

# Correlations between experimental and theoretical adiabatic ionization energies for organic compounds and rate constants for atmospheric reactions with hydroxyl radicals

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*Adiabatic ionization energy (AIE) calculations were performed at the AM1, PM3, PM6, PDDG, HF/QZVP, and B3LYP/QZVP levels of theory on 722 atmospherically relevant organic compounds with available experimental  $k_{OH}$ . From the starting set of molecules, a final suite of 114 mono- and polyfunctionalized compounds provided converged neutral and cationic geometries without imaginary frequencies for all six levels of theory. NIST evaluated AIEs were available for 54 compounds, providing mean absolute AIE prediction errors of 0.31 (AM1), 0.28 (PM3), 0.50 (PM6), 0.36 (PDDG), 1.22 (HF/QZVP), and 0.20 eV (B3LYP/QZVP). Modest correlations were found between the experimental ( $r=-0.68$ ,  $SE=0.81$ ) and computationally estimated ( $r=-0.77$  [AM1],  $-0.75$  [PM3],  $-0.83$  [PM6],  $-0.79$  [PDDG],  $-0.83$  [HF/QZVP], and  $-0.82$  [B3LYP/QZVP];  $SE=0.75$  [AM1],  $0.78$  [PM3],  $0.66$  [PM6],  $0.73$  [PDDG],  $0.67$  [HF/QZVP], and  $0.68$  [B3LYP/QZVP]) AIEs and the corresponding experimental  $\log k_{OH}$ . Univariate AIE versus  $k_{OH}$  correlations are of lower predictive ability than state-of-the-art multivariate techniques, and are limited by the inability to calculate reliable AIEs for large numbers of atmospherically relevant compounds due either to convergence failures at various levels of theory or the presence of imaginary frequencies for converged cationic geometries.*

*Keywords: hydroxyl radical, atmospheric chemistry, quantitative structure-activity relationship, ionization energy, theoretical methods*

The hydroxyl radical ( $\cdot OH$ ) plays a fundamental role in the abiotic cycling of organic, organometallic, and inorganic compounds in the troposphere [1–4]. In addition to experimental approaches, theoretical methods for predicting the rate constants for reaction of organic compounds with the hydroxyl radical ( $k_{OH}$ ) have been the focus of a number of studies. In general, these predictive investigations have taken one of three general tactics [5–24]: (1) rigorous and time-intensive medium- through high-level computational studies (e.g., density functional theory, composite methods) on all possible mechanistic pathways for the reaction of a particular compound with the hydroxyl radical (i.e., addition to unsaturated groups, hydrogen abstractions, etc.); (2) regression based quantitative structure-activity relationship (QSAR) models employing a range of two- and three-dimensional molecular descriptors; and (3) univariate correlations with physicochemical properties (e.g., ionization energies [IEs], bond dissociation enthalpies [BDEs]).

In the absence of experimental data, high-level theoretical studies typically offer the most accurate approach. However, they are not suitable for screening large numbers of potential atmospheric contaminants due to the computational costs and substantial user-interaction/expert judgement required on an individual compound case-by-case basis to ensure all relevant mechanistic pathways have been rigorously investigated. Multivariate QSAR models are amenable to rapid screening techniques, and many offer reasonable accuracy. Because of the often arbitrary nature of the variables chosen for multivariate QSARs (which also may have little or no physicochemical relevance towards the process(es) under study), and potential concerns regarding statistical rigor and model under-/overfitting, the true applicability domain of such models can be the subject of debate. Among the univariate models, the two most relevant physicochemical descriptors are IEs and BDEs. Such univariate models are not

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subject to the same types of statistical concerns as their multivariate analogs, and it may be reasonable to assume their applicability domains are much more robust. These two properties often correlate well against each other, but the IE is the easier to obtain - particularly as molecules become more complex. For example, even a relatively small semi-volatile organic compound may have >10 different BDEs, but only a single IE value.

For this reason, several studies have investigated univariate correlations between IEs and  $k_{OH}$  [5,7,12,15]. Gaffney and Levin [5] found high correlation coefficients between experimental IEs and  $\log k_{OH}$  for a small set of 18 alkenes and dienes that react via hydroxyl radical addition ( $r=0.97$ ,  $m=-0.61\pm 0.04$ ,  $b=-4.68\pm 0.37$ ), as well as a separate minimal set of 4 oxygenated and halogenated alkenes that also react via the addition mechanism ( $r=0.95$ ,  $m=-0.57\pm 0.13$ ,  $b=-5.42\pm 1.24$ ). Subsequently, Gusten et al. [7] reported separate aromatic and aliphatic based correlations between experimental vertical IEs and experimental  $-\log k_{OH}$  for larger sets of organic compounds: aromatics,  $n=32$ ,  $r=0.95$ ,  $s=0.29$ ,  $m=1.52\pm 0.10$ ,  $b=-2.06\pm 0.84$ ; and aliphatics,  $n=129$ ,  $r=0.95$ ,  $s=0.36$ ,  $m=0.79\pm 0.02$ ,  $b=3.06\pm 0.24$ . More recently, Grosjean and Williams [12] published a correlation between the  $\log k_{OH}$  for various unsaturated organic compounds and IE ( $n=36$ ,  $r=0.89$ ,  $m=-0.44\pm 0.04$ ,  $b=-6.23\pm 0.34$ ), along with a separate correlation for a small subset of chlorinated olefins ( $n=7$ ,  $r=0.81$ ,  $m=1.44\pm 0.47$ ,  $b=-25.6\pm 4.6$ ). For a suite of 13 hydrofluorocarbons (and methane), Percival et al. [15] also reported the following correlation between the  $\log k_{OH}$  and IE:  $n=14$ ,  $r=0.96$ ,  $m=-1.12$ ,  $b=0.85$ .

With the exception of the work by Gusten et al. [7] on aliphatics ( $n=129$ ), the datasets to date have been limited in size and scope, and have not considered in detail the use of theoretical methods for estimating IEs within these types of models. This latter consideration is critical, as the majority of compounds for which estimated  $k_{OH}$  values are desired have either not been synthesized experimentally, or do not have experimental IEs available in the open literature. Thus, IE versus  $k_{OH}$  correlations for atmospheric persistence screening will generally need to employ estimated IEs as inputs, whether or not the model was developed and trained with experimental or theoretical IEs. Furthermore, unless computationally expensive high-level theoretical methods are used, which are prohibitive for screening large numbers of molecules and/or compounds with >15-20 heavy atoms, there are known systematic biases between experimental and predicted IEs using many of our current computational methods [25]. In this context, the most internally consistent path forward appears to be using predicted IEs to develop and train a univariate  $k_{OH}$  prediction model, along with predicted IEs (at the same level of theory) for subsequent screening efforts.

In addition, separating compounds by class (e.g., unsaturated/aromatic, saturated, halogenated [partially or fully], heteroatom substituted, caged/cyclic or having low-energy conformations that may provided hitherto unforeseen kinetic limitations for oxidants reaching the preferred reaction center, etc.) is often difficult for polyfunctionalized molecules (necessitating time-consuming expert judgement, thereby possibly defeating the purpose of the chosen modeling approach), or even inaccurate (if property versus  $k_{OH}$  model development correlations cross in the chemical space for different classes of compounds, the correct classification for a new polyfunctional molecule may be difficult to determine). For these reasons, we investigated the feasibility of developing reliable unclassified univariate IE versus  $k_{OH}$  correlations using estimated IEs obtained at computationally tractable levels of theory (semiempirical, Hartree-Fock, density functional theory) as could be applied in atmospheric persistence screening models with a training set of molecules from a large ( $n>700$ ) experimental  $k_{OH}$  database.

Calculations were conducted in Gaussian 09 (G09) [26] using the AM1 [27, 28], PM3 [29, 30], PM6 [31], and PDDG [32–36] semiempirical methods as reimplemented [37–39] in G09, and the Hartree-Fock (HF) and B3LYP density functional theory (DFT) [40–42] model chemistries with the QZVP [43] basis set. For developing broad and robust  $k_{OH}$  prediction correlations using theoretical methods, basis sets with the largest practical range of applicability with reasonable completeness are preferred. The QZVP basis set extends through the sixth period (H-Rn), beyond that of comparable Pople (e.g., 6-311G level [H-Kr]) or Dunning (e.g., cc-pVQZ [H-Ar, Ca-Kr]) basis sets. Semiempirical methods are computationally inexpensive, and thus attractive for potential structure-activity relationships that may comprise large molecules. Conversely, MPn and composite method calculations are prohibitively expensive for compounds with many heavy atoms. HF and DFT model chemistries often offer an acceptable compromise between accuracy and cost for larger compounds. The large variety of density functionals presently available precludes a rigorous examination of all potential methods at this level of

Table 1: Summary error statistics for AIE estimation accuracy at each of the six levels of theory under study against 54 compounds with NIST evaluated AIEs.

	MSD <sup>a</sup>	MAD <sup>b</sup>	RMSD <sup>c</sup>	MAXD <sup>d</sup>
AM1	-0.21	0.31	0.40	1.30 [difluoromethane]
PM3	-0.04	0.28	0.36	1.11 [chlorodifluoromethane]
PM6	-0.24	0.50	0.66	2.17 [p-dichlorobenzene]
PDDG	-0.16	0.36	0.48	1.26 [ethanethiol]
HF/QZVP	-1.18	1.22	1.27	1.84 [ethylene oxide]
B3LYP/QZVP	-0.15	0.20	0.25	0.61 [hexafluorobenzene]

<sup>a</sup> mean signed deviation. <sup>b</sup> mean absolute deviation. <sup>c</sup> root mean squared deviation. <sup>d</sup> maximum deviation with compound name in brackets.

Table 2: Regression statistics for linear correlations between theoretical AIE and the corresponding experimental  $k_{OH}$  at each of the six levels of theory under study for 114 compounds with experimental  $k_{OH}$ .

	r	p	CV	SE	m	b
AM1	-0.77	$<10^{-23}$	-0.07	0.75	$-0.90\pm 0.07$	$-3.01\pm 0.64$
PM3	-0.75	$<10^{-21}$	-0.07	0.78	$-0.91\pm 0.07$	$-2.73\pm 0.70$
PM6	-0.83	$<10^{-29}$	-0.06	0.66	$-0.96\pm 0.06$	$-2.60\pm 0.55$
PDDG	-0.79	$<10^{-24}$	-0.07	0.73	$-0.86\pm 0.06$	$-3.28\pm 0.59$
HF/QZVP	-0.83	$<10^{-28}$	-0.06	0.67	$-0.73\pm 0.05$	$-5.22\pm 0.39$
B3LYP/QZVP	-0.82	$<10^{-28}$	-0.06	0.68	$-0.83\pm 0.05$	$-3.64\pm 0.50$

theory. In previous benchmarking efforts on ionization energy prediction ability, the B3LYP functional displayed above average performance compared to a range of other density functionals [25], and was therefore chosen for the present task. All enthalpies and free energies include thermal and zero-point corrections; all final geometries comprise local minima absent any imaginary frequencies.

From a starting suite of 722 organic compounds with experimental  $k_{OH}$  in the database from Wang et al. [44], a set of 114 final compounds provided converged neutral and cationic geometries without imaginary frequencies for all six levels of theory (Supporting Information Table S1). Of these 114 compounds, 54 have NIST evaluated [45] adiabatic ionization energies (AIEs) for comparison. Riley et al. [25] reported mean absolute deviations (MAD) ranging from 0.20 eV (MPWB95) to 0.83 eV (cSVWN5), with an average error of 0.25 eV and a B3LYP MAD of 0.23 eV, using the 6-31+G\* basis set on a suite of 37 compounds and across 37 different functionals. Similar errors were obtained by these authors using the aug-cc-pVDZ basis set. With our 54 compounds, we obtain similar error metrics with the B3LYP functional (MAD=0.20 eV; Table 1), slightly worse performance for the four semiempirical methods (AM1 MAD=0.31 eV; PM3 MAD=0.28 eV; PM6 MAD=0.50 eV; and PDDG MAD=0.36 eV), and unacceptable performance with the HF method (MAD=1.22 eV).

For the 54 compounds with NIST evaluated AIEs, we find a relatively low correlation against the corresponding experimental  $k_{OH}$  ( $r=-0.68$ ,  $p<10^{-7}$ ,  $CV=-0.07$ ,  $SE=0.81$ ,  $m=-0.78\pm 0.12$  [ $\pm SE$ ],  $b=-3.89\pm 1.11$ ; Figure 1). This modest quality correlation demonstrates the inherent difficulty in generating reliable univariate predictive relationships for  $k_{OH}$  based on theoretically obtained physico-chemical property descriptors. Using the various theoretical methods, we find slightly improved qualities of fit between the estimated AIEs and corresponding  $k_{OH}$  (Figure 2(a)-(f); Table 2). However, with standard errors of about 0.7 log  $k_{OH}$  units (about five-fold error in  $k_{OH}$ ), these regressions are outside the desired accuracy of 0.3 log  $k_{OH}$  units (two-fold error in  $k_{OH}$ ) that can be obtained by multivariate approaches and bond additivity methods [9, 10, 13, 16]. Consequently, general univariate IE versus  $k_{OH}$  prediction approaches for organic compounds appear inferior to current state-of-the-art multivariate approaches. Not only are univariate IE versus  $k_{OH}$  correlations of lower predictive ability than the multivariate techniques (which often offer similar computational expense), but a key limitation is the inability to calculate reliable IEs for large numbers of atmospherically relevant compounds due either to convergence failures at various levels of theory or the presence of imaginary frequencies for converged cationic geometries.

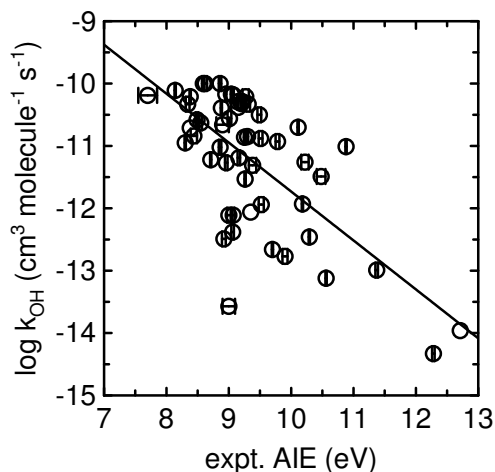


Figure 1: Correlation between NIST evaluated experimental AIE and corresponding experimental  $k_{OH}$ . Quoted errors in the experimental AIE are shown; in most cases, these error bars are smaller than the size of the symbols.

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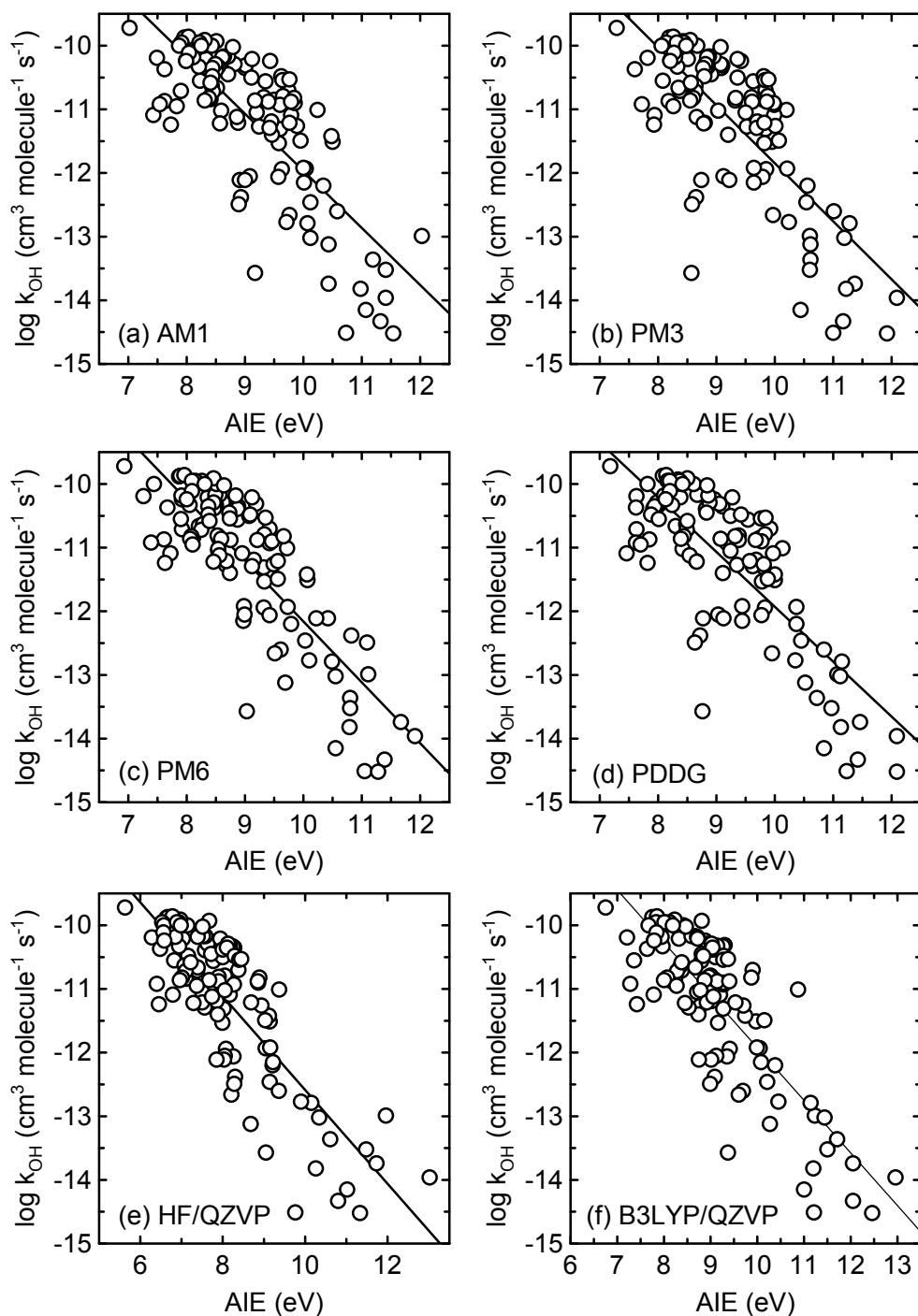


Figure 2: Correlations between theoretical AIEs obtained at the (a) AM1, (b) PM3, (c) PM6, (d) PDDG, (e) HF/QZVP, and (f) B3LYP/QZVP levels of theory and corresponding experimental  $k_{OH}$ .

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