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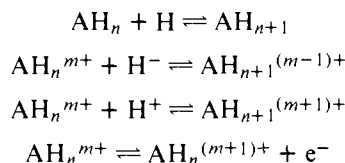
A Systematic Study of the Ionization Potentials and Electron, Proton, Hydrogen, and Hydride Affinities of OH_n Molecules and Ions

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Abstract: Ab initio LCAO-MO-SCF computations with large Gaussian basis sets have been performed on oxygen hydrides with one to three hydrogen atoms. Both the bond lengths (r) and bond angles (ϕ) were varied to produce energy surfaces $E(r, \phi)$. The resulting energies were used to determine ionization potentials and electron, proton, hydrogen, and hydride affinities.

A knowledge of accurate ionization potentials and electron, proton, hydrogen, and hydride affinities can be obtained by studying the reactions illustrated below.



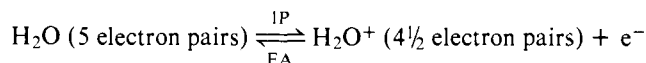
These energy difference quantities are important for studies in areas such as ion hydration, acid-catalyzed reactions, and electron scattering. Unfortunately, many of the species in the above reactions are not amenable even to experimental detection. It is exactly this kind of problem where theoretical means might be used to their greatest advantage.

Although self-consistent molecular orbital theory, with a well defined set of basis functions, gives a generally successful account¹⁻³ of nonenergy one-electron properties such as multipole moments, diamagnetic shielding, etc., the calculation of properties dependent on energy differences have not been as successful. This is because the SCF energy (E_{SCF}) is no more than an approximation to the Hartree-Fock energy (E_{HF}), which is itself only one component of the electronic energy (E_{el}) written as:

$$E_{\text{el}} = E_{\text{SCF}} + (E_{\text{HF}} - E_{\text{SCF}}) + E_{\text{C}} + E_{\text{R}}$$

where E_{C} is the correlation energy and E_{R} is the relativistic energy. Our ability to compute E_{el} and resulting energy differences is limited by our knowledge of the last three terms. Since the number of atoms is conserved in chemical reactions, differences in E_{R} can be assumed to be negligible. But, because the correlation energy (E_{C}) is generally related to the number of electron pairs in a molecule, systematic errors are un-

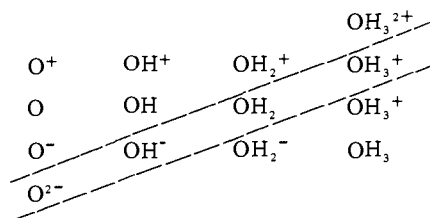
avoidable in the calculation of energy differences in processes where closed electronic shells are either created or destroyed as in the electron detachment, attachment process illustrated below:



Estimating the correlation energy changes by comparing calculated results to experimental results, whenever both are reasonably accurate, is a way to reduce the influence of these systematic errors. If in a given system, neither experimental measurements nor theoretically calculated correlation energies of sufficient accuracy exist, a method of making approximate correlation energy corrections is through an extrapolation from similar systems which are better characterized. Both these combinations of circumstances are present in the oxygen hydride situation; that is, only some of the set of oxygen hydrides and their ions have been characterized experimentally and/or theoretically. This paper focuses on the oxygen hydrides for their inherent interest and importance and because it is worthwhile studying the entire set of species in a systematic manner.

In order to transfer correlation energy estimates from one hydride to another, one must be assured that the quantity ($E_{\text{HF}} - E_{\text{SCF}}$) is either known or is of the same relative magnitude for both hydrides. Numerous ab initio LCAO-MO-SCF calculations have been previously performed⁴⁻¹⁰ to predict energy-dependent properties of some oxygen hydrides. Except for two cases,^{4,5} these calculations have not been concerned with a comprehensive study of more than a few hydrides, and since it is difficult to estimate ($E_{\text{HF}} - E_{\text{SCF}}$) for these isolated calculations, no correlation energy corrections have been attempted. Also, because the ($E_{\text{HF}} - E_{\text{SCF}}$) term differs for each calculation, it is impossible to collate their results to determine

trends. Thus, in the present study, a uniform basis set (which included both d and p polarization functions on the oxygen and hydrogen atoms) was employed so as to minimize and reduce fluctuations in $(E_{HF} - E_{SCF})$ in the prediction of a series of ionization potentials (IP) and electron (EA), proton (A_{H^+}), hydrogen (A_H), and hydride (A_{H^-}) affinities for a few of the monooxygen hydrides. This involved the calculation of equilibrium geometries and energies for the following species, where the ten-electron closed-shell systems are enclosed by the broken line.



Method

For singlet states of molecules, normal closed-shell theory with real molecular orbitals is used, leading to the well-known equations of Roothaan.¹¹ For states of higher multiplicity, restricted single determinant¹² theory is used. This method has not been widely used, since iterative convergence of the energy is not always assured. However, no such problems were encountered with the present calculations and it is believed that all of the energies quoted represent the minima obtainable with both methods. Here, the term Hartree-Fock energy (E_{HF}) refers to the minimum restricted closed- or open-shell energy which would be obtained with a complete basis set. Correlation energy thus refers to the difference between E_{HF} and the nonrelativistic energy of the molecular species in question.

In a preliminary study¹³ of the effects of polarization functions on calculated energy differences, it was found that unless these functions were used on both the oxygen and hydrogen atoms, little confidence could be placed on the relative as well as the absolute magnitudes of the calculated energy differences. This is caused by the varying effect that a given polarization function will have on the $(E_{HF} - E_{SCF})$ energy term of each molecular species. For example, the calculated proton affinities of OH^- and OH_2 changed by -11.8 and 3.9 kcal/mol, respectively, when polarization functions were added to the basis set. Recent calculations on negative ions¹⁴⁻¹⁶ indicate that additional diffuse s and p basis functions are required on the heavier atom to properly describe negative ions. No diffuse basis functions were used in the present calculations and the lack of these diffuse basis functions appears to be only partially offset by the added polarization functions.

The actual Gaussian basis sets used in these calculations included a (10s,5p,1d) basis set on oxygen contracted by a (4s,2p,1d) basis set. The hydrogen atom was described by a (4s,1p) basis set contracted to a (2s,1p) basis set. The oxygen d exponent (0.706 328) was obtained by extrapolating optimized C and N d exponents.¹⁷ The hydrogen p exponent (0.9) was obtained from previous CI results.¹⁸ All other exponents and contraction coefficients were those suggested by Basch et al.¹⁹

For the species investigated, the above basis sets represented the following basis set sizes:

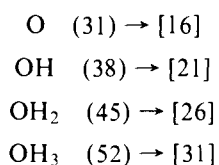


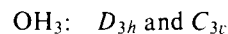
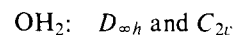
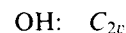
Table I. Computed Total Atomic Energies

Atomic species	State	Total energy, hartree		
		Present	Hartree-Fock	Exptl
H ⁻	1S	-0.405 271	-0.4878 ^a	-0.5245 ^a
H	2S	-0.497 639	-0.5	-0.5
O ⁺	4S	-74.355 627	-74.3726 ^b	-74.6097 ^e
O	3P	-74.793 186	-74.8094 ^c	-75.1101 ^e
O ⁻	2P	-74.748 716	-74.7895 ^d	-75.1639 ^e
O ²⁻	1S	-74.277 585	-74.3184	

^a A. W. Weiss, *Phys. Rev.*, **122**, 1826 (1961). ^b E. Clementi, *J. Chem. Phys.*, **38**, 1001 (1963). ^c E. Clementi et al., *Phys. Rev.*, **127**, 1618 (1962). ^d Reference 25. ^e Reference 6.

No distinction was made in the basis sets for ionic or neutral species.

The potential surfaces $E(r, \phi)$, generated by variation of the O-H bond length (r) and the HOH bond angle (ϕ), were calculated for all of the hydrides listed in the introduction. For economic reasons, these variations were restricted to the following symmetries:



Results and Discussion

Total Energies. The calculated total energies for all of the grid points considered are listed in Table I for atoms, Table II for diatomic hydrides, Table III for triatomic hydrides, and Table IV for quaternary hydrides. In order to economize on the amount of computer time required to compute an energy surface for each species, the increments in both bond angle and bond length variations were deliberately chosen to be quite large. Then, to determine the equilibrium geometries from these surfaces, two methods were employed to determine the significance of the interpolated equilibrium geometries.

First, a polynomial of the form

$$E(r, \phi) = \sum_{i,j=0} a_{ij} r^i \phi^j$$

was fitted to the calculated points by means of least-squares fitting. Generally, a_{ij} was found to be significant only for $i = 0, 2$, and 4 and j varying from 0 to 4 . The minimum of the polynomial was then determined. Second, a third-order spline function fitting routine was used to generate a 51-point square interpolated energy surface. The minimum energy computed by each method agreed to four decimals with the exception of H_2O , where the second method gave an energy 0.0023 hartree higher. The equilibrium bond lengths determined by both methods agreed to three significant figures, whereas the equilibrium bond angles differed by as much as 5° . Again the largest discrepancy occurred in the calculation of the equilibrium bond angle for H_2O . Although the significance of the interpolated equilibrium bond angle could be improved by computing more energy points near the minimum, this was not done, since we were primarily interested in minimum energies which were reproduced to a sufficient accuracy by both fitting methods. Furthermore, in instances where data points are widely spread, the spline function fitting did not always produce a smooth curve along the whole surface. Thus, the equilibrium energies and geometries listed in the tables and used henceforth were those determined by the polynomial least-squares fitting method.

In Tables V-IX no figures are listed under the heading best MO when it was felt that the present calculations were in fact the best.

Table II. Computed Total Energies of Diatomic Oxygen Hydrides

Diatomic species	State	Bond length, bohr			
		1.7	1.8	1.9	2.0
OH ⁺	³ Σ	-74.970 287	-74.979 682	-74.982 651	-74.981 145
OH	² Π	-75.395 631	-75.399 762	-75.397 644	-75.391 203
OH ⁻	¹ Σ	-75.362 878	-75.366 488	-75.364 261	-75.358 129

Table III. Computed Total Energies for H₂O⁻ (²Σ⁻ and ²A₁), H₂O (¹Σ_g and ¹A₁), and H₂O⁺ (²Π and ²B₁)

Bond angle, deg	Species	Bond length, bohr			
		1.7	1.8	1.9	2.1
180.000 000	H ₂ O ⁻	-75.764 339	-75.788 691	-75.802 158	-75.813 431
	H ₂ O	-75.987 121	-75.987 198	-75.975 482	
132.720 720	H ₂ O ⁺	-75.589 613	-75.602 101	-75.602 616	-75.581 579
	H ₂ O ⁻	-75.791 005	-75.812 770	-75.824 526	-75.828 687
124.392 864	H ₂ O	-76.022 428	-76.025 304	-76.016 309	
	H ₂ O ⁺	-75.615 910	-75.628 816	-75.629 455	-75.607 991
120.000 000	H ₂ O ⁻	-75.796 838	-75.817 583	-75.828 006	-75.830 256
	H ₂ O	-76.029 288	-76.032 868	-76.024 488	
109.471 202	H ₂ O ⁺	-75.620 180	-75.633 337	-75.634 108	-75.612 678
	H ₂ O	-76.032 041	-76.036 013	-76.027 969	
95.842 972	H ₂ O ⁻	-75.805 776	-75.824 890	-75.833 108	-75.830 205
	H ₂ O ⁺	-75.613 564	-75.628 779	-75.631 158	-75.611 815
82.952 420	H ₂ O ⁻	-75.799 231	-75.819 535	-75.828 602	-75.826 519
	H ₂ O	-76.015 742	-76.024 552	-76.020 793	

Table IV. Computed Total Energies for H₃O⁻ (¹A₁), H₃O (²A₁), H₃O⁺ (¹A₁), and H₃O²⁺ (²A₁)

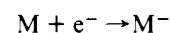
Bond angle, deg	Species	Bond length, bohr				
		1.7	1.8	1.9	2.0	2.2
120.0	H ₃ O ⁻	-76.176 517	-76.222 128	-76.252 650	-76.272 725	-76.288 587
	H ₃ O		-76.420 923	-76.434 554	-76.436 625	-76.416 563
	H ₃ O ⁺	-76.308 506	-76.321 396	-76.316 005	-76.298 147	
	H ₃ O ²⁺	-75.442 970	-75.480 436	-75.498 775	-75.503 959	-75.489 500
117.5	H ₃ O ⁻	-76.178 594	-76.223 221	-76.252 609	-76.271 293	-76.285 492
	H ₃ O		-76.422 098	-76.435 394	-76.436 949	-76.416 580
	H ₃ O ⁺	-76.309 096	-76.322 484	-76.317 518	-76.299 924	
	H ₃ O ²⁺	-75.436 031	-75.473 390	-75.492 225	-75.497 433	-75.482 340
115.0	H ₃ O ⁻	-76.180 467	-76.224 227	-76.252 593	-76.270 092	-76.282 573
	H ₃ O		-76.422 932	-76.435 937	-76.437 100	-76.416 353
	H ₃ O ⁺	-76.309 017	-76.322 925	-76.318 401	-76.301 135	
	H ₃ O ²⁺	-75.428 300	-75.466 028	-75.484 897	-75.490 324	-75.476 360
110.0	H ₃ O ⁻	-76.183 386	-76.225 281	-76.252 483	-76.268 160	-76.277 312
	H ₃ O		-76.423 514	-76.436 094	-76.436 783	-76.415 242
	H ₃ O ⁺	-76.306 707	-76.321 737	-76.318 161	-76.301 706	
	H ₃ O ²⁺	-75.411 100	-75.448 945	-75.467 966	-75.473 906	-75.461 740
105.0	H ₃ O ⁻		-76.226 484	-76.252 001	-76.266 301	-76.272 711
	H ₃ O			-76.434 919	-76.435 362	-76.413 308
	H ₃ O ⁺		-76.317 584	-76.315 073	-76.299 518	
	H ₃ O ²⁺		-75.428 372	-75.448 219	-75.454 599	-75.443 810
95.0	H ₃ O ⁻			-76.247 460	-76.260 755	-76.265 006
	H ₃ O			-76.427 998	-76.428 901	-76.407 262
	H ₃ O ⁺					
	H ₃ O ²⁺				-75.406 371	-75.397 099

Ionization Potentials and Electron Affinities. The adiabatic ionization potential (I_a) for a molecule or ion (M) is defined as the energy absorbed when an electron is removed from a parent molecule or ion while the electron affinity (EA) is defined as the energy released when an electron is captured by a molecule or ion (M). In order to avoid confusion, the thermodynamic conventions will be used to specify energy differences. Thus, all endothermic processes will show a positive energy difference, while exothermic processes will show a negative energy difference.

In the following two reactions



and



since the electronic energy of a bare electron is zero, one may define the following:

$$I_a(M) = E^{M^+}(\text{Re}) - E^M(\text{Re})$$

$$EA(M) = E^{M^-}(\text{Re}) - E^M(\text{Re})$$

Subdividing the total energies into Hartree-Fock, correlation,

Table V. Equilibrium SCF Energies for Oxygen Hydrides As Determined by Least-Squares Polynomial Fitting

Species	SCF energies, hartree			Exptl
	Present	Best MO	Hartree-Fock ^a	
OH ⁺ (³ Σ ⁻)	-74.9827	-75.0004 ^b	-75.001	-75.300
OH (² Π)	-75.3998	-75.4213 ^b	-75.422	-75.780 ^b
OH ⁻ (¹ Σ _g)	-75.3665	-75.4175 ^c	-75.418	-75.847 ^b
OH ₂ ⁺ (² B ₁)	-75.6375		-75.668	
OH ₂ (¹ A ₁)	-76.0410	-76.066 ^d	-76.068	-76.485
OH ₂ ⁻ (² A ₁)	-75.8342		-75.865	
OH ₃ ²⁺ (² A ₁)	-75.5039		-75.534	
OH ₃ ⁺ (¹ A ₁)	-76.3233	-76.3433 ^e	-76.350	
OH ₃ (² A ₁)	-76.4380		-76.468	
OH ₃ ⁻ (¹ A ₁)	-76.2886 ^f			

^a Hartree-Fock energies are estimated from either best MO or present results. ^b Reference 6. ^c Reference 7. ^d H. Popkie, H. Kistenmacher, and E. Clementi, *J. Chem. Phys.*, **59**, 1325 (1973). ^e Reference 8. ^f Calculated at $r = 2.2$ bohr and $\phi = 120^\circ$.

Table VI. Bond Lengths for Oxygen Hydrides

Molecule	r_e , bohr		Exptl
	Theoretical		
	Present	Best MO	
OH ⁺ (³ Σ ⁻)	1.909	1.795 ^a	1.9443
OH (² Π)	1.811	1.795 ^a	1.8342
OH ⁻ (¹ Σ _g)	1.806	1.781 ^b	1.834
OH ₂ ⁺ (² B ₁)	1.86		1.89 ^f
OH ₂ (¹ A ₁)	1.79	1.778 ^c	1.81
OH ₂ ⁻ (² A ₁)	1.95		
OH ₃ ²⁺ (² A ₁)	2.00		
OH ₃ ⁺ (¹ A ₁)	1.82	1.823 ^d	1.91 ^e
OH ₃ (² A ₁)	1.96		
OH ₃ ⁻ (¹ A ₁)	∞		

^a Table V, footnote a. ^b Table V, footnote b. ^c Table V, footnote d. ^d Reference 10. ^e T. H. Dunning, R. M. Pitzer, and S. Aung, *J. Chem. Phys.*, **57**, 5044 (1972). ^f H. Lew and I. Heiber, *ibid.*, **58**, 1246 (1973).

Table VII. Bond Angles (ϕ) for Oxygen Hydrides

Molecule	ϕ , deg		Exptl
	Theoretical		
	Present	Best MO	
OH ₂ ⁺	113.4		110.50 ^d
OH ₂	105.2	106.6 ^a	104.5 ^b
OH ₂ ⁻	105.4		
OH ₃ ²⁺	120.0		
OH ₃ ⁺	114.2		110.4 ^c
OH ₃	113.0		
OH ₃ ⁻	120.0		

^a Table V, footnote d. ^b Table V, footnote e. ^c L. Basile, P. La-Bonville, J. R. Ferraro, and J. M. Williams, *J. Chem. Phys.*, **60**, 1981 (1974). ^d Table VI, footnote f.

relativistic, and zero-point energy contributions, the I_a of a molecule may be written as

$$I_a(M) = \Delta E_{\text{HF}}^M(\text{Re}) + \Delta E_C^M(\text{Re}) + \Delta E_R^M(\text{Re}) + \Delta E_{\text{ZP}}^M(\text{Re})$$

where

$$\Delta E_{\text{HF}}^M(\text{Re}) = E_{\text{HF}}^{M+}(\text{Re}) - E_{\text{HF}}^M(\text{Re})$$

and where the remaining energy differences are written in an analogous manner.

For a stable molecule (M), it is generally assumed that both $\Delta E_{\text{HF}}^M(\text{Re})$ and $\Delta E_C^M(\text{Re})$ are both greater than zero. For the present discussion, it will be assumed that both $\Delta E_R^M(\text{Re})$

Table VIII. Inversion Barriers for Nonplanar Oxygen Hydrides

Molecule	Inversion barrier, kcal/mol	
	Present	Best MO
OH ₂ ⁺	20.6	
OH ₂	31.6	
OH ₂ ⁻	13.1	
OH ₃ ⁺	1.2	1.5 ^a
OH ₃	0.6	

^a Table V, footnote e.

Table IX. Hartree-Fock Ionization Potentials of Oxygen Hydrides

Molecule	Theoretical, eV		Exptl, eV
	Present	Best MO	
OH	11.3	11.4 ^a	13.36
OH ₂	11.0		12.65 ^b
OH ₃ ⁺	22.3		
OH ₃	3.1		

^a Table V, footnote b. ^b W. L. Smith, *Mol. Phys.*, **26**, 361 (1973).

and $\Delta E_{\text{ZP}}^M(\text{Re})$ are negligible and can be ignored. Thus, considering the known experimental ionization potentials of OH and OH₂ and the Hartree-Fock energies listed in Table V, $\Delta E_C^M(\text{Re})$ may be estimated as 1.90 eV for OH and 1.77 eV for OH₂. Based on these results, the ionization potentials listed in Table IX and illustrated in Figure 1 may be considered to differ from the experimental values by approximately 1.75 ± 0.25 eV.

The electron affinity of a molecule (M) may be subdivided into energy differences in a manner analogous to the subdivision of the ionization potential.

$$\text{EA}(M) = \Delta E_{\text{HF}}^{(M)}(\text{Re}) + \Delta E_C^{(M)}(\text{Re}) + \Delta E_R^{(M)}(\text{Re}) + \Delta E_{\text{ZP}}^{(M)}(\text{Re})$$

where

$$\Delta \text{EA}_{\text{HF}}^{(M)}(\text{Re}) = E_{\text{HF}}^{(M-)}(\text{Re}) - E_{\text{HF}}^{(M)}(\text{Re})$$

and where the other total energy component differences are defined similarly. As before, we shall assume that $\Delta E_R^{(M)}(\text{Re})$ and $\Delta E_{\text{ZP}}^{(M)}(\text{Re})$ are negligible. For a stable negative ion to be formed in this electron capture process, $\Delta E_{\text{HF}}^{(M)}(\text{Re})$ must generally be a negative number or a small positive number. In the event that $E_{\text{HF}}^{(M)}(\text{Re})$ is positive and the negative ion is stable, then the binding energy of the excess electron must be attributed to correlation, relativistic, and zero-point energy contributions.

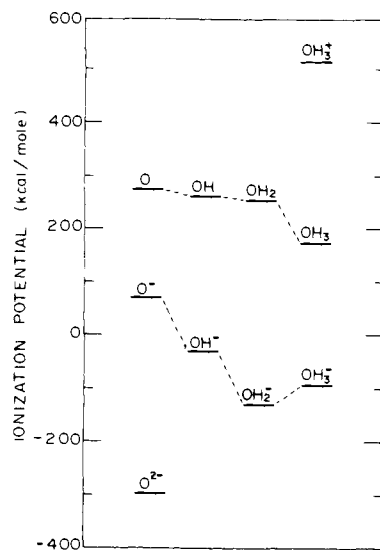


Figure 1. Ionization potentials of oxygen and its simple hydrides.

The electron affinities (eV) calculated from the SCF energies listed in Tables I and V are 2.51, 1.21, 0.91, and 5.63 for H, O, OH, and OH₂, respectively, and a number <4.06 eV for OH₃. The corresponding experimental²⁰ electron affinities (eV) are -0.7542, -1.456, and -1.83 for H, O, and OH, respectively. From the experimental and Hartree-Fock EA of H, O, and OH, one may deduce a value of -1.00, -2.01, and -1.94 eV for the respective correlation energy ($\Delta E_C^{(M)}(\text{Re})$) contributions to the EA. Combining these correlation energy estimates with the SCF results above leads to a predicted EA of 1.51 eV for H, -0.80 eV for O, and -1.03 eV for OH. These results are still in error by 300, 45, and 44%. This error is principally due to the inability of an LCAO-MO-SCF method to describe both ionic and neutral species equally well without modifications being made in the exponents of the basis functions. Even so, it is possible to more accurately estimate the EA of OH₂ and OH₃ by making two assumptions: that the respective SCF error and correlation energy corrections of O and OH may be averaged and then, that this average (-2.70 eV) does not materially change for other hydrides. (Due to its anomalous behavior, H is excluded from the averaging.) Using this average correction, the EA of OH₂ and OH₃ may be estimated to be 2.9 and <1.4 eV. The value of 2.9 eV and especially the positive sign of the EA of OH₂ is in accord with a previous²¹ interpretation of the electron scattering spectra of H₂O where it was stated that OH₂⁻ decays to H₂O ($X^{-1}A_1$) + e⁻. It should be noted that the SCF energy differences here do not preclude dissociation of OH₂⁻ to H(²S) + OH(¹ Σ^+). This is in contradiction to studies by Webster¹⁶ and Claydon, Segal, and Taylor.²¹

Proton Affinities. The proton affinity (A_{H^+}) is here defined as the energy difference between the protonated species and the parent molecule in the following reaction: $M + H^+ \rightarrow MH^+$.

Noting that the energy of a bare proton is zero, the A_{H^+} of a molecule may be defined in a manner analogous to the previous definition for the ionization potential

$$A_{H^+}(M) = \Delta E_{\text{HF}}^{(M)}(\text{Re}) + \Delta E_C^{(M)}(\text{Re}) + \Delta E_R^{(M)}(\text{Re}) + \Delta E_{\text{ZP}}^{(M)}(\text{Re})$$

Summing the correlation and relativistic terms

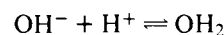
$$A_{H^+}(M) = \Delta E_{\text{HF}}^{(M)}(\text{Re}) + \Delta E_{C+R}^{(M)}(\text{Re}) + \Delta E_{\text{ZP}}^{(M)}(\text{Re})$$

The above formula can then be applied either to obtain the experimental A_{H^+} or, given the experimental A_{H^+} and two other quantities, to determine the third theoretical quantity.

Unfortunately, few experimental oxygen hydride proton affinities have been determined to reasonable accuracies. Thus, the formulation of A_{H^+} in terms of theoretical components is of little use for the determination of exact molecular correlation and relativistic energy corrections. However, if one determines a single correlation-relativistic correction for the hydride series, then, assuming the $\Delta E_{C+R}^{(M)}(\text{Re})$ remains constant for each increased oxygen-hydrogen bond, one can make an effort to more exactly approximate experimental A_{H^+} from approximate Hartree-Fock calculations.

One of the more recent experimental determinations²² of the proton affinity of OH₂ lists a value of -166 ± 2.3 kcal/mol. The zero-point energy difference between OH₃⁺ and OH₂ has been previously estimated²³ as 8.8 kcal/mol. Using these values and the Hartree-Fock energies, $\Delta E_{C+R}^{(OH_2)}$ may be calculated to be 2.2 kcal/mol.

For the reaction



ΔE_{HF} may be calculated to be -408 kcal/mol from the Hartree-Fock energies, and assuming that $\Delta E_{\text{ZP}}^{(OH^-)} = 7.1$ kcal/mol leads to a value of 8.9 or 30.9 kcal/mol for $\Delta E_{C+R}^{(OH^-)}$ depending upon whether $A_{H^+}(OH^-)$ is taken as -392 or -370 kcal/mol,²⁴ respectively.

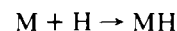
Both of the above results are contrary to an assumption that an increase in the number of oxygen-hydrogen bonds leads to an increase in the magnitude of the correlation energy. One rationalization of the positive $\Delta E_{C+R}^{(M)}(\text{Re})$ can be made by assuming that $\Delta E_{\text{HF}}^{(M)}(\text{Re})$ is, in fact, incorrect. Hopkinson et al.²⁴ have shown that as the quality of the basis set used to describe a molecule is increased, the calculated A_{H^+} converges to the experimental in the sense that $\Delta E_{\text{HF}}^{(M)}(\text{Re})$ is increased (decreased in magnitude) when the quality of the basis set is increased. However, in the above calculations for H₂O and OH⁻ a negative $\Delta E_{C+R}^{(M)}(\text{Re})$ could only be obtained by increasing $\Delta E_{\text{HF}}^{(M)}(\text{Re})$ by approximately 10 kcal/mol or 0.016 hartree. Assuming that the Hartree-Fock limit for H₂O is exact, this increase in ΔE_{HF} implies a decrease in the Hartree-Fock energy of H₃O⁺ from -76.350 to -76.366 hartree. Similarly, assuming that the Hartree-Fock limits for both H₂O and OH⁻ are correct, then one would have to estimate the A_{H^+} of OH⁻ as <-402 kcal/mol. Neither of the above possibilities is as reasonable as assuming that for the isoelectronic series

$$E_C(OH^-) < E_C(H_2O) < E_C(H_3O^+) \\ \text{or } |E_C(OH^-)| > |E_C(H_2O)| > |E_C(H_3O^+)|$$

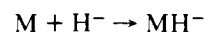
A recent CI calculation²⁵ gives numerical confirmation to the above statement for the H₂O-H₃O⁺ pair.

The proton affinities listed in Table X and illustrated in Figure 2 are computed without including any contributions due to correlation and relativistic effects. It is understood that these A_{H^+} will be less than the experimental A_{H^+} by at least 10 kcal/mol.

Hydrogen and Hydride Affinities. The hydrogen (A_H) and hydride affinities (A_{H^-}) can be defined for the reactions



and



in a manner analogous to the definition of proton affinities. For both cases, the relativistic energy differences will be assumed to be negligible and $\Delta E_{C+R}^{(M)}(\text{Re})$ may be reduced to $\Delta E_C^{(M)}(\text{Re})$.

For hydrogen affinities, since the bare hydrogen atom possesses no correlation energy, $\Delta E_C^{(M)}(\text{Re})$ will in general be a negative number. A reliable estimate to the correlation energy contribution to the A_H of a molecule M can be made by

Table X. Proton Affinities of Oxygen and Its Hydrides

Species	Theoretical, kcal/mol		Exptl or best estimate, kcal/mol
	Present	Hartree-Fock	
O	-119	-120	-107 ^a
O ⁻	-409	-397	-384 ^a
O ²⁻	-684		
OH	-149	-154	
OH ⁻	-423	-408	-395 ^a
OH ₂	84	84	
OH ₂ ⁺	-177	-177	-166 ^b
OH ₂ ⁻	-379	-379	

^a Estimated. ^b Reference 20.

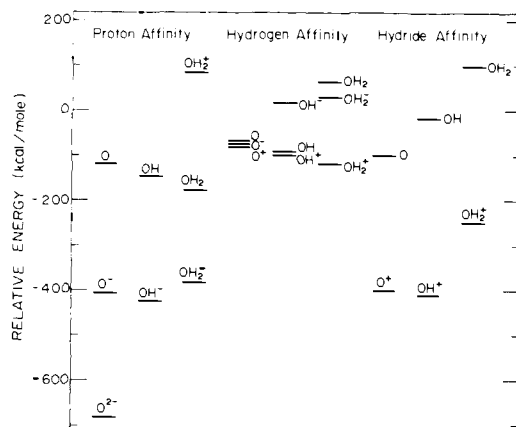


Figure 2. Proton, hydrogen, and hydride affinities of oxygen and its hydrides.

recognizing that the A_H of M is the negative of the dissociation energy of MH. Thus,

$$-\Delta E_C^{(M)}(\text{Re}) = \Delta E_{\text{HF}}^{(M)}(\text{Re}) + \Delta E_{\text{ZP}}^{(M)}(\text{Re}) + D_0^0(\text{M-H})$$

Using the experimental values²⁶ of D_0^0 and zero-point energies for OH and OH₂ and the listed Hartree-Fock energies,

$$-\Delta E_C^{(\text{O})} = -71.5 + 5.08 + 100.35 = 33.9 \text{ kcal/mol}$$

$$-\Delta E_C^{(\text{OH})} = -92.28 + 8.07 + 117.88 = 33.7 \text{ kcal/mol}$$

As an approximation to the A_H of those atoms or molecules for which no experimental observations could be found, the best estimate in Table XI is determined by adding -34 kcal/mol (estimated contribution of ΔE_C) to the Hartree-Fock A_H . It must be noted that although the value of E_C remained constant for O and OH, there might be a more marked change for E_C of ions. Thus, the estimated A_H values for the ions may deviate from experimental values more than the estimated A_H for neutral species.

Hydride affinities (A_{H^-}), calculated in a manner analogous to hydrogen affinities, are listed in Table XII and illustrated in Figure 2. On comparing the calculated and Hartree-Fock hydrogen and hydride affinities, one may note the excellent agreement of the hydrogen affinities and the very poor agreement of the hydride affinities. As previously stated, to obtain experimentally meaningful results by calculating correlation energy corrected SCF energy differences between reactants and products, it must be assumed that the calculated SCF energy do not deviate from their respective Hartree-Fock limits to significantly different degrees. For example, in the calculation of the hydrogen affinity of OH₃ the SCF energies of H, OH, and OH₂ differ by 1.5, 13.9, and 16.9 kcal/mol from their respective Hartree-Fock limits. However, in the calculation of the hydride affinity of OH⁺, the SCF energies of H⁻,

Table XI. Hydrogen Affinities of Oxygen Hydrides

Molecule	Theoretical, kcal/mol		Exptl or best estimate
	Present	Hartree-Fock	
O ⁺	-80.7	-80.7	-115 ^a
O	-69.2	-71.5	-100.4 ^b
O ⁻	-76.1	-80.7	-115 ^a
OH ⁺	-99.2	-104	-138 ^a
OH	-90.1	-91.6	-117.9 ^b
OH ⁻	18.8	33.3	-0.7 ^a
OH ₂ ⁺	-118	-115	-149 ^a
OH ₂	63.2	62.8	28.3 ^a
OH ₂ ⁻	<27.1		

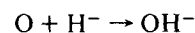
^a Estimated results obtained by adding -34 kcal/mol to Hartree-Fock value. ^b Reference 24.

Table XII. Hydride Affinities of Oxygen Hydrides

Species	Present	Hartree-Fock
O ⁺	-401	-352
O	-105	-76
OH ⁺	-410	-364
OH	-18	28
OH ₂ ⁺	-248	-196
OH ₂	<99	

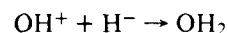
OH⁺, and OH₂ differ by 51.8, 11.5, and 16.9 kcal/mol from their respective Hartree-Fock limits. Thus, while in the calculation of hydrogen affinities the deviations of the SCF energies from their Hartree-Fock limits tend to cancel, this is not the case in the calculation of hydride affinities where the calculated SCF energy of the hydride ion is anomalously inaccurate. Although the addition of correlation energy corrections to the calculated SCF hydride affinities would be superfluous, the good agreement between the SCF and Hartree-Fock proton and hydrogen affinities does imply that the present estimates of the Hartree-Fock energies are reasonably accurate and can be corrected for correlation energy differences.

Assuming that the relativistic energy of OH⁺, OH⁻, and OH₂ is identical with that of the oxygen atom,²⁷ and using the Hartree-Fock and experimental energies listed in Tables I and V, the correlation energy differences for the following reactions are as follows:



$$E_C (\text{au}) -0.258 -0.037 -0.376$$

$$\Delta E_C (\text{kcal/mol}) -50.8$$



$$E_C (\text{au}) -0.250 -0.037 -0.368$$

$$\Delta E_C (\text{kcal/mol}) -50.8$$

Then, assuming that ΔE_C remains constant for all of the species listed in Table XII, the experimental hydride affinities may be estimated to be approximately 51 kcal/mol lower than the Hartree-Fock affinities listed in Table XII.

Summary

Figure 3 shows all of the hydrides which were studied and summarizes the relative SCF energy changes which have been calculated here. The arrows in this figure show the energetically most favored direction for any reaction under the appropriate conditions. Horizontal arrows indicate hydrogen atom attachment or detachment reactions,

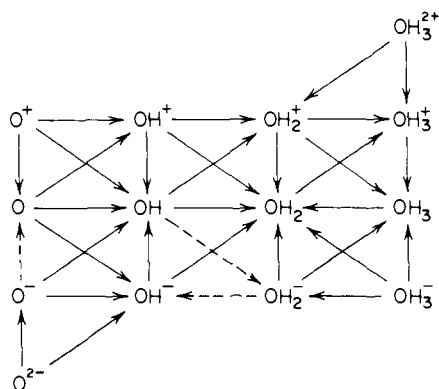
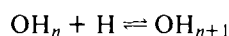
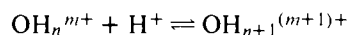
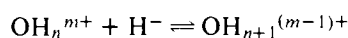


Figure 3. Energetically favored processes of oxygen hydrides.



diagonal arrows indicate either hydride ion or proton attachment or detachment reactions,

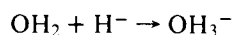
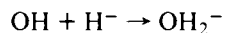


and vertical arrows indicate electron attachment or detachment reactions.

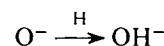
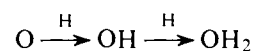
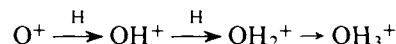


Also, the broken arrows indicate energy differences which were calculated here, but which are either so small in magnitude as to leave the true direction in doubt or do not conform with better theoretical or known experimental data.

The more certain conclusions shown in Figure 3 may be summarized as follows: (1) The attachment of a proton to a negative or neutral species always leads to a product which is lower in energy than the reactants. (2) The attachment of a hydride ion to a positive or neutral species leads to a decrease in energy except for the reactions



(3) The attachment of a hydrogen atom is energetically favored for the series



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