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Is Water Electron Withdrawing or Electron Donating: Acid-Base Properties of Different Water Related Species Treated by Taft Equation

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Abstract Water (HOH), hydroxyl radical ($HO^{\bullet}$), hydroxide ion (HO^{-}), hydrogen peroxide (HHO_2), hydroperoxyl radical ($HO_2^{\bullet}$), hydroperoxide anion (HO_2^{-}) and hydronium ion (HH_2O^{+}) are all water related species and are environmentally important. The corresponding acid -base couples are represented as HOH/OH^{-}, $HO^{\bullet}/O^{\bullet-}$, HO^{-}/O^{2-}, HHO_2/HO_2^{-}, $HO_2^{\bullet}/O_2^{\bullet-}$, HO_2^{-}/O_2^{2-} and H_3O^{+}/H_2O. Therefore, the corresponding conjugate bases are hydroxide ion OH^{-}, mono oxygen radical anion $O^{\bullet-}$, oxide dianion O^{2-}, hydroperoxide anion HO_2^{-}, peroxyl radical anion $O_2^{\bullet-}$, peroxide dianion O_2^{2-} and H_2O respectively. The acid-base properties are well characterized by treating the p*K*a data with Taft σ* values of the corresponding conjugate bases of these couples using Taft **linear free-energy relationship** (LFER). Positive Taft ρ* value of 17.7 indicates that electron withdrawing species facilitate the deprotonation and vice-versa. **The present study is a good class-room exercise for both undergraduate and graduate advanced physical-organic chemistry level.**

Keywords: *Species of water, Taft equation*

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1. Introduction

Water is an inorganic molecule with the molecular formula H_2O. It is a translucent, tasteless, odorless, and colorless substance. It is the main component of Earth's streams, lakes, and oceans and the fluids of all known living organisms, in which it acts as a universal solvent. Water, being a polar molecule with a dipole moment of 1.8546 D, undergoes strong intermolecular hydrogen bonding. Therefore, it contributes largely to its physical and chemical properties. It is an essential beverage for all known forms of life. Due to its presence in all organisms, its chemical stability, its worldwide abundance, and its strong polarity relative to its small molecular size, water is often referred to as the "universal solvent" [1,2]. In the present work the pK_a data of different acid-base couples of the species of water is collected and shown to obey Taft LFER.

2. Methods

KaleidaGraph is used to draw the straight-line graphs. Taft σ* values and pK_a values are from different sources or if not available are estimated. The pK_a of Hydroxide ion was also determined by DFT method. It came out to be 63.44. The Quantum mechanical calculations were performed using Gaussian 09 [3] program. The G4 method [4] was utilized to determine the Gibbs free energy for the reaction:

$$OH^- \rightleftharpoons O^{2-} + H^+$$

The G4 is a high-accuracy composite *ab initio* quantum chemical method [5] developed by Pople's group. It makes use of geometries and thermochemical corrections calculated at B3LYP/6-31G (2df,p) level, a highest-level single point calculation at CCSD(T) **(Coupled Cluster with Single and Double excitations and perturbative Triple excitations)** instead of QCISD(T) **(Quadratic Configuration Interaction with Single and Double excitations and perturbative Triple excitations)** level, and addition of extra polarization functions in the largest-basis set MP2 calculations. It is an improvement of G3X. After finding the Gibbs free energy (using G4 method) of the reactants and products pK_a was determined using the formula

$$\Delta G = -2.303\ RT \log K_a$$

Or

$$pK_a = \frac{\Delta G}{2.303RT}$$

3. Discussion

In the following table 1 different acid-base couples of water species along with their pK_a values and Taft σ* values are presented.

Table 1. different acid-base couples of water species along with their pK_a values and Taft σ* values

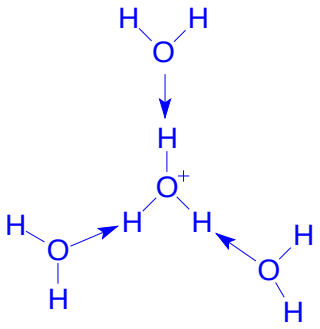
Sl. NO.	Acid species: Dissociable proton is shown in blue	R (substituent) or conjugate base	Taft σ* of R	pK_a
1	Water: HOH	HO^-	1.67[a]	15.7[b]
2	Hydroxyl radical: $HO^\bullet$	$O^{\bullet-}$	1.89[c]	11.9[d]
3	Hydroxide ion: HO^-	O^{2-}	–0.683[e]	57.7[f]
4	Hydrogen peroxide: HHO_2	HO_2^-	1.91[g]	11.75[h]
5	Hydroperoxyl radical: $HO_2^\bullet$	$O_2^{\bullet-}$	2.30[i]	4.88[j]
6	Hydroperoxide anion: HO_2^-	O_2^{2-}	0.962[k]	28.5[l]
7	Hydronium ion: $(HH_2O)^+$	H_2O	2.57	0.00[m]
8	Hydronium ion: $(HH_2O)^+$	H_2O	2.67	-1.74[n]
9	Hydroxide ion: HO^-	O^{2-}	–0.683[e]	63.44[o]

[a]from reference 6; [b]from reference 7; [c]calculated using pK_a of $HO^{\bullet(d)}$ and the Taft plot of pKa vs Taft σ* of our paper from Resonance (ref. 8); **[d]from reference 9**; [e]calculated from the ratios of Taft σ* values of COO^- and COOH, and O^- and OH: $\frac{\sigma^*\text{of } COO^-}{^*\text{of COOH}} = \frac{^*\text{of } O^-}{^*\text{of OH}}$ in this equation except σ* of O^- all other three values are from reference 10; [f]obtained from the Taft plot and using Taft σ* of –0.683; [g]obtained from the Taft plot (Ref. 8) and using pK_a of H_2O_2 of 11.75[h], **[h]for pK_a of H_2O_2 see ref. 11**;[i]evaluated from the pK_a and Taft plot of reference 8; **[j]from ref. 12**; [k]calculated using the approximate value of pK_a of 28.5[l]; **[l]from ref. 20**; [m]from reference 24, [n]from reference 25; [o]from DFT method

Various water related species are explained as follows:

The abondance of water is already explained in the introduction. Hydroxyl radical can be denoted as $^\bullet OH$ or $HO^\bullet$ is short lived species with a half-life of less than a second [13]. As a short-lived species, it plays an important role in radical chemistry [14]. The self-dissociation of a water molecule in liquid water is the fundamental event in acid-base chemistry, determining the pH of water. The hydroxide ion is naturally produced from water by the self-ionization reaction $2H_2O \rightleftharpoons H_3O^+ + OH^-$ [15]. The concentrations of H_3O^+ and OH^- are each close 10^{-7} mole/L. So, the pH at equilibrium will be 7.00. Hydrogen peroxide is a chemical compound with the molecular formula H_2O_2. It is a non-planar molecule with book-like structure shown by IR spectroscopy [16]. Hydrogen peroxide is about 1000 times stronger acid than water [17]. The hydroperoxyl radical is the protonated form of superoxide with the molecular formula $HO_2^\bullet$. This species plays an important role in the atmosphere and as a reactive oxygen species in cell biology [18]. It is an angular molecule [19]. It can exist in equilibrium with its conjugate base peroxide radical anion $O_2^{\bullet-}$ with a pK_a of 4.88 [12]. Hydroperoxide anion is a negatively charged molecular species with molecular formula HO_2^-. Its estimated pK_a is 28.5 [20].

And lastly about hydronium ion $(HH_2O)^+$. There is lot of discussion about the structure of hydrated proton. Three main structures for the aqueous proton have experimental support: the first one is Eigen cation, is a tetrahydrate, $H_3O^+(H_2O)_3$, the second one Zundel cation, is a dihydrate, $H^+(H_2O)_2$, and the third one Stoyanov cation, an expanded Zundel cation, is hexahydrate, $H^+(H_2O)_2(H_2O)_4$ [21,22]. In fact, one of the authors (VJ) have shown that the proton is a tetrahydrate $(H_9O_4)^+$ from the entropy change of hydration of a proton [23]. The structure of the tetrahydrate could be as shown below:



At 25°C, the pK_a of H_3O^+ is approximately 0.0 [24]. The values commonly given for pK_a of H_3O^+ in water solution are 0 or −1.74. The former is based on the activity of the solvent in a dilute solution (in this case, water) is 1, while the latter uses the value of the concentration of water in the pure liquid of 55.5 M. Silverstein has shown that -1.74 is thermodynamically unsupportable [25]. The disagreement comes from the ambiguity that to define pK_a of H_3O^+ in water, H_2O has to act simultaneously as a solute and the solvent. The IUPAC has not given an official definition of pK_a that would resolve this ambiguity. On the other hand, Silverstein has shown that Ballinger and Long's experimental results [26] support a pK_a of 0.0 for the aqueous proton [27]. Neils and Schaertel provide added arguments for a pK_a of 0.0 [28]. Figure 1 is the Taft plot.

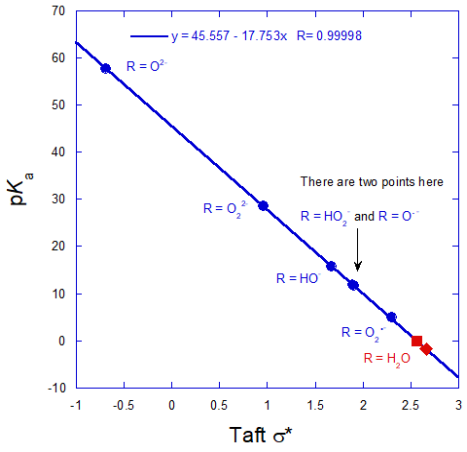


Figure 1. Plot of pK_a versus Taft σ* of different species of water

Water can act as either an electron-donating group (EDG) or an electron-withdrawing group (EWG), depending on how it is attached and the chemical context [7]. As a Hydroxy Group (–OH) it has both the effects. When water is attached to a molecule as a hydroxy group

(–OH), such as in alcohols or phenols, it exerts two opposing electronic effects. Oxygen is highly electronegative, so it pulls electron density through sigma bonds. If the oxygen lone pair can overlap with a π system (e.g., in Phenol), it donates electron density by resonance. So, which effect dominates? In aliphatic alcohols (e.g., methanol): the inductive electron-withdrawing effect dominates. In aromatic systems (e.g., phenol): the resonance electron-donating effect dominates, making the –OH group an activating substituent. Water itself is best described as a Lewis electron donor because oxygen donates a lone pair. However, when present as an –OH substituent, it can be electron withdrawing by induction and electron donating by resonance. The dominant effect depends on the molecular environment. As a conclusion, the classification of the hydroxyl group (–OH), and by extension water-derived substituents, as both inductively withdrawing and resonance donating is well established in organic chemistry [7].

Using the value of pK_a = 63.44 for the equilibrium $OH^- \rightleftharpoons O^{-2} + H^+$ obtained by DFT method did not change the trends in the Taft plot (Figure 2) indicating that our calculation by DFT is correct.

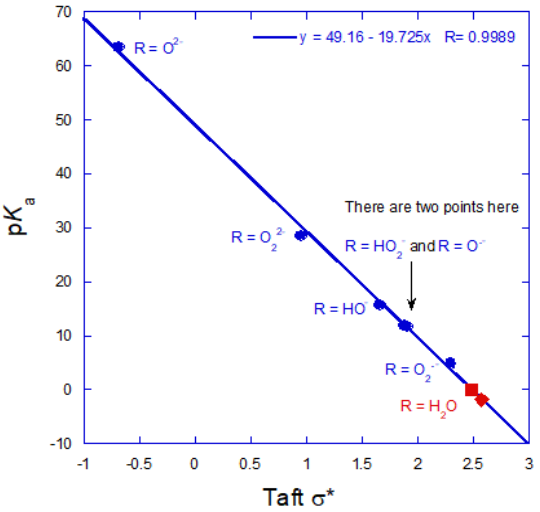


Figure 2. Plot of pK_a versus Taft σ^* of different specis of water using DFT derived pK_a for OH^-

Red square is by taking pK_a of water as 0.00 and red diamond with -1.74. In either case the Taft σ* of water did not change much. The two values change by a difference of 0.10. The positive Taft σ* value of water indicates that water is an electron withdrawing in nature. But it is known that in the formation of hydronium ion it is electron donating.

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Conflict of Interest

We don't have any conflict of interest.

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