

# Quantum Chemical Estimation of the Acidities of Silanols

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**Abstract.** The acidities of silanol groups have long been of interest in chromatography, and more recently the catalytic activity of these groups has become recognized. Silanols are more acidic than their corresponding alkanols. This difference is examined in terms of the electronic structures of the compounds as determined using density functional theory at the B3LYP/6-31+G\* level. Alterations in the structures of these compounds in aqueous solution compared to vacuum are also examined using the SM8/water solvent model of Marenich et al.

**Keywords:** Acidity,  $pK_a$ , Silanol, Alkanols, Quantum Chemistry, Descriptors

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## Introduction

The acidities of silanol groups have been of interest for some time from a number of perspectives. In particular the acidities of the silanol groups on silica surfaces have attracted interest because of their importance in chromatography,<sup>1</sup> although there has been disagreement over the quantitative values (pK<sub>a</sub>s) to be attributed to these groups.<sup>2</sup> In early work Hair and Hertl<sup>3</sup> found the pK<sub>a</sub> of the silanol group to be about 7.1. Later, Ong et al.<sup>4</sup> applied surface second harmonic generation techniques and discerned two sets of surface silanol groups, with pK<sub>a</sub>s near 4.5 and 8.5. More recent studies by Mendez et al.<sup>5</sup> identified two types of sites on the silica surface, the first with pK<sub>a</sub>s in the range 3.5-4.6 and the second with pK<sub>a</sub>s from 6.2-6.8. Additional interest in the properties of silanol groups comes from the recent identification by Schafer et al.<sup>6</sup> of a new class of silanediol catalysts characterized by their strong hydrogen bonding strengths.

In general silanols are more acidic than their hydrocarbon counterparts, and it is to be expected that this difference should be reflected in the electronic structures of the compounds. Silicon is less electron-attracting (Pauling electronegativity  $\chi = 1.90$ ) than the other elements involved: carbon ( $\chi = 2.55$ ), oxygen ( $\chi = 3.44$ ), and hydrogen ( $\chi = 2.20$ ). Moreover, silicon has a larger charge capacity—the ability to absorb or donate charge--than these other elements,

## Computational Methods

Calculations were performed at the B3LYP/6-31+G\* level using the Spartan'10 program suite (Wavefunction, Inc., Irvine, Cal., U.S.A.). This level was chosen so that the SM8 aqueous solvent model<sup>7</sup> could be implemented within Spartan'10 program.

Partial atomic charges were natural charges, as described by Reed et al.<sup>8</sup> These charges have been found to be relatively insensitive to the basis set used<sup>9</sup> and have displayed good correlations with pK<sub>a</sub>s in earlier studies.<sup>9 10</sup>

## Results and Discussion

*Charge distributions and structures.* Figure 1 compares the natural charge distributions of methanol and silanol. In this figure the effects of the different electronegativities and charge capacities of the carbon and silicon atoms are readily apparent. The charges on the silanol hydroxyl group are much more extreme than those on the methanol hydroxyl group. In methanol the methyl hydrogens bear much of the positive charge and the carbon atom is negative, whereas in silanol the silicon atom, with its low electronegativity and large charge capacity, is strongly positive (depleted of electronic charge) and the silyl hydrogens are actually negative.

Figure 2 compares the natural charges and structures of the methanol and silanol anions in vacuum and in the SM8/water solvent model. The most obvious features are (a) the elongation of the C-O and Si-O bonds in the aqueous solvent and (b) the increased charge on the oxygen atom in the solvent.

## Conclusions

## Figures

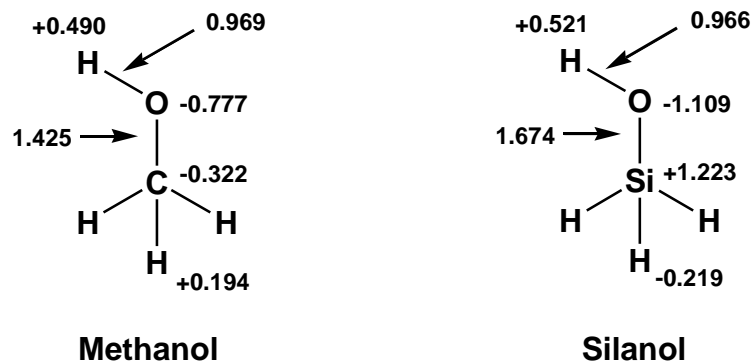


Figure 1. B3LYP/6-31+G\* natural charges and bond lengths of methanol and silanol.

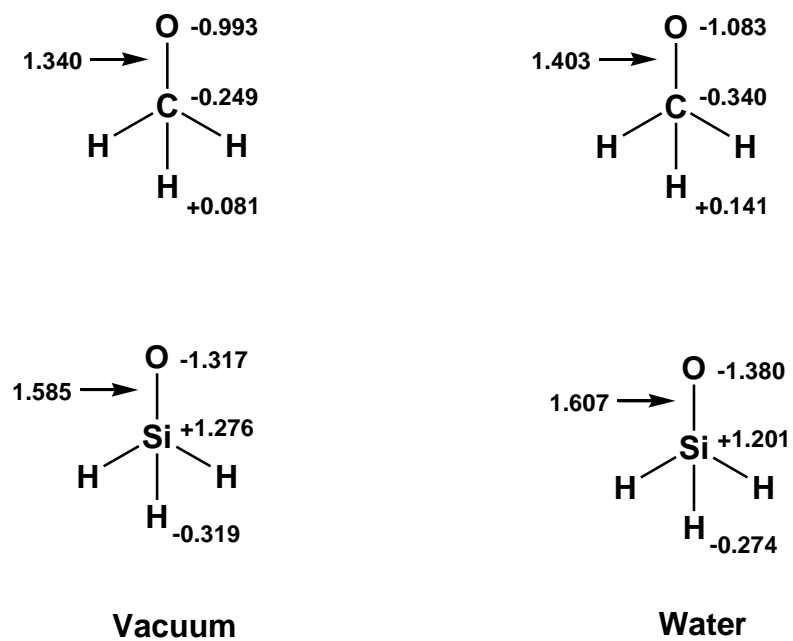


Figure 2. Calculated natural charges and bond lengths of the methanol and silanol anions in vacuum and in the SM8/water solvent model.

## References

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- <sup>1</sup> J. Nawrocki, *J. Chromatog. A* **779** (1997) 29-71.
- <sup>2</sup> J. Nawrocki, *Chromatographia* **31** (1991) 177-191.
- <sup>3</sup> M. L. Hair and W. Hertl, *J. Phys. Chem.* **74** (1970) 91-94.
- <sup>4</sup> S. W. Ong *Chem. Phys. Lett.* **191** (1992) 327-335.
- <sup>5</sup> A. Méndez, E. Bosch, M. Rosés. U. D. Neue, *J. Chromat. A* **986** (2003) 33-44.
- <sup>6</sup> A. G. Schafer, J. M. Wieting, and A. E. Mattson, *Org. Lett.* **13** (2011) 5228-5231.
- <sup>7</sup> A. V. Marenich, R. M. Olson, C. P. Kelly, C. J. Cramer, and D. G. Truhlar, *J. Chem. Theory Comput.* **3** (2007) 2011-2033.
- <sup>8</sup> A. E. Reed, R. B. Weinstock, and F. J. Weinhold, *J. Chem. Phys.* **83** (1985) 735-746.
- <sup>9</sup> K. C. Gross and P. G. Seybold, *Int. J. Quantum Chem.* **80** (2000) 1107-1115.
- <sup>10</sup> K. C. Gross, P. G. Seybold, and C. M. Hadad, *Int. J. Quantum Chem.* **90** (2002) 445-458.