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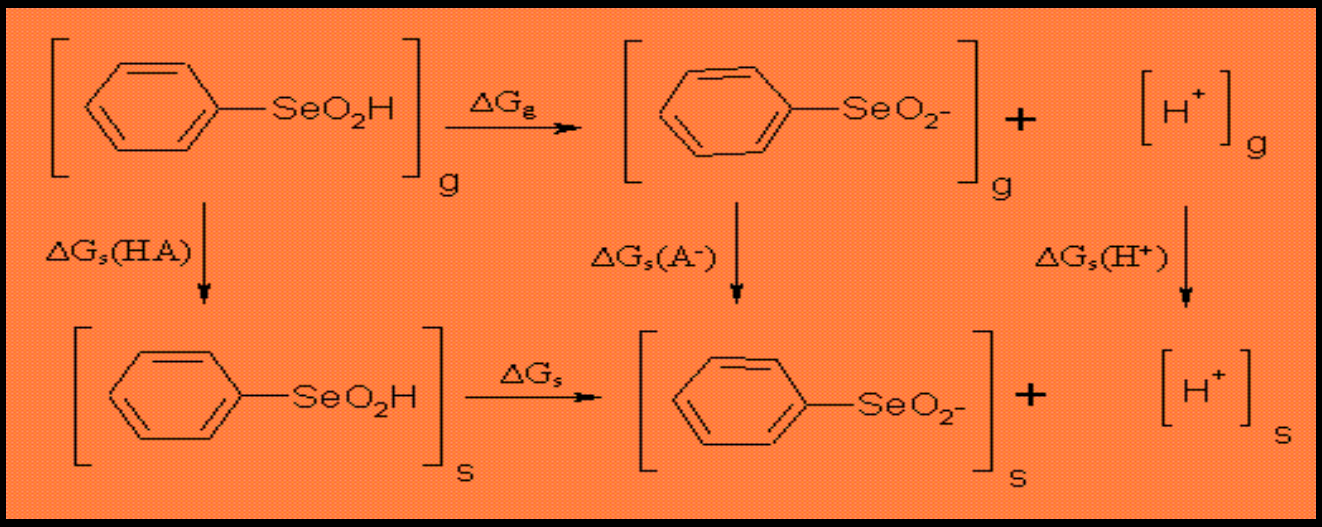
p*Ka* of organoselenium compounds: Ab initio and DFT calculations

Sajjad Karamat, Walter M.F.Fabian, Juraj Kona

Introduction

The exact ionization state of biologically important organoselenium compounds, e.g. those involved in the catalytic cycle of peroxidases is still incompletely known.[1] As a first step to the modelling of catalytic mechanism of glutathione peroxidase, the pK_a – values of a series of selenols R-SeH, seleninic acids R-SeO_2H and selenenic acids R-SeOH were calculated by ab initio (MP2) and DFT (B3LYP) methods using a thermodynamic cycle.[2] Here we are presenting results for seleninic acids R-SeO_2H only.



The pK_a calculated on the basis of the thermodynamic cycle is expressed as

$$2.303\ RT\ pK_a = G_g(A^-) + G_g(H^+) - G_g(HA) + \Delta G_s(H^+) + \Delta G_s(A^-) - \Delta G_s(HA)$$

where HA = Ph-SeO_2H and A^- = Ph-SeO_2^-

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Acknowledgment

S.K. thanks the Higher Education Commission of Pakistan for a scholarship.

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Computational Details

All computations have been performed with the Gaussian 03 suite of programs.[3] Four different model chemistries were employed, B3LYP/6-31G(d,p), MP2/6-31G(d,p), B3LYP/aug-cc-pVDZ, MP2/aug-cc-pVDZ.

All structures were characterized by frequency calculations as true minima and thermal corrections to Gibb's free energy are added as unscaled. Solvent effects (H_2O) were estimated by the single-point IEF-PCM procedure.[4] The pK_a values were calculated according to the above equation and experimental value for ΔG_s (H^+) was taken as -264.0 kcal/mol.[5] The value for G_g (H+) was taken from Sackur-Tetrode equation as -6.28 kcalmol^{-1}. The pK_a values are calculated at a temperature of 298.15 K.

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Results and Discussions

The experimental values of seleninic acids R-SeO_2H as well as those calculated by four different model chemistries are given in Table 1. The correlation between the experimental and theoretical pK_a values is given in Figure 1.

Table 1

	Exp.Value[6]	B3LYP 6-31G(d,p) Calc. Value	MP2 6-31G(d,p)	B3LYP aug-cc-pVDZ	MP2 aug-cc-pVDZ
Ph-SeO_2H	4.8	24.1	23.8	12.4	10.1
p-CH_3- Ph-SeO_2H	4.9	24.4	24.0	12.7	10.2
m-CH_3- Ph-SeO_2H	4.8	24.5	24.0	12.8	10.3
p-F- Ph-SeO_2H	4.5	23.7	23.3	12.0	9.8
m-F- Ph-SeO_2H	4.3	23.1	22.7	11.6	9.4
p-Cl- Ph-SeO_2H	4.5	23.1	23.0	11.8	9.6
m-Cl- Ph-SeO_2H	4.5	22.5	22.4	11.3	9.2
p-Br- Ph-SeO_2H	4.5	23.1	22.8	11.8	9.6
m-Br- Ph-SeO_2H	4.4	22.5	22.3	11.5	9.2
p-CH_3O- Ph-SeO_2H	5.1	26.0	24.9	14.1	11.4
m- CH_3O- Ph-SeO_2H	4.6	24.0	23.6	12.7	10.2
m-NO_2- Ph-SeO_2H	4.1	21.3	21.4	10.7	8.5
o- C_6H_5- Ph-SeO_2H	4.7	24.7	25.5	13.3	11.0

None of the methods used is capable to provide a reasonable agreement with the experimental values. Additions of diffuse funtions significantly improve the results. Reasonable trends but not absolute pK_a values are obtained as shown in Figure 1 . The correlation seems to be better described by B3LYP/6-31G(d,p) than MP2/aug-cc-pVDZ as indicated by the correlation coefficient R^2. The absolute values are better described by MP2/aug-cc-pVDZ than B3LYP/6-31G(d,p) but at much expense. *p*-CH_3-Ph-SeO_2H and *o*-C_6H_5-Ph-SeO_2H show large deviation.

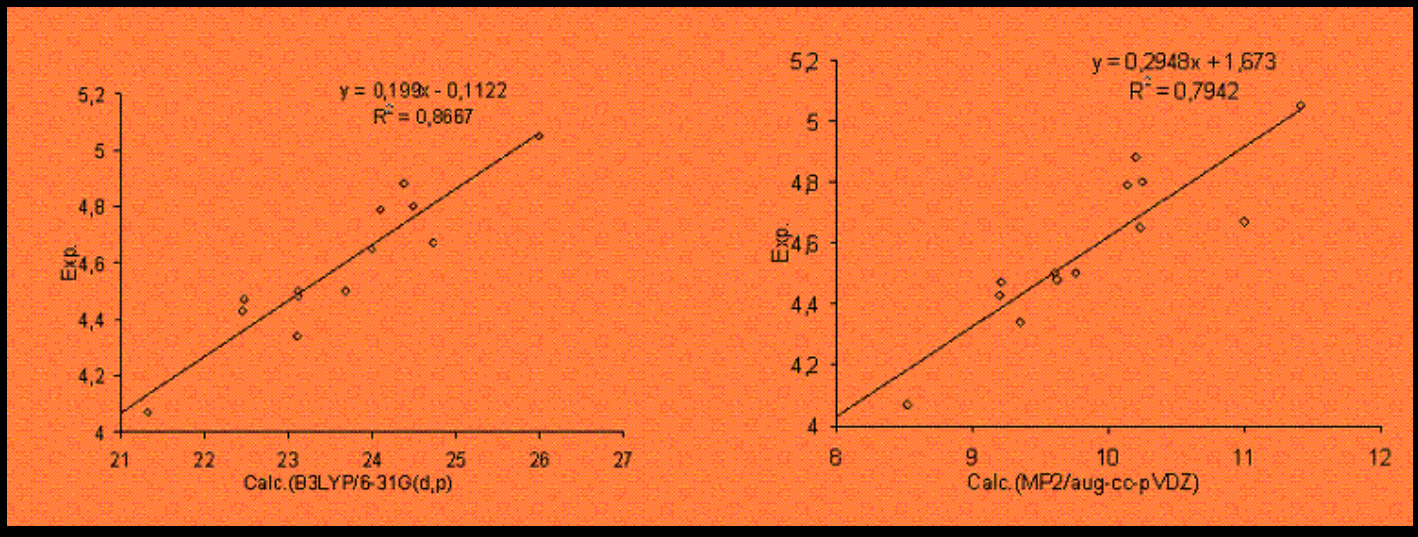

Figure 1 The correlation between the experimental and theoretical pK_a (The correlation coefficient R^2 for B3LYP/aug-cc-pVDZ and MP2/6-31G(d,p) is 0.8252 and 0.7156 respectively)

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