values. Among the different versions of PCM, the CPCM is determined to provide better results for the pK_a of the acids that were studied here.

Using a stepwise multi-regression analysis a simple relation is presented to calculate the pK_a for carboxylic acids in aqueous solution. The root-mean-square of error is only 0.37 in pK_a units.

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