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COMPARISON OF ABSOLUTE ACIDITIES AND BASICITIES OF METHANOL AND SILANOL CALCULATED BY THE AB INITIO MO METHOD

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Abstract

Absolute gas-phase basicities and acidities were calculated at the RHF/3-21G//3-21G, RHF/3-21+G//3-21G, RHF/3-21+G//3-21+G and RHF/3-21+G(*)//3-21G(*) levels of ab initio theory. The effect of the use of diffuse and polarization functions on the calculated geometries, acidities and basicities was studied. The use of diffuse functions is necessary to calculate accurate acidity and it has a 10 kcal/mol effect on the calculated basicity. The use of *d*-functions (3-21G(*) basis set) for silanol has an important effect on the calculated acidity and basicity. The *d*-functions play a lesser role if the polarization functions are used. The absolute gas-phase acidity and basicity of silanol have not been measured until now; we give a prediction for those values within 3 kcal/mol. According to the calculations, silanol is more acidic than methanol, the difference being 22 kcal/mol. The basicity of the two molecules is closer to each other, the protonation energy of silanol being 6 kcal/mol less. According to the 3-21G(*) calculations the Si-O bond length increase is very important during protonation of silanol.

Keywords: quantum chemical calculation, ab initio, methanol, silanol.

Introduction

The Broensted acidity or deprotonation energy and basicity or protonation energy are very important and extensively used properties both in solution and in gas phase chemistry. The development of measuring techniques such as ion cyclotron resonance (ICR) spectroscopy and high-pressure mass spectrometry have made it possible to obtain a reliable scale of acidity and basicity in the gas phase [1, 2]. In this way the acid and base strength of isolated molecules can be measured.

The development of theory [3], in parallel with experimental techniques, can provide a better understanding of acidity and basicity. Absolute acidity is the energy difference between the total energy of a neutral molecule and the total energy of the corresponding anion. The basicity is the energy difference between the protonated and neutral molecule. Complete geometry optimization is necessary to obtain the correct energies. The knowledge of absolute acidity and basicity is useful for comparisons, and it can give an explanation of the different chemical behaviour. If calculated and measured values are compared, an impression of the performance and the predictive force of the theoretical model used may be obtained. The calculated acid and base strengths are related to the isolated gas phase molecules. If the effect of solvation is considered, the acid and base strength in solution can be predicted, too [4–8].

The acidities calculated at the MP4/6-311++G(3df,2pd)//6-31G(d) level for 9 binary hydrides [9] practically agree with measured values. This level of theory can be used only in the case of small molecules. It is too expensive for larger, chemically more interesting molecules.

The STO 3G, the simplest basis set that can be used in ab initio calculations, performs rather poorly in this field [3]. For larger molecules such as trimethyl substituted silanol the use of STO 3G is more feasible. It is planned to investigate the applicability of the STO-3+G basis set, with results to be published later.

The STO 3-21G basis set is more promising [3, 10]. The 3-21+G//3-21G basis set proved to have reliable predictive power, and experimental acidities can be calculated with 3 kcal/mol uncertainty [10], which is acceptable compared to 1 or 2 kcal/mol experimental error. The 3-21+G(*) basis set [3] can be used for silanol. The additional *d*-functions usually improve the quality of the 3-21G basis set for second row elements. It is interesting that the 3-21G basis set is composed of the same number of Gaussians as STO-3G, the difference being in the larger number of atomic orbitals.

To compare the calculated and measured absolute protonation and deprotonation energies in the gas phase, some corrections have to be added to the ab initio energy differences, The largest correction term is the zero point energy difference (ΔZPE) between the ions and the neutral molecule. Another far from negligible term is the electron correlation energy difference (ΔEcorr). But the 3-21G basis set is not suitable for the calculation of electron correlation effects. Even the 6-311G** basis set can have problems in giving correct electron correlation contributions. For example IKUTA proposes -4 kcal/mol [7] for the acidity correction of methanol, while according to SIGGEL et al. the correction is -9.6 kcal/mol [10]. For the basicity of methanol the ΔEcorr is -1, -2 kcal/mol calculated at the 6-31G** level [3]. The error due to neglect of ΔEcorr is small compared to protonation or deprotonation energies within a homologous series, e.g. alcohols. In this work the ΔEcorr was not used directly, but clearly the ΔEcorr would lower the calculated acidities and basicities by a few kcal/mol. The translation, rotation, vibration and PV work terms are neglected, these values (<1kcal/mol) do not contribute significantly to the determination of relative acidity and basicity.

The aim of the present paper is to give a reliable prediction for the unmeasured acidity and basicity of silanol, and the 3-21G basis set was selected for the calculations. To obtain data for the silanol the measured protonation and deprotonation energy of methanol was corrected according to the calculated energy difference. The acid and base strength of silanol is interesting from the point of view of chemical differences compared to methanol. Methanol is rather stable while silanol is not, since it reacts readily and disiloxane is formed. The starting step of the ionic process may be the deprotonation of silanol. The silanol should be a stronger acid than methanol; for example trimethylsilanol is more acidic than the corresponding t-butyl-alcohol [11].

Calculation Details

The calculations were done using the MICROMOL [12] program on an IBM/AT compatible 24 MHz 386 computer equipped with co-processor, 8 MB RAM and a 155 MB ESDI fixed disk with 25 ms access time. The four center integral coding and decoding subroutines of the original MICROMOL were modified. The relative speed increase was 60 per cent on that part of the program. If the source code was compiled with a MS-Fortran 4.1 optimizing compiler, the speed increase was 2-fold compared with the original executable code. The best results were obtained when 386 compilers were used. For example a double zeta energy, gradient and property calculation on water took 91 seconds compared with 1200 seconds on the 8 MHz AT. The MS-Fortran version took 130 seconds for the same problem. A large disk cache (400 kB) was also used, to eliminate the file writing and reading overhead.

To run substantial ab initio calculations some more power is required. We plan to experience with the microway's number smasher 860. We expect at least 15 times speed increase, which will make quite large calculations possible on a microcomputer. The parallel processing capability of that system is very promising.

Ab Initio Geometries and Energies

The results of 3-21G, 3-21+G and 3-21G(*) geometry optimization are summarized in *Table 1*. Methanol and its ions were studied extensively, the geometries having been calculated earlier at a high level of theory [7, 10, 13]. The geometries are published here to show the effect of adding diffuse functions to the 3-21G basis set, and to draw some conclusions.

Table 1
Hartree-Fock equilibrium structures, methanol derivatives

Molecule	Point group	Parameter	3-21G	3-21+G	Expt.[14]
CH_3O^-	C_{3v}	r(CO)	1.349	1.413	
		r(CH)	1.134	1.104	
		<(HCO)	117.3	113.5	
CH_3OH	C_s	r(CO)	1.441	1.457	1.421
		r(OH)	0.966	0.964	0.963
		r(CHg)	1.079	1.077	1.094
		r(CHt)	1.085	1.083	1.094
		<(HOC)	110.3	112.8	108.0
		<(OCHg)	112.2	110.8	110.4
		<(OCHt)	106.3	105.8	107.2
		<(HgCHt)	108.6	109.7	108.5
$CH_3OH_2^+$	C_s	r(CO)	1.537	1.558	
		r(OH)	0.973	0.974	
		r(CH)	1.075	1.075	
			1.073	1.073	
			1.073	1.073	
		<(HOC)	121.3	121.8	
		<(HOH)	116.4	115.9	
		<(HCH)	112.7	113.0	
			113.7	114.2	
			113.7	114.2	

Bond distances (r) in Å, bond angles (<) in degree. In the case of $CH_3OH_2^+$ the diffuse functions are used only on the oxygen. Hg: gauche hydrogen, Ht: trans hydrogen compared to O-H in methanol.

The adding of diffuse functions has the largest effect for the methanolate anion. The CO bond length $\{r(\mathrm{CO})\}$ is increased by 0.064 Å, the CH bond length is shortened by 0.030 Å and the hydrogen atoms are moved toward planarity by 4.2° (*Table 1*). The geometry of the anion was published by SIGGEL et al. [10] at the RHF/6-311++G(2d,p) level. This calculation can be accepted as a reference, as it is very close to the Hartree-Fock limit. The published values are the following: r(CO) = 1.325 Å, r(CH) = 1.122 Å and <(HCO) = 115.1°. If we compare this r(CO) distance to the r(CO) distances in *Table 1*, the introduction of diffuse orbitals has changed the bond length in the wrong direction. Similar erroneous r(CO) bond lengthening can be found for methanol (*Table 1*). The errors in r(CH) and <(HCO) are overcompensated. The 3-21G geometry is closer to the higher level ab initio calculations and/or to the experimental values.

The total energies calculated can be found in *Table 2*. It can be seen from the data that the introduction of the diffuse functions has the largest effect on the energy of the anion, lowering it by 0.0747 a.u. (46 kcal/mol) (*Table 3*). An additional geometry optimization lowers the energy only by 0.0039 a.u. (2 kcal/mol). The effect of geometry optimization is even smaller (in the case of methanol 0.0004 a.u.), and we may suppose it to be negligible in the case of cation. The published geometry of the cation (*Table 1*) was calculated with diffuse functions on the oxygen only.

Table 2

Total energies of Hartree-Fock equilibrium structures of CH_3O^-, CH_3OH and $CH_3OH_2^+$

	Compound		
Basis (RHF)	CH_3O^-	CH_3OH	$CH_3OH_2^+$
3-21G//3-21G	-113.7248	-114.3980	-114.7249
3-21+G//3-21G	-113.7995	-114.4256	-114.7367
3-21+G//3-21+G	-113.8034	-114.4260	

Total energies in Hartrees

Table 3

The influence of adding diffuse functions to the 3-21G basis set on the total energy in kcal/mol

	Compound		
Basis (RHF)	CH_3O^-	CH_3OH	$CH_3OH_2^+$
3-21G → 3-21+G	-46	-17	-7

The following considerations can be drawn from the results: if diffuse functions are introduced, the changes in geometry are large (mainly bond lengthening, resulting in worse values), and the energy changes are very small. The introduction of diffuse functions makes the energy hypersurface more flat around the energy minima, so the geometry changes have minor influence on the total energy of the molecule. If acidity is calculated without reoptimization of the geometry, the error is small (less than 2 kcal/mol) and it is certainly positive. The geometry reoptimization has no influence on the calculated basicity. Those facts suggest not to reoptimize the 3-21G geometry with diffuse functions. In this way a lot of computer time and work were saved in the case of silanol.

The optimized geometries of silanol and its ions can be found in *Table 4*. The use of *d*-functions on the silicon (3-21G(*) basis set) has a large effect on the equilibrium geometry calculated. In the case of the anion the Si-O bond shortens by 0.052 Å, while the Si-H bonds shorten by 0.010–0.012 Å. The H-Si-H bond angle does not change. Similar but smaller bond length shortenings appear in the silanol and the cation. The Si-O bond length in silanol is supposed to be between 1.63–1.64 Å, from similar compounds. For example the same bond length in the disiloxane is 1.633 Å[15]. The introduction of *d*-functions is improving the calculated geometry.

Table 4

Hartree-Fock equilibrium structures, silanol derivatives

Molecule	Point group	Parameter	3-21G	3-21G(*)
SiH_3O^-	C_3v	r(SiO)	1.602	1.550
		r(SiH)	1.538	1.527
		<(HSiO)	117.9	117.7
SiH_3OH	Cs	r(SiO)	1.674	1.633
		r(OH)	0.960	0.959
		r(SiHt)	1.479	1.467
		r(SiHg)	1.488	1.478
		<(HOSi)	126.7	128.8
		<(OSiHg)	112.1	112.1
		<(OSiHt)	106.9	107.5
		<((HgSiHt)	109.2	108.9
$SiH_3OH_2^+$	Cs	r(SiO)	1.839	1.814
		r(OH)	0.976	0.974
		r(SiH)	1.463	1.455
			1.463	1.452
			1.463	1.452
		<(HOSi)	123.9	123.5
		<(HOH)	112.3	112.9
		<(HSiH)	115.9	115.5
			115.9	115.5
			116.1	116.8

In the case of neutral alcohols there is a very large difference between the Si-O-H and the C-O-H bond angles, the former being larger by 18°.

It is very interesting to compare how the geometry is changed after protonation of methanol and silanol. Both cations are quasi-planar around the oxygen atom, but in protonated silanol the H-O-H angle is closer to the same bond angle in water. Another characteristic change is the C-O and Si-O bond lengthening. From *Table 1* the C-O bond is longer by 0.096 or 0.101 Å, calculated on the 3-21G and 3-21+G basis set, respectively. The corresponding Si-O bond lengthening is 0.165 Å(3-21G) and 0.181 Å(3-21G(*)) (*Table 4*). The latter is probably closer to reality. The effect is larger by more than 80% in the case of protonated silanol, and the Si-O bond weakened considerably. Because of this weak Si-O bond, the cation can lose water more readily. The H-O-H part in protonated silanol is closer to the free water and the SiH_3 part is more pyramidal, leaving more room for nucleophilic attack.

Table 5 contains the calculated total energies for the silicon derivatives. The diffuse and *d*-functions are added to the 3-21G basis set first, without geometry reoptimization. It can be seen from the data of *Table 6*, that the inclusion of *d*-orbitals has larger effect than the use of diffuse orbitals. But in the latter case, the energy decrease is much larger for the anion, while in the former case the energy decrease is very large for all compounds. It is very interesting that the energy decrease caused by the *d* and the diffuse functions are additive within a few kcal/mol.

Table 5
Total energies of Hartree-Fock equilibrium structures of SiH_3O^-, SiH_3OH and $SiH_3OH_2^+$

	Compound		
Basis (RHF)	SiH_3O^-	SiH_3OH	$SiH_3OH_2^+$
3-21G//3-21G	-363.5573	-364.1806	-364.5084
3-21+G//3-21G	-363.6132	-364.2091	-364.5247
3-21G(*)//3-21G	-363.6804	-364.2920	-364.6055
3-21G(*)//3-21G(*)	-363.6833	-364.2932	-364.6058
3-21+G(*)//3-21G	-363.7380	-364.3187	-364.6195
3-21+G(*)//3-21G(*)	-363.7384	-364.3186	-364.6195

Total energies in Hartrees

Table 6
The influence of adding polarization and diffuse functions to the 3-21G basis set on the total energy in kcal/mol

	Compound		
Basis (RHF)	SiH_3O^-	SiH_3OH	$SiH_3OH_2^+$
3-21G → 3-21+G	-35	-18	-11
3-21G → 3-21G(*)	-77	-70	-61
3-21G → 3-21+G(*)	-114	-87	-70

Reoptimizing the 3-21G geometry with *d*-functions has a small effect on the total energy of the anion: -0.0029 a.u. (-2 kcal/mol). The effect is less than half in the case of silanol, and it is practically zero in the case of the protonated anion (*Table 5*). If diffuse functions are used with *d*-functions, there is no practical difference between the total energies of 3-21G and 3-21G(*) geometry.

Acidities and Basicities

The calculated acidity difference between methanol and silanol is 31 kcal/mol on the 3-21G basis set (*Table 7*). Acidities calculated without the use of diffuse functions are certainly in error and the values are too high. This is because the 3-21G basis set is not flexible enough to give a correct description of the anion. If diffuse functions are included, the difference between the acidities is only 19 kcal/mol. This behaviour can be easily explained by comparison of the data in *Table 3* and *Table 6*. The energy decrease of the methanolate anion is larger by 11 kcal/mol than the energy decrease of the corresponding deprotonated silanol. The 3-21G basis set can describe the anion of silanol better, because of the larger number of orbitals on the silicon atom. If *d*-functions are added to the basis set, the difference is increased to 27 kcal/mol. Supposing that the valence shell energy description is the best in the latter case, the latter value can be accepted as the acidity difference between silanol and methanol. According to SIGGEL et al. the linear regression slope of the acidities calculated on the 3-21+G basis set is 1.22 [10]. With this correction, the difference being divided by 1.22, the calculated acidity difference is 22 kcal/mol. The expected experimental acidity of silanol is around 357 kcal/mol at 298 K. According to this value silanol is less acidic than phenol or HCN and its acidity is close to the corresponding value of thiols [2] in the gas phase.

The calculated basicity of methanol and silanol show no significant difference according to the 3-21G and 3-21+G calculations (*Table 7*). It is very interesting that the inclusion of diffuse functions in the basis set has a large effect (10 kcal/mol) and brings the calculated basicity of methanol closer to the experimental value. The agreement is surprisingly good. The diffuse functions were applied even in the case of cations, to calculate all the three energies on the same basis set. If *d*-functions are added to the 3-21+G basis set, the basicity of silanol is lowered below the basicity of methanol by 6 kcal/mol. The energy of silanol is decreased more than the energy of the cation. Accepting the latter value, it is probable that silanol is less basic than methanol, but the difference is only a few kcal/mol.

For better comparison of the experimental and calculated acidities and basicities, the experimental values were corrected with zero point energy difference (ΔZPE). The ΔZPE correction of methanol is taken to be 9 kcal/mol for acidity and 6 kcal/mol for basicity, in good agreement with

Table 7
Hartree-Fock and experimental deprotonation and protonation energies

	Deprotonation energy (acidity)		Protonation energy (basicity)	
Basis (RHF)	CH_3OH	SiH_3OH	CH_3OH	SiH_3OH
3-21G//3-21G	422	391	205	206
3-21+G//3-21G	393	374	195	198
3-21+G//3-21+G	391	–	–	–
3-21G(*)//3-21G		384		197
3-21G(*)//3-21G(*)		383		196
3-21+G(*)//3-21G		364		189
3-21+G(*)//3-21G(*)		364		189
Experiment	(379 ± 1) [2]	–	(185 ± 2) [1]	–
Corrected (ZPE, 0K)	387		191	

Energies in kcal/mol

the literature data [10, 13]. The experimental protonation and deprotonation energies are in parentheses and the corrected values are in the last row of *Table 7*.

Conclusion

The geometry optimization after adding *d*-functions and/or diffuse functions to the 3-21G basis set has no significant influence on the calculated acidity and basicity. The 3-21G geometry is applicable because of the very flat energy hypersurface around the equilibrium geometry. For relative acidity and basicity comparisons the error is probably even smaller.

The geometry calculated by the 3-21G(*) basis set is better in the case of silanol, in agreement with the previous experience in the literature [3]. A very important bond lengthening is found in the protonated silanol. The Si-O bond becomes weak and this may partly account for the high reactivity of silanol.

Silanol is more acidic than methanol, the difference being 27 kcal/mol calculated on the RHF/3-21+G(*) basis set. The corrected value is 22 kcal/mol, the correction factor proposed by SIGGEL et al. [10] being used. This again supports a higher reactivity. The silanol basicity is less by 6 kcal/mol than the basicity of methanol, if calculated at the 3-21G(*) level. There is no practical difference between the basicities if they are calculated at the 3-21G or 3-21+G level.

The basicity of methanol calculated at the 3-21+G level shows a better agreement with the experimental value than the basicity calculated at the 3-21G level.

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