International Journal of Chemical Studies

Dr. Ashok Kumar Acharya
Assistant Professor
PG Department of Chemistry
Ranchi College, Ranchi,
Jharkhand, India

Comparison of theoretical and experimental value of pK$_a$ of mixed hetero oxomolybdates by quantum chemical calculation

Dr. Ashok Kumar Acharya

Abstract

Some synthesized trihetero-oxomolybdates were studied by the DFT studies. Pk$_a$ of these oxomolybdates shown with Continuum model of solvent polarisation is shown. The method is useful for predicting Pk$_a$ of selective molecules where the ionization of proton is basically controlled by the lone pair electron of atomic site. However it fails to predict pK$_a$ of very strong and weak acids. The result is very closely agreed to theoretical and experimental value.

Keywords: Experimental value, hetero oxomolybdates, quantum chemical

1. Introduction

Quantum chemical calculation is a tool by the researchers to investigate molecular structure, Properties, kinetics and reactivity. Now a day's advanced computer programs are used for performing quantum chemical calculation. The solute-solvent and solvent-solvent interactions are important aspects to understand the reactivity of the molecules during a phase of reactions. Hammett constant has been successfully used in analysing many kind of chemical reaction in different solvent medium. Recent literature review ensures more desirable approaches and the quantum chemical methods are used to determine pK$_a$ and other related physiochemical properties of molecules [1, 2]. The hybrid quantum mechanical/molecular modelling method with semi empirical level of theory is found to be useful for predicting ground and excited states pK$_a$ values [3]. The MP2 calculation with cluster continuum model some time produces good results. 6-31G representation minimization has been carried out at the MP2 level rather than at the Hartree-Fock level. In the calculation of absolute acidity electrons may only loosely associated with specific atoms. The definite feature of dissociation of proton from a particular acidic site explicitly taken in pK$_a$ calculation. More over the solvent dielectric field also contributes to the dissociation of the acidic site.

2. Methodology: The dissociation ability of H$^+$ from active site of molecule is determining pK$_a$ value. The dissociation of proton from active site was selectively taken in the pK$_a$ calculation. In the present study HF/6-31G** and B3LYP/6-31** rotates are used for complete geometry optimization of both, the acids and the conjugate bases is the dissociation energy.

Table 1: Type of calculation/basis set// Type of calculation/ basis set

6-31G*/AMI	Hartree-Fock 6-31G* calculation of energy preceded by AMI calculation of geometry
B3LYP/6-31G*//3-21G	B3LYP 6-31G* density functional preceded by Hartree-Fock 3-21G calculation of geometry
LMP2/6-311+G**//BP/6-31G*	Localized MP2 calculation of energy with 6-311+G** basis set preceded by BP 6-31G* density functional calculation of geometry

The dissociation energy $\Delta E_1 = (E_{AH}-E_A) +\Delta ZPE+\Delta S$, E_{AH} and E_a are the energies of an acid and conjugate base, and ΔS the difference of solvation energies for these molecules. The volume of acid and conjugate bases was estimated before computing solvation energies. The dielectric constant value of 78 was taken for solvent effect. pK$_a$=-logK$_a$=ΔE_1/2.303RT

We have taken 10-molybdo, Vanado Zinco Cobalate (III), 11-Molybdonickelo cuprate (II) which were being synthesized earlier in our laboratory for comparing their acidic strength.

Correspondence
Dr. Ashok Kumar Acharya
Asst. Professor PG Department
of Chemistry Ranchi College,
Ranchi, Jharkhand, India

The pHs were measured with a pH meter which is combined with a glass and calomel-saturated electrodes. Ater calibration in pH 4 and 7 pH was measured for stock solutions at different temperatures. The pH values obtained allow calculation of pKa value of acids. The dielectric constant of a solvent is the measure of a solvent efficiency to separate oppositely charges ions. $F = 8.988 \times 10^9 q^2/cr^2$, Larger the value of Dielectric constant smaller the attraction forces between the ions larger acidity constant lower be its pK_a value. $pK_a = AD_1 + BD_2 + CD_3 + E$, $D_i = 1, 2, 3, \ldots$, A, B, C, E are linear regression co-efficients.

3. Result and Discussion: To determine pK_a in a solute solvent interaction the dissociation energy of H^+ from hetero poly acid has to be determined. We have selected small molecules whose pK_a value is known. The proton dissociation energies of these molecules extensively studied in table-2.

Table 2: Mullikan net charge on proton active sites of acid and conjugate base and dissociation energies of proton.

Molecules	H^+	O^-	O^-	ΔE(a.u)
CH_3COOH	0.36	-0.59	-0.76	0.592
$C_2H_5CH(OH)(COOH)$	0.37	-0.62	-0.78	0.566
H_2CO_3	0.38	-0.61	-0.78	0.566
C_6H_5OH	0.35	-0.66	-0.81	0.596
H_2SO_4	0.41	-0.66	-0.81	0.519
$(COOH)_2$	0.37	-0.57	-0.73	0.588
$H_4[Mo_{11}VZnCo]$	0.30	-0.68	-0.94	0.834

The computed pK_a values of molecules are given in table-2. The variation in solvation energies of conjugate acids and bases are shown in table-3. The difference between the solvation energies after dissociation proton to form anion may be analysed from these results. The zero point energies of AH and A^- and their difference are shown. In has been observed the additional solvent field that contributes to the dissociation of acid is obtained from the solvation energies computed in aqueous medium at dielectric constant 78. Calculations of the discrepancy of theoretical pK_a value from the experimental values due to the variation of the approaches used in detailed description. SCRF (Self Consistent Reaction Field) dipole method is used for computing pK_a of these molecules. The theoretical values obtained for selected acidic sites in fact in fair agreement with experimental results.

Table 3: the computed pK_a of molecule with HF/6-31G** and B3LYP/6-31G** and B3LYP/6-31G** along with experimental pK_a.

Acid	Conjugate base	Theoretical pK_a	Expt. pk_a
CH_3COOH	CH_3COO^-	4.67	4.76
$C_2H_5CH(OH)(COOH)$	$C_2H_5CH(OH)COO^-$	4.47	3.86
$(COOH)_2$	$HOOCCO_2^-$	4.39	1.25
$H_4[Mo_{11}VZnCo]$	$H_3[Mo_{11}VZnCo]^-$	4.66	5.12

The theoretical pK_a values obtained for selected acidic sites shown in table 2 are in fact fair agreement with experimental results. The deviation is very small. The variability of pK_a values for some molecules obtained from both HF/6-31G** and DFT (6-31G**/B3LYP) methods was studied. As we can see pK_a values obtained for some molecules clearly depend on the ionisation of proton from the active site but the same approach cannot predict the experimentally observed pK_a of all types of molecules. It requires some additional modification in the computational methodology used to calculate the dissociation energy of comparatively strong

acids and bases. In case of strong acids, the dissociation controlled by electrostatic interactions, in which solute-solvent and solvent polarity may predominately contribute to the dissociation of proton from active site. The study reflects this methodology can predict pK_a of small molecule rather than bigger molecule in a slight variation from the theoretical and experimental value. These theoretical data correlated with the experimentally pH metry data.

4. References
1. Toth AM, Liptak MD, Shields GC. Jam chem. Soc. 2001; 123:2314
2. Jang YH, Sowers LC, Cagin T, Goddard WA. Jphys chem. 2001; 105:274.
3. Pliego JR, Riveros JM. J Phys Chem A. 2001; 105:7241.
4. Atkinns PW, Physical chemistry, 5th edn, (oxford University press, UK). 1994.
5. Jang YH Sowers LC, Cagin T, Goddard WA. J Phys chem. 2001; 105:274.
6. Pliego JR Jr, Riveros JM. Chem. Eur J. 2002; 8:1945.