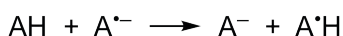


Acidities of Carboxylic Acids

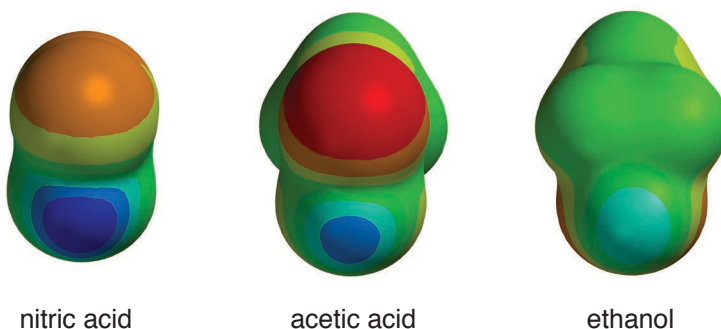
Acid strength is among the most important molecular properties. It is readily available from calculation, either in terms of absolute deprotonation energy,



or, more commonly, as the deprotonation energy relative to that of some standard acid (A'H).









The energy calculations discussed so far apply strictly to gas-phase acidities* and may or may not reflect acidities in solution. This prompts a search for alternative descriptions. One possibility is the value of the electrostatic potential in the vicinity of the acidic hydrogen in the neutral acid. Electrostatic potential maps certainly reveal gross trends in acidity, for example, the acidic hydrogen in a strong acid, such as nitric acid, is more positive than that in a weak acid, such as acetic acid, which in turn is more positive than that in a very weak acid, such as ethanol.




In this tutorial, you will use electrostatic potential maps to quantify changes in acid strength due to subtle variations in structure. You will use the Spartan Spectra and Properties Database (SSPD) to eliminate the need for quantum calculations.

* This is not to say that quantum chemical treatments of solvated molecules have not been developed or have not been implemented within *Spartan*, but rather that in our opinion are not reliable enough to provide quantitative data.






1. One after another, build or sketch trichloroacetic, dichloroacetic, chloroacetic, formic, benzoic, acetic and pivalic acids. Put all molecules into the same document. Use **New Build** () or **New Sketch** () both from the **File** menu for the first molecule and use **Build New Molecule** () or **Sketch New Molecule** () both from the **File** menu for each successive molecule. *Click* on  when you are done.
2. All of the molecules that you have built are available in SSPD. *Click* on the name of whichever molecule is selected at the bottom of the screen, make sure that ω B97X-D/6-31G* is selected from the menu in the dialog that results, *click* on **Replace**, and finally on **All**. Structures obtained from ω B97X-D/6-31G* density functional calculations will replace those you have built. The wave function is also provided with the database entry.
3. Select **Spreadsheet** from the **Display** menu (). Expand it so that you can see all seven molecules, and that two data columns are available. *Double click* inside the header cell of the first available data column, *type* **pK_a** and *press* the **Enter** key (**return** key on Mac). Enter the experimental pK_a's (given in the table below) into the appropriate cells under this column. You need to *press* the **Enter** (**return**) key following each entry.

acid	pK _a	acid	pK _a
trichloroacetic (Cl ₃ CCO ₂ H)	0.7	benzoic (C ₆ H ₅ CO ₂ H)	4.19
dichloroacetic (Cl ₂ CHCO ₂ H)	1.48	acetic (CH ₃ CO ₂ H)	4.75
chloroacetic (ClCH ₂ CO ₂ H)	2.85	pivalic ((CH ₃) ₃ CCO ₂ H)	5.03
formic (HCO ₂ H)	3.75		

Experimental data from: E.P. Sargeant and B. Dempsey, *Ionization Constants of Organic Acids in Aqueous Solution*, IUPAC no. 23, Pergamon Press, 1979.

4. To display all molecules at once, *check* the box to the left of the molecule name (**Label** column) in the spreadsheet for each entry. To manipulate the molecules independently of one another, *click* to deselect **Coupled** from the **Model** menu (). Arrange the seven molecules on screen such that you can clearly see the

acidic hydrogen on each.

5. Select **Surfaces** from the **Display** menu () and then *click* on **Add** and select **electrostatic potential map**. When the electrostatic potential map calculations complete (they will be marked “completed”), *check* the box at the left of **electrostatic potential map** in the **Surfaces** dialog. Select **Properties** from the **Display** menu () and *click* on the electrostatic potential map to display the **Surface Properties** dialog. *Click* on  (the **Post** icon) to the right of **Max** inside the **Surface Properties** dialog. The maximum value of the electrostatic potential (corresponding to the acidic proton) will be posted to the spreadsheet. Leave the dialog on screen.
6. Plot experimental pK_a vs. maximum in the electrostatic potential. Select **Plots** from the **Display** menu () and then select **pKa** under the **X Axis** menu and **Property Max (Surface)** from the **Y Axes** list. *Click* on **Create**. *Click* on  to edit the plot and *check* the box next to **Curve**. Choose the **Least Squares** option and *click* on **Done**. Does there appear to be a correlation between pK_a and the maximum value of the electrostatic potential?
7. Close the document and any open dialogs.