

## Supplementary Material

### Uranyl monocarboxylates of aromatic acids:

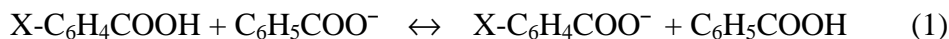
#### A density functional model study of uranyl humate complexation

Rupashree Shyama Ray, Sven Krüger, and Notker Rösch

##### Acidity of aromatic carboxylic acids:

We studied the substitution effects on the acidity of benzoic acid as a check of the accuracy of our computational approach and to support the interpretation of corresponding effects in uranyl monocarboxylate complexes. Guided by available experimental results, we examined the substitution effects for methyl, hydroxyl, and fluoro benzoic acid in ortho, meta, and para positions. We considered only the low-energy conformers for each acid.<sup>1</sup> We optimized structures without symmetry constraints at the LDA level, and we calculated energies in single-point fashion with the BP functional. Thermodynamic parameters were calculated both for systems in the gas phase and in aqueous solution, and compared with experimental values. Experimental  $\Delta G$  values of deprotonation in solution were calculated from  $pK_a$  values.<sup>2</sup>

We chose the isodesmic reaction



to describe the differences of acidity of substituted acids  $XC_6H_4COOH$ ,  $X = CH_3, OH, F$ , with benzoic acid as a reference (Table 1).

**Table 1.** Gibbs free energies  $\Delta G$  of the proton exchange reaction between substituted benzoic acids  $XC_6H_4COOH$  and the benzoate anion, Eq (1), in  $\text{kJ mol}^{-1}$ , for the reaction in the gas phase and in aqueous solution (PCM). The differences  $\Delta$  between experimental and calculated value are also given.

X	Gas phase			Solution			
	$\Delta G_{\text{exp}}^a$	$\Delta G_{\text{calc}}$	$\Delta$	$pK_a^b$	$\Delta G_{\text{exp}}^c$	$\Delta G_{\text{calc}}$	$\Delta$
o-F	-10	-7	3	3.27	-5	-3	2
m-F	-16	-18	2	3.87	-2	-8	-6
p-F	-12	-13	-1	4.14	0	-3	-3
o-OH	-56	-68 <sup>d</sup>	—	2.98	-7	-34 <sup>d</sup>	—
m-OH	-6	-7	-1	4.08	-1	-2	-2
p-OH	-17	-18 <sup>e</sup>	-1	4.58	2	6	3
o-CH <sub>3</sub>	-3	-3	0	3.91	-2	2	4
m-CH <sub>3</sub>	3	-2	5	4.24	0	-4	-4
p-CH <sub>3</sub>	5	1	4	4.34	1	-1	-2

<sup>a</sup> Ref. 2. <sup>b</sup> Ref. 7. <sup>c</sup> Calculated from  $pK_a$ ; The  $pK_a$  value of benzoic acid is 4.18. <sup>d</sup> Calculated value provided for the most stable isomer (phenolate). <sup>e</sup> In line with experiment, averaged over the most stable isomers of carboxylate and phenolate anions (see text).

In the gas phase, fluoro benzoic acids show a little stronger acidity compared to benzoic acid owing to the electron withdrawing nature of the F substituent. The rather high acidity of o-hydroxy benzoic acid is caused by a strong intramolecular hydrogen bond between hydroxyl and carboxyl groups in the anion. Meta and para isomers lack this effect, but one notes an increased acidity of p-hydroxy benzoic acid due to resonance stabilization of the corresponding anion.<sup>3,4</sup> For p-hydroxy benzoate, carboxylate and phenolate anions coexist in about equal amounts.<sup>5</sup> Thus, also in our calculations, we averaged the results for deprotonated carboxyl and hydroxyl groups and obtain reasonable agreement with experiment. For o-hydroxy benzoate the situation is more complicated due to the existence of an intramolecular hydrogen bond. Nevertheless, we found similar results for the phenolate and the carboxylate isomers of o-hydroxy benzoate, with a negligible preference for the former, 0.2 kJ mol<sup>-1</sup>, as also noted in another computational study.<sup>6</sup> As the distribution of isomers is not clear in experiment, we subsequently excluded that case from our comparison. The experimentally observed variation<sup>7</sup> of acidity among the various derivatives of benzoic acids are well reproduced in our calculations; the corresponding average absolute deviation of the Gibbs free energy of proton exchange for the systems shown in Table 1 is 2 kJ mol<sup>-1</sup>. Also the trends between different substituents and their positions are qualitatively recovered.

In solution the variation of proton exchange energies of differently substituted benzoic acids relative to benzoic acids is considerably smaller than in the gas phase (Table 1). For p-hydroxy benzoate, deprotonation of the carboxyl group is favored.<sup>5</sup> For the o-hydroxy substituent we calculated a strong deviation from experiment, which may be due to the coexistence of several isomers. A similar difference had also been obtained by other computational methods.<sup>8,9</sup> Although the average absolute deviation of calculated from experimental data in solution, 4 kJ mol<sup>-1</sup>, is still acceptable, trends between different isomers are not reproduced. As an example we mention meta-fluoro and meta-methyl isomers, which are calculated to be slightly more acidic than their ortho and para congeners, at variance with the experimental trend which shows the ortho substituted species to be most acidic. Similar deviations in relative acidities have been obtained before for chloro-substituted benzoic acids<sup>10</sup> and most probable can be traced back to the inherent accuracy of the PCM model applied.

Overall we conclude from these results that small differences in acidity of substituted benzoic acids are not well reproduced by a standard density functional approach that includes a PCM treatment of solvation effects. Thus, similarly small differences, below ~5 kJ mol<sup>-1</sup>, in complexation energies of uranyl with this type of ligands should be interpreted with due care.

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