

Perfluoroarylated Cyclopentadiene Tautomer Thermochemistry – Theory and Experiment

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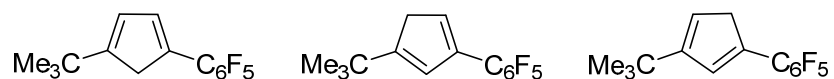
Background. Several years ago, one of my graduate students, Matt Thornberry, initiated a project in which the acidities of various perfluoroaryl-substituted cyclopentadienes were measured. The procedure is simple. A mixture of a cyclopentadiene of unknown (but roughly estimable) acidity, a well-characterized standard (HA), and less than one equiv of a strong base (fluorenyllithium) are dissolved in THF. An equilibrium (eq 1) is established and the acidity of the unknown acid, $K_a(\text{HB})$ is simply the ratio of the observed K_{eq} and the acidity constant of the standard acid, $K_a(\text{HA})$ (eq 2). All four species in eq 1 are fluorinated, so their *relative* concentrations can be established by ^{19}F NMR spectrometry. What makes this work so beautifully is that with cyclopentadienes as the two acids (HA and HB), the reaction is in slow exchange on the NMR timescale, and all four of the relative concentrations can be established simultaneously. This eliminates the need to determine the concentrations of any species by mass balance.



$$K_{\text{eq}} = K_a(\text{HA}) / K_a(\text{HB}) \quad (2)$$

Matt was interested in strong carbon acids, so his primary focus was comparing HA to HB, then HB to HC, and so on, working his way through a library of available compounds that we had made until he had identified some with very low $\text{p}K_a$ values (near 0). The measurement cannot bridge gaps in $\text{p}K_a$ of more than about 2 units because of experimental errors associated with the dynamic range of the NMR experiment.

Tautomers. With cyclopentadienes, the two acids can actually be isomeric (tautomers). A good example is shown below. Again, these compound interconvert slowly on the NMR time scale, but rapidly enough that they cannot be separated by liquid chromatography. In crystal structures they often appear as random solid solutions.



Using published methods based on UV-Vis spectrometry, one can only obtain an “average” acidity of these compounds because the conjugate base, which is in common to all three acids, is the quantified species (arylcyclopentadienyl anions are yellow). But with the NMR method, all of the species are easily quantified. Of course, the relative K_a values of two tautomers is directly related to their relative ground-state free energies.

Project. Therefore I propose to synthesize several fluoroarylated cyclopentadiene compounds that are known (or predicted) to exhibit tautomerization, measure their relative acidities (and therefore their relative free energies) by NMR spectrometry, and calculate their relative free energies using electronic structure calculations. The synthesis will require the purchase of fluoroaromatic compounds (hexafluorobenzene, perfluoropyridine, and perfluorotoluene). Other expenses include THF as a reaction solvent, and hexane and silica gel for chromatographic purification. The project is perfect for a first-year undergraduate who wants to learn basic synthetic methods, computational chemistry, and NMR.