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Calculated ionization energies, orbital eigenvalues (HOMO), and related QSAR descriptors of organic molecules: a set of 61 experimental values enables elimination of systematic errors and provides realistic error estimates—Supporting Information

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Text S1	Vibrational and thermal contributions to the AIE
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The difference in zero-point vibrational energy was evaluated using the computed vibrational frequencies from the DFT calculations described above, using the GoodVibes v3.2¹ package. Frequencies were scaled with scaling factors of 0.96 for B2PLYPD and

0.9675 for B3LYP, based on the scaling factors for similar basis sets in the CCCBDB². To evaluate the effects of temperature, the difference in the Gibbs free energy G when including vibrational-rotational effects for a temperature of 298 K were also evaluated. Its impact on the IE is denoted $\Delta AIE_{0K \rightarrow 298K}$, corresponding to the change in the calculated AIE going from 0 K to 298 K. For the vibrational frequencies, the quasi-harmonic approximation of Grimme³ was used for vibrational frequencies $< 100 \text{ cm}^{-1}$.

Text S2 Details on CCSD(T) calculations

The CBS extrapolation used the augh-cc-pVXZ(2df)^{4–7} (X=D,T,Q) basis sets, where “h” refers to the augmentation of only non-hydrogen atoms. For As and Br, regular aug-cc-pVXZ was used instead. The HF energy and the CCSD correlation energy were extrapolated as a (T,Q) extrapolation and the (T) correlation energy as a (D,T) extrapolation:

$$E_{HF}/CBS = E_{HF/Q} + \frac{E_{HF/Q} - E_{HF/T}}{\left(\frac{4}{3}\right)^5 - 1} \quad (1)$$

$$\Delta E_{HF}^{CCSD}/CBS = \Delta E_{HF/Q}^{CCSD} + \frac{\Delta E_{HF/Q}^{CCSD} - \Delta E_{HF/T}^{CCSD}}{\left(\frac{4}{3}\right)^{3.22} - 1} \quad (2)$$

$$\Delta E_{CCSD}^{CCSD(T)}/CBS = \Delta E_{CCSD/T}^{CCSD(T)} + \frac{\Delta E_{CCSD/T}^{CCSD(T)} - \Delta E_{CCSD/D}^{CCSD(T)}}{\left(\frac{3}{2}\right)^{3.22} - 1} \quad (3)$$

For some larger molecules (1-naphtol, azulene, benzimidazole, naphtalene, DABCO, and dibenzofuran), the cc-pVXZ (X=T,Q) basis set was used for $\Delta E_{HF}^{CCSD}/CBS$. For dibenzofuran, the cc-pVXZ (X=D,T) basis set was also used for $\Delta E_{CCSD}^{CCSD(T)}/CBS$, whereas the augh-cc-pVXZ(2df) basis sets were used for the other components.

ΔE_{FC}^{AE} was calculated either with the MTSmall basis set as defined in the W1 method (essentially an uncontracted pVTZ basis), or with the cc-pwCVTZ⁸ basis set, and for some larger molecules (1-naphtol, azulene, dibenzofuran, naphtalene, benzimidazole, and thymine) with the cc-pwCVDZ⁸ basis set. For Br, the cc-

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pwCVQZ⁸ basis set was used, and for As, the HGBSP1-5⁹ basis set was used (an uncontracted basis set by design), whereas cc-pwCVTZ⁸ was used for the other atom types.

ΔE_{NR}^{SR} was calculated with the second order Douglas-Kroll-Hess method¹⁰. It was either calculated as $E_{SR}/MTSmall - E_{nonrel}/MTSmall$ or as $E_{SR}/Jorge - TZP - DKH - E_{nonrel}/Jorge - TZP$ using Jorge's basis sets^{11,12} optimized for the respective type of calculation. Unless otherwise mentioned, the calculations on open-shell species were performed based with a restricted open shell (ROHF) reference determinant. Additional calculations with the unrestricted reference determinant (UHF) were carried out to calculate CCSD(T)/CBS energies in the frozen-core, non-relativistic approximation. These were combined with ΔE_{FC}^{AE} and ΔE_{NR}^{SR} from ROHF-based calculations form a combined electronic energy, which is referred to as UHF-CCSD(T) hereafter.

Text S3 Iodine-containing organic molecules

Molecules containing iodine were deliberately excluded in this work, since they require major changes in methodology. For iodoalkanes, SO effects are large (0.583 eV for iodoethene¹³) and also severely impact the geometry of the cation.¹⁴ However, ionization of the halogen lone electron pairs is not of practical relevance when Iodine is attached to a conjugated π -system. For the practically more relevant iodobenzene, a CCSD(T)/CBS calculation was carried out as follows: CCSD(T)/CBS with the augh-cc-pVXZ-PP basis set^{15,16} and pseudopotentials, ΔE_{FC}^{AE} with the cc-pwCVTZ-PP¹⁷ basis set, and ΔE_{NR}^{SR} with the Jorge-TZP(-DKH) basis set. ΔE_{FC}^{AE} and ΔE_{NR}^{SR} both accounted for 0.01 eV). The final, composite AIE was 8.83 eV as opposed to the experimental value of 8.7580(6) eV¹⁸. The larger deviation could be caused by the use of pseudopotentials or by the insufficient treatment of relativistic effects.

Text S4 Relationship between descriptors

Ionization potential (IP) is often used instead of *ionization energy* (IE). However, they are equivalent, since an IE (eV) is the energy needed to move one electron across a potential difference (V).

In the gas phase:

$$AIE_g = VIE_g - \lambda_{ox,g} \quad (4)$$

where the adiabatic and vertical IEs are connected by the reorganization energy $\lambda_{ox,g}$, which is the energy required to distort the n-1 electron species to the structure of the n-electron species. For a hypothetical single electron transfer (SET) reaction in the gas phase, a reaction partner needs to be reduced:

$$AEA_g = VEA_g - \lambda_{red,g} \quad (5)$$

where *EA* refers to the adiabatic or vertical electron affinity of the oxidant. The Gibbs free energy of electron transfer is then given by:

$$\Delta G_{SET,g}^{\circ} = AIE(\text{reductant}, g) + AEA(\text{oxidant}, g) \quad (6)$$

In the solution phase, absolute AIE_{aq} s are not experimentally accessible and are reported as *relative* standard half-cell reduction

or oxidation potentials (mind the sign!) *versus* the normal hydrogen electrode (NHE), often denoted $E_{1/2}$. They are related to the free energy of removing the electron by:

$$E_{1/2} = \left(\frac{-\Delta G_{ox}^{\circ}}{nF} + E_H^{\circ} \right) \quad (7)$$

where ΔG_{ox}° is the (absolute) ionization energy, n the number of transferred electrons, F is the Faraday constant that converts ΔG_{ox}° to V, and E_H° the absolute potential of the NHE, estimated to be 4.28 V.¹⁹ Therefore, apart from a constant, unit conversion (potential/energy), and possibly different standard state conventions, ΔG_{ox}° is equivalent to AIE_{aq} , and I will use ΔG_{ox}° and AIE_{aq} interchangeably.

The free energy of a single electron transfer is related to both half-cell reactions:

$$\Delta G_{SET}^{\circ} = E_{1/2}^{red} + E_{1/2}^{ox} = AEA_{red} + AIE_{ox} \quad (8)$$

For a series of reactions with the same oxidant, AIE_{aq} differs from ΔG_{SET}° only by a constant. For the linear model sketched above, the slope is identical, regardless of whether AIE_{aq} or ΔG_{SET}° is used.

With $VIE_{aq} = AIE_{aq} + \lambda_{ox,aq}$, a regression model that uses VIE_{aq} differs only by $\lambda_{ox,aq}$ from a regression model that uses the AIE_{aq} , assuming that $\lambda_{ox,aq}$ is constant among a set of structurally related molecules. Since $-\epsilon_{HOMO} \approx VIE$, models that use either $-\epsilon_{HOMO}$ or VIE as a descriptor are equivalent but may exhibit different slopes and intercepts because of the relationship between VIE and $-\epsilon_{HOMO}$ (Table 4 in the main text).

Text S5 Details on illustrative QSAR applications

Singlet quenching by arenes

Rate constants and thermodynamics for quenching of singlet excited states by arenes in acetonitrile were taken from the literature (see references in the main text). The set included 14 quenching reactions of excited singlet states involving 10 different reductants:

- 2,9,10-tricyanoanthracene* by *m*-xylene
- 1-cyanonaphthalene* by 1,2,4-trimethylbenzene
- 9,10-dicyanoanthracene* by biphenyl
- 1,4-dicyanonaphthalene* by toluene
- 1-cyanonaphthalene* by biphenyl
- 9,10-dicyanoanthracene* by *p*-xylene
- 2,6,9,10-tetracyanoanthracene* by benzene
- 2,9,10-tricyanoanthracene* by toluene
- 1,2-benzanthracene* by 1,4-dimethoxybenzene
- 1,2-benzanthracene* by 1-trifluoromethyl-4-N(CH₃)₂-benzene
- 3,4-benzacridine* by 1,3-dimethoxybenzene

- 3,4-benzacridine* by 1,3,5-trimethoxybenzene
- 1-pyrenecarboxylic acid* by 1,3-dimethoxybenzene
- 1-pyrenecarboxylic acid* by 1,3,5-trimethoxybenzene

The experimental reduction potentials of the excited singlet state of the oxidant were taken from the literature.

For Fig. 5. (a) in the main text, ΔG_{SET} was calculated from the difference between the experimental reduction potential and the experimental one-electron oxidation potential of the arene.

For Fig. 5. (b), The one-electron oxidation potential was replaced by $-\epsilon_{HOMO}$. For this calculation, the geometry of the reductant was optimized at the B3LYP/6-311+G(2df,2pd) level of theory, with solvation effects accounted for by the SMD implicit solvation model. $-\epsilon_{HOMO}$ used the same level of theory. For $-\epsilon_{HOMO} - E_{red}^{\circ}$, a shift of -4.28 eV (the absolute potential of the SHE) and -0.241 eV (the potential of the calomel electrode) was applied. This shifts the scale of the x-axis to that of the experimental data, but has no influence on the regression.

For Fig. 5 (c), the AIE_{aq} was calculated at the B3LYP/6-311+G(2df,2pd) level of theory, and accounted for solvation effects with the SMD model. AIE_{aq} was calculated as the difference of Gibbs' free energies at 298 K, i.e., rotational and vibrational contributions to G from a normal mode analysis were considered. The resulting AIE_{aq} was adjusted for electrode potentials (see above).

For Fig. 5 (d), AIE_{aq} was evaluated as the sum of AIE_{gas} and $\Delta\Delta G_{solv}$. For all solutes, the geometries were optimized in the gas phase using B3LYP/6-311+G(2df,2pd), and vibrational/rotational contributions to G were evaluated at this level of theory. Where available, an experimental gas phase $AIE_{gas, 0 K}$ from PFI/MATI experiments was corrected with thermal contributions (from the B3LYP calculations) to yield $AIE_{gas, 298 K}$ (1,3-dimethoxybenzene, 1,4-dimethoxybenzene, benzene, toluene, p-xylene). For the other compounds, the electronic IE was estimated using eq. 9 in the main text, with electronic energies evaluated at the PWPB95/def2-TZVPPD level of theory. $AIE_{gas, 298 K}$ was complemented with ΔG_{solv} from separate SMD calculations at the B3LYP/6-31+G(d,p) level of theory and using the (frozen) gas phase geometries. The resulting AIE_{aq} was adjusted for electrode potentials (see above).

Aqueous oxidation of organics by ClO_2^{\cdot}

Experimental second order rate constants were taken from the NIST solution kinetics database. The chosen reactants were 2,4-hexadiene-1-ol, 2,5-dimethylfuran, 2-methoxyphenolate, 4-methoxyphenol, aniline, anthracene, DABCO, dimethylamine, furfuryl alcohol, hydroquinone, indole, isobutylthiolate, methylamine, N,N-dimethylaniline, phenolate, phenol, piperidine, and trimethylamine.

For Fig. 6 (a), $-\epsilon_{HOMO}$ was calculated at the B3LYP/def2-TZVPPD level of theory. A regression correction was applied to $-\epsilon_{HOMO}$, but this has no impact on the quality of the fit.

For Fig. 6 (b), the best estimate of AIE_{aq} was calculated in the same way as for Fig. 5 (c), but using B3LYP/def2-TZVPPD for gas phase geometries and ΔG_{solv} with the SMD model. For almost

all compounds in the set, $AIE_{gas, 0 K}$ from PFI/MATI experiments or an estimate of the (gas phase) electronic IE at W1 level was available.

For Fig 6. (c), the AIE_{aq} from Fig. 6 (b) was used. Reorganization energies λ were calculated using B3LYP/def2-TZVPPD as follows. $\lambda_{gas} = VIE_{gas} - AIE_{el.,gas}$, that is, only electronic energies were considered. λ_{aq} was evaluated using the (frozen) gas phase geometry of the neutral molecule and the cation, as $\lambda_{aq} = E(n-1, R(neutral)) - E(n-1, R(cation))$ where R refers to the (gas phase) optimized geometry of either the neutral or the cation. For $E(n-1, R(neutral))$, a VIE calculation with non-equilibrium solvation was performed. The solvation contribution to λ was evaluated as $\lambda_{solv} = \lambda_{aq} - \lambda_{gas}$. The expression used for the energy on the x-axis is similar to those used by Marcus or Rehm and Weller. However, the former usually employ free energies and λ that refer to the whole SET reaction, whereas here, only the oxidation half-cell reaction was considered. To correct the quadratic term, 5.215 eV were subtracted, which is close to a correction for the (absolute) reduction potential of ClO_2^{\cdot} . Note that the reorganization energy of ClO_2^{\cdot} is missing from the expression. $\lambda_{solv, SET}$ of the overall SET reaction cannot be cleanly partitioned between both reactants. $\lambda_{solv, SET}$ refers to the encounter complex, where SET yields a zwitterion. In contrast, λ_{solv} of the reductant yields a solvated radical cation, which is likely an overestimation of the solvent effect. Consequently, λ_{solv} was scaled by an empirical factor of 0.16, which yielded the best fit (the other parameters were kept fixed). Real applications of this type of equation should further explore how $\lambda_{solv, SET}$ is best approximated.

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Table S1 Components of CCSD(T)/CBS adiabatic ionization energies [eV]

Compound	IE_{HF}	ΔIE_{HF}^{CCSD}	$\Delta IE_{CCSD}^{CCSD(T)}$	ΔIE_{FC}^{AE}	Basis ^a	ΔIE_{NR}^{SR}	Basis ^a	ΔIE_{ZPVE}	ΔAIE_{calc}^{exp}	$IE_{el..NR}$
DABCO	6.818	0.482	-0.092	0.000	pwCVTZ	-0.002	Jorge-TZP	0.030	0.041	7.168
Radical-Benzyl	6.271	0.910	-0.001	0.017	MTSmall	-0.002	MTSmall	0.062	0.007	7.190
Azulene	6.134	1.094	0.154	0.009	pwCVDZ	-0.005	Jorge-TZP	0.025	-0.001	7.392
N-methylaniline	6.548	0.786	0.053	0.010	pwCVTZ	-0.006	Jorge-TZP	0.044	0.018	7.379
Aniline	6.779	0.862	0.069	0.008	pwCVTZ	-0.004	Jorge-TZP	0.026	0.020	7.698
1-naphtol	6.758	0.961	0.045	0.009	pwCVDZ	-0.005	Jorge-TZP	0.025	0.027	7.746
Thioanisole	7.120	0.796	0.025	0.008	pwCVTZ	-0.008	Jorge-TZP	0.007	0.025	7.925
Hydroquinone	6.869	0.964	0.071	0.011	pwCVTZ	-0.002	Jorge-TZP	0.044	0.021	7.894
Piperidine	6.962	1.059	0.051	0.002	pwCVTZ	-0.003	Jorge-TZP	-0.027	0.022	8.053
Dibenzofuran	7.177	0.935	0.037	0.012	pwCVDZ	-0.004	Jorge-TZP	-0.017	0.028	8.132
Radical-Allyl	6.916	1.127	0.024	0.020	MTSmall	-0.004	MTSmall	0.057	0.009	8.077
Naphtalene	7.173	0.955	0.033	0.011	pwCVDZ	-0.005	Jorge-TZP	0.006	0.029	8.143
Pyrrole	6.976	1.141	0.109	0.018	MTSmall	0.000	MTSmall	-0.005	0.028	8.215
Anisole	7.235	0.945	0.066	0.014	pwCVTZ	-0.005	Jorge-TZP	-0.001	0.021	8.238
E-hexatriene	7.098	1.076	0.079	0.019	MTSmall	-0.001	MTSmall	0.014	0.015	8.255
Benzimidazole	7.332	1.016	0.059	0.011	pwCVDZ	-0.005	Jorge-TZP	-0.014	0.024	8.394
Radical-Cyclopent.	6.905	1.350	0.093	0.017	MTSmall	0.000	MTSmall	0.053	-0.009	8.374
Phenol	7.444	0.990	0.079	0.014	pwCVTZ	-0.003	Jorge-TZP	0.011	0.027	8.501
(CH ₃) ₂ S	7.696	0.974	0.067	0.001	MTSmall	-0.009	MTSmall	-0.036	0.003	8.736
Radical-Propargyl	7.822	0.853	-0.018	0.019	MTSmall	-0.003	MTSmall	0.039	0.011	8.665
Pyridazine	8.110	0.619	-0.003	-0.003	pwCVTZ	0.003	Jorge-TZP	0.011	0.027	8.696
Thiophene	7.770	1.063	0.086	0.017	MTSmall	-0.004	MTSmall	-0.025	0.032	8.904
Furan	7.627	1.177	0.100	0.022	MTSmall	-0.003	MTSmall	-0.016	0.019	8.906
Thymine	8.026	0.895	0.051	0.009	pwCVDZ	-0.007	Jorge-TZP	-0.032	0.024	8.956
Bromobenzene	8.118	0.878	0.043	0.012	pwCVT(Q)Z	0.011	Jorge-TZP	-0.011	0.053	8.998
Methylamine	7.863	1.178	0.083	0.000	MTSmall	-0.001	MTSmall	-0.066	0.014	9.109
Butadiene	7.823	1.146	0.101	0.021	MTSmall	0.000	MTSmall	-0.009	0.013	9.077
Chlorobenzene	8.105	0.945	0.059	0.016	MTSmall	-0.006	MTSmall	-0.013	0.034	9.091
Phenylsilane	8.041	1.071	0.100	0.020	pwCVTZ	-0.003	Jorge-TZP	-0.062	0.031	9.200
Pyridine	8.127	1.093	0.059	0.003	MTSmall	0.000	MTSmall	-0.052	0.032	9.250
Fluorobenzene	8.090	1.056	0.084	0.020	MTSmall	-0.003	MTSmall	-0.017	0.027	9.223
Benzene	8.143	1.083	0.091	0.021	MTSmall	0.000	MTSmall	-0.085	0.009	9.329
Pyrazine	9.647	-0.034	-0.209	0.004	pwCVTZ	-0.001	Jorge-TZP	-0.080	0.039	9.369
Tetrachloroethene	8.522	0.818	0.007	0.011	MTSmall	-0.015	MTSmall	0.008	0.025	9.333
Pyrimidine	9.297	0.245	-0.133	0.003	MTSmall	0.002	MTSmall	-0.037	0.045	9.367
Thiazole	8.243	1.094	0.072	0.021	MTSmall	-0.008	MTSmall	-0.037	0.022	9.409
Methanethiol	8.441	0.983	0.069	0.004	MTSmall	-0.010	MTSmall	-0.033	-0.001	9.498
Oxazole	8.269	1.257	0.097	0.026	MTSmall	-0.003	MTSmall	-0.033	0.017	9.632
E-1,2-diCl-ethene	8.671	0.967	0.043	0.012	MTSmall	-0.010	MTSmall	-0.003	0.022	9.671
Oxetane	8.579	1.180	0.059	0.005	MTSmall	-0.006	MTSmall	-0.111	0.037	9.785
Benzonitrile	8.827	0.919	0.050	0.020	pwCVTZ	-0.003	Jorge-TZP	-0.041	0.041	9.776
Bromoethene	8.765	1.041	0.060	0.009	pwCVT(Q)Z	-0.019	Jorge-TZP	-0.017	0.019	9.856
AsH ₃	8.566	1.077	0.076	0.002	HGBSB1-5	0.069	Jorge-TZP	-0.005	-0.040	9.761
Radical-CH ₃	8.867	0.854	0.060	0.021	MTSmall	-0.002	MTSmall	0.042	0.002	9.799
PH ₃	8.620	1.150	0.082	0.021	MTSmall	0.008	MTSmall	-0.011	-0.008	9.881
Diacetylene	9.239	0.929	0.032	0.024	MTSmall	0.001	MTSmall	-0.011	0.038	10.185
NH ₃	8.775	1.348	0.101	0.005	MTSmall	-0.001	MTSmall	-0.041	0.001	10.228
H ₂ S	9.379	1.025	0.079	0.009	MTSmall	-0.011	MTSmall	-0.016	-0.003	10.495
Ethene	8.948	1.458	0.152	0.022	MTSmall	-0.002	MTSmall	-0.053	0.011	10.569
Bromomethane	9.712	0.986	0.061	-0.007	pwCVT(Q)Z	-0.031	Jorge-TZP	-0.074	-0.036	10.789
Acetic acid	9.133	1.481	0.107	0.010	MTSmall	-0.006	MTSmall	-0.047	0.026	10.705
Methanol	10.064	0.901	0.035	0.002	MTSmall	-0.004	MTSmall	-0.118	0.040	10.962
Formaldehyde	9.651	1.247	0.084	0.007	MTSmall	-0.005	MTSmall	-0.071	0.027	10.962
Chloromethane	10.443	0.928	0.048	0.005	MTSmall	-0.012	MTSmall	-0.107	0.002	11.422
Ethyne	9.868	1.395	0.146	0.027	MTSmall	-0.002	MTSmall	-0.021	0.012	11.423
Cyanoacetylene	10.691	0.983	0.021	0.026	MTSmall	-0.002	MTSmall	-0.025	0.051	11.670
Acetonitrile	10.951	1.290	0.089	0.019	MTSmall	0.001	MTSmall	-0.139	0.008	12.342
SO ₂	12.277	0.237	-0.135	0.015	MTSmall	-0.002	MTSmall	-0.016	0.030	12.364
Fluoromethane	12.084	0.659	-0.022	0.006	MTSmall	-0.004	MTSmall	-0.163	0.025	12.703
H ₂ O	11.090	1.494	0.104	0.010	MTSmall	-0.006	MTSmall	-0.069	0.006	12.692
HCl	11.682	1.053	0.075	0.010	MTSmall	-0.013	MTSmall	-0.019	0.042	12.778

^aIf no basis set is indicated in the table, the MTSmall basis set was used. ^bAlso accounts for the experimental spin-orbit splitting, see text for details.

Table S2 Temperature contribution to the AIE; CCSD(T)/CBS values for VIE and λ [eV]

Compound	$\Delta AIE_{0K \rightarrow 298K}^a$	$\Delta IE_{el. \rightarrow AIE_{298K}}^b$	$VIE_{el.NR}^c$	λ_{NR}^d
DABCO	-0.015	0.015	7.548	0.380
Radical-Benzyl	0.015	0.077	7.291	0.101
Azulene	-0.021	0.004	7.517	0.125
N-methylaniline	-0.031	0.013	7.517	0.139
Aniline	0.002	0.028	8.082	0.384
1-naphtol	-0.019	0.006	7.916	0.170
Thioanisole	-0.022	-0.015	8.076	0.151
Hydroquinone	-0.011	0.033	8.208	0.314
Piperidine	-0.023	-0.050	8.807	0.754
Dibenzofuran	-0.024	-0.041	8.306	0.174
Radical-Allyl	0.015	0.072	8.141	0.063
Naphtalene	-0.023	-0.016	8.270	0.127
Pyrrrole	-0.018	-0.023	8.428	0.213
Anisole	-0.027	-0.027	8.482	0.244
E-hexatriene	-0.018	-0.004	8.436	0.181
Benzimidazole	-0.022	-0.036	8.640	0.246
Radical-Cyclopentadienyl	0.049	0.102	8.550	0.176
Phenol	-0.020	-0.009	8.747	0.246
(CH ₃) ₂ S	-0.029	-0.065	8.803	0.068
Radical-Propargyl	0.015	0.054	8.700	0.035
Pyridazine	-0.016	-0.006	9.317	0.621
Thiophene	-0.022	-0.048	9.122	0.218
Furan	-0.020	-0.036	9.109	0.203
Thymine	-0.025	-0.057	9.251	0.295
Bromobenzene	-0.023	-0.034	9.231	0.233
Methylamine	-0.032	-0.098	9.789	0.680
Butadiene	-0.019	-0.028	9.254	0.177
Chlorobenzene	-0.024	-0.037	9.319	0.227
Phenylsilane	-0.003	-0.066	9.416	0.216
Pyridine	-0.021	-0.073	9.772	0.522
Fluorobenzene	-0.026	-0.043	9.469	0.245
Benzene	-0.072	-0.157	9.474	0.146
Pyrazine	-0.002	-0.083	9.736	0.367
Tetrachloroethene	-0.013	-0.005	9.665	0.332
Pyrimidine	-0.018	-0.056	9.840	0.473
Thiazole	-0.023	-0.060	9.656	0.247
Methanethiol	-0.018	-0.051	9.548	0.050
Oxazole	-0.020	-0.054	9.913	0.281
E-1,2-diCl-ethene	-0.018	-0.021	9.977	0.306
Oxetane	0.000	-0.111	9.935	0.150
Benzonitrile	-0.030	-0.070	9.939	0.163
Bromoethene	-0.019	-0.037	10.062	0.206
AsH ₃	-0.016	-0.021	10.489	0.727
Radical-CH ₃	0.019	0.061	9.807	0.008
PH ₃	-0.017	-0.028	10.605	0.724
Diacetylene	-0.020	-0.031	10.313	0.129
NH ₃	-0.001	-0.042	10.939	0.712
H ₂ S	-0.019	-0.035	10.501	0.006
Ethene	-0.022	-0.076	10.765	0.196
Bromomethane	-0.049	-0.123	10.791	0.003
Acetic acid	-0.018	-0.065	11.007	0.302
Methanol	-0.017	-0.135	11.175	0.214
Formaldehyde	-0.019	-0.090	11.014	0.052
Chloromethane	-0.048	-0.155	11.492	0.071
Ethyne	-0.019	-0.039	11.537	0.114
Cyanoacetylene	-0.022	-0.048	11.820	0.150
Acetonitrile	-0.055	-0.194	12.590	0.248
SO ₂	-0.015	-0.032	12.580	0.216
Fluoromethane	-0.045	-0.208	13.505	0.801
H ₂ O	-0.020	-0.089	12.781	0.089
HCl	-0.019	-0.038	12.841	0.063
All species:				
MIN	-0.072	-0.208		0.003
MAX	0.049	0.102		0.801
Non-radical, Non-hydride, non-haloalkane species:				
MIN	-0.072	-0.194		0.050
MAX	0.002	0.033		0.754

^aCalculated thermal energy to bring the AIE from 0 K to 298 K. ^bCalculated energy to bring the electronic (A)IE to 298 K. ^cCCSD(T)/CBS estimate of the non-relativistic VIE. ^dCCSD(T)/CBS estimate of the non-relativistic λ . MIN and MAX refer to the minimum and maximum values explored by each quantity.

Table S3 Deviation of electronic AIE (ROHF/ROKS) from the electronic, non-relativistic reference values ($IE_{el,NR}$, †Table S1) before and after linear regression [eV]

Method	MAD	RMSD	ΔAIE_{\min}	ΔAIE_{\max}	Slope	Intercept	RMSD _{reg}	$\Delta AIE_{\min,reg}$	$\Delta AIE_{\max,reg}$
HF	1.035	1.082	-1.623	0.420	0.972	1.255	0.354	-0.669	1.403
B3LYP	0.154	0.172	-0.332	0.060	0.984	0.300	0.088	-0.211	0.198
B2PLYPD	0.165	0.177	-0.328	-0.018	0.988	0.278	0.061	-0.160	0.127
BHandHLYP	0.249	0.268	-0.447	0.695	0.999	0.194	0.197	-0.267	0.879
LC-PBE	0.188	0.223	-0.110	0.481	1.020	-0.372	0.129	-0.232	0.364
LC- ω PBE	0.086	0.108	-0.180	0.268	1.019	-0.209	0.100	-0.193	0.260
M06	0.168	0.193	-0.431	0.019	1.001	0.153	0.097	-0.264	0.187
M06-2X	0.072	0.092	-0.256	0.255	1.008	-0.072	0.091	-0.257	0.278
M06-HF	0.292	0.339	-0.327	0.920	0.981	-0.061	0.227	-0.574	0.601
M11	0.083	0.104	-0.158	0.294	1.003	-0.056	0.100	-0.185	0.276
MP2	0.180	0.374	-0.261	1.980	0.920	0.683	0.346	-0.461	1.756
PBE0	0.177	0.195	-0.375	0.097	1.006	0.119	0.086	-0.194	0.275
PM3	0.445	0.637	-2.396	1.552	1.207	-1.853	0.592	-2.182	1.506
ω B97XD	0.131	0.148	-0.300	0.055	0.999	0.138	0.073	-0.173	0.181

Table S4 Experimental AIEs (at 0 K) from PFI experiments [eV].

Quantity	Descriptor	Slope [eV ⁻¹]	Ref.
Aqueous phase oxidation reactions			
log(k), CO ₃ ^{•-} + phenolate	ΔG_{SET}°	-2.03	20
log(k), CO ₃ ^{•-} + anilines	ΔG_{SET}°	-2.89	20
log(k), O ₃ + phenol/phenolate	$VIE_{aq,DFT}$	-3.78	21
log(k), O ₃ + aromatics	$-\epsilon_{HOMO}$	-2.2	22
log(k), O ₃ + aromatics	$-\epsilon_{HOMO}$	-4.7	22
ln(k _{app}), [FeO ₄] ²⁻ + organics	$IE_{DFT}^{\circ a}$	-4.8 ^b	23
log(k _{app}), ^c H ₂ O ₂ (activated) + organics	$-\epsilon_{HOMO}$	-1.95	24
		-4.53	24
log(k), ¹ O ₂ + phenols/phenolates	$\Delta G_{1/2,calc}^{\circ}$	-2.46	25
log(k), CO ₃ ^{•-} + phenols/phenolates	$\Delta G_{1/2,calc}^{\circ}$	-1.54	25
log(k), MnO ₂ + anilines	$-\epsilon_{HOMO}$	-6.2	26
log(k), MnO ₂ + anilines	$\Delta G_{1/2,calc}^{\circ}$	-5.4	26
log(k), CO ₃ ^{•-} + anilines	$\Delta G_{1/2,calc}^{\circ}$	-1.95	27
log(k), CO ₃ ^{•-} + aliphatic amines	$\Delta G_{1/2,calc}^{\circ}$	-1.51	27
log(k), ³ benzophenone + N-containing organics	$\Delta G_{1/2,calc}^{\circ}$	-1.41	27
log(k), ³ MAP + N-containing organics	$\Delta G_{1/2,calc}^{\circ}$	-4.68	27
log(k), HO [•] + phenols, alkanes, alcohols	$-\epsilon_{HOMO}$	-0.50	28
Gas phase oxidation reactions			
log(k), NO ₃ ^d	$-\epsilon_{HOMO}$	-1.0	29
	VIE_{calc}	-1.49	29

^aMethods section doesn't detail the type of IE. ^bNo unit given in reference, [eV] assumed.

^cTwo slopes for log(k_{app}) at pH 7 and 10. ^dQSAR model containing both VIE_{calc} and $-\epsilon_{HOMO}$, among other descriptors.