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ON SIMPLIFYING THE AIIR METHOD FOR DETERMINING THE H-R BOND ENTHALPY BASED ON COMPUTATIONAL RESULTS

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Abstract

A simplified method of calculating AIIR bond dissociation energies is derived and applied. The results presented can be used to calculate 298 K H-R bond dissociation energies at CBS-QB4, CBS-4M, G1, G2, G2MP2, G3, G3B3, G3MP2, G3MP2B3, G4, and G4MP2 levels of theory.

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Introduction

A recent paper [1] described the Averaged Isodesmic Isogyric Reactions (AIIR) method for calculating a high-accuracy H-R (where R can represent any type of fragment) bond enthalpy based on computational data. Briefly, the method suggests combining the calculated reaction enthalpy for a set of isodesmic, isogyric reactions of the form

$$H\text{-}R + X \rightarrow H\text{-}X + R \qquad (1)$$

by choosing a set of hydrogen abstractors X for which the bond enthalpy D(H-X) is well known experimentally. Using computational values for the thermally-corrected total energies of the molecules H-R, X, H-X, and R, the reaction enthalpy can be calculated from

$$\Delta_{rxn}H = E_{H\text{-}R} + E_X - E_{H\text{-}X} - E_R \qquad (2)$$

where E_q represents the thermally corrected total energy of the species q. The reaction enthalpy can also be determined from bond enthalpies.

$$\Delta_{rxn}H = D(H\text{-}R) - D(H\text{-}X) \qquad (3)$$

The AIIR method uses the reaction enthalpy calculated using equation (2) in conjunction with a well-known bond dissociation energy D(-H-X) taken from the literature to determine the bond enthalpy of interest, D(H-R) using equation (3).

The paper suggests thirteen examples of choices for the hydrogen abstractor X and presents results comparing calculated H-R bond enthalpies to experimental values taken from the literature. The H-R bond energy D(H-R) is the calculated as an averaged value over the set of results obtained for each choice of the abstractor X. The authors also compare the results to 31 values taken from the literature and determine Mean Absolute Deviations (MAD) to gauge the reliability of the method.

In this letter, we show that this method can be greatly simplified by recognizing that the values of E_X, $E_{H\text{-}X}$, and D(H-X) are independent of the H-R molecule of interest. As such, their contributions to the averaged value of D(H-R) will be the same for a given level of theory.

Simplifying AIIR

The fact that E_x, $E_{H\text{-}X}$, and D(H-X) are independent of the choice of the H-R molecule of interest greatly simplifies the calculation of the averaged calculated value of the dissociation energy D(H-R) by reducing the number of parameters for each level of theory to two, instead of the 39 required in the original presentation. Demonstration of this is straight forward.

The bond dissociation energy of interest, D(H-R), can be calculated from the reaction enthalpy and experimental value of D(H-X) by rearranging equation (3)

$$D(H\text{-}R) = \Delta_{rxn}H + D(H\text{-}X) \qquad (4)$$

Substituting the expression for $\Delta_{rxn}H$ from equation (2) produces

$$D(H\text{-}R) = E_{H\text{-}R} + E_X - E_{H\text{-}X} - E_R + D(H\text{-}X) \qquad (5)$$

The averaged value D_{AIIR}(H-R) is then determined by adding the results for each X employed and dividing by the number of abstractors (N_X) used.

$$D_{AIIR}(H\text{-}R)=\frac{1}{N_X}\sum_X\left\{E_{H-R}+E_x-E_{H-X}-E_R+D(H-X)\right\} \qquad (6)$$

Using the commutative property of addition, equation (6) can be re-written

$$D_{AIIR}(H\text{-}R)=\frac{1}{N_X}\left\{\sum_X E_{H-R}+\sum_X E_x-\sum_X E_{H-X}-\sum_X E_R+\sum_X D(H-X)\right\} \qquad (7)$$

Noting that $E_{H\text{-}R}$ and E_R are completely independent of the choice of X, the sums involving these terms can be simplified.

$$\sum_X E_{H-R} = N_X\left(E_{H-R}\right) \qquad (8)$$

$$\sum_X E_R = N_X\left(E_R\right) \qquad (9)$$

And so equation (7) becomes

$$D_{AIIR}(H-R)=\frac{1}{N_X}\left\{N_X(E_{H-R})+\sum_X E_X-\sum_X E_{H-X}-N_X(E_R)+\sum_X D(H-X)\right\} \qquad (10)$$

This expression can be rearranged to a sum of two terms.

$$D_{AIIR}(H\text{-}R)=\left\{E_{H-R}-E_{R}\right\}+\frac{1}{N_{X}}\left\{\sum_{X}\left[E_{X}-E_{H-X}+D(H-X)\right]\right\} \quad (11)$$

The second term in this expression is, of course, independent of the choice of the fragment R and thus really only need to be determined once. It can then be applied to the calculation of D_{AIIR}(H-R) simply as a correction to the difference between E_{H-R} and E_R.

This also implies that for a desired set of units, the calculation of D_{AIIR}(H-R) is can be reduced to a simple linear function of the difference between E_{H-R} and E_R.

$$D_{AIIR}(H\text{-}R) = a(E_{H-R}-E_{R}) + b \quad (12)$$

In this project, we have fit the results of calculations presented by Khorasani and Fleming [1] to this expression in order to determine the values of *a* and *b* for a simplified version of the calculation of D_{AIIR}(H-R) based on computational data. Dissociation enthalpies calculated using these coefficients will be identical to those calculated using the more complete method discussed in reference [1]. We also provide an example calculation to demonstrate the simplicity and utility of the method.

Methodology and Results

Using the data from Khorasani and Fleming [1], Blanksby and Ellison [2], and also data taken from the Active Thermochemical Tables [3], values of *a* and *b* in equation (12) can be determined by a simple least-squares fit. G4 [4] data used for a fit to equation (12) are shown in Table I and Figure 1. Briefly, Equation (12) uses thermally corrected, single-point total energies as reported by Gaussian 16 [5] at one of the eleven levels of theory included in reference [1]. The bond energies are calculated as the reaction enthalpy for a reaction of the form

$$H\text{-}R\ (g) \quad \rightarrow \quad H(g) + R(g) \quad (13)$$

using enthalpies of formation taken from the Active Thermochemical Tables (ATcT)[3] where the data are available. Additional experimental values, where ATcT data do not exist, were taken from reference [2].

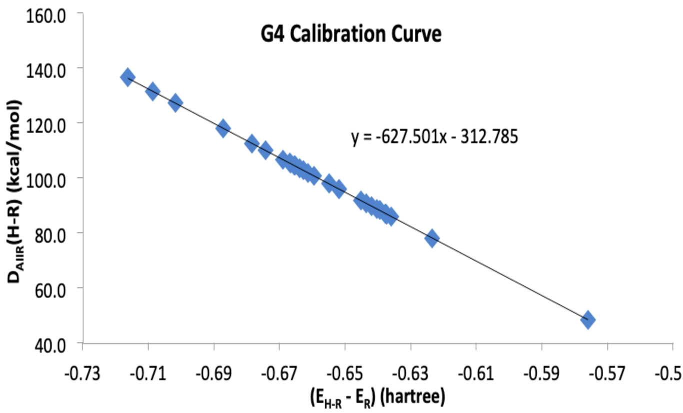

Figure 1. Relationship between 31 calculated DAIIR(H-R) and (EH-R - ER) values calculated at the G4 level of theory at 298 K.

The results of fitting the data for all eleven levels of theory presented by Khorasani and Fleming are shown in Table II. All molecular energy calculations have been performed using the Gaussian 16 [5] package on an Intel Core i5 based PC running Debian Linux [6].

Example Calculation

As an example of the application of these results, consider the calculation of the bond enthalpy for the first C-H bond broken in methane, as well as mono-, di-, and tri-fluoro substituted methane molecules at the G3B3 [4] level of theory. To find this difference, one must calculate the thermally corrected total energy (reported by Gaussian 16 [5] as the G3 Energy) of each parent molecule, and each of the corresponding radicals. From these data, the bond enthalpy can be calculated using the expression

$$D_{AIIR}(H\text{-}R)=-627.117\frac{kcal}{mol\ hartree}\left(E_{H-R}-E_{R}\right)-312.395\frac{kcal}{mol} \quad (14)$$

These results are shown in Table III. For comparison, The literature values of D(H-CH_3) and D(H-CF_3) are 104.916 ±0.013 and 106.58 ± 0.61 kcal/mol at 298 K respectively, based on data found in the ATcT [3]. Given the estimated uncertainty of AIIR calculations at the G3B3 level of theory of 0.69 kcal/mol, the values agree within the combined uncertainties.

Conclusion

The results from this project greatly simplify the application of the AIIR method to calculate H-R bond dissociation energies. The simplification reduces the problem to simply finding the difference between he thermally corrected total energy of the H-R molecule and the R fragment, and applying equation (12) using parameters for the chosen level of theory.

This same methodology can be used for any level of theory for which thermally corrected total energies for the species R and H-R can be determined. However, because the values of E_R, E_{H-R}, E_x, and E_{H-X} can only be compared when calculated at the same level of theory, the determination of the coefficients a and b need to be determined separately for each unique level of theory. However, as new results are generated at as of yet impracticable levels of theory, the simplification outlined in this paper can be used to make the calculation of H-R bond dissociation energies quite simple.

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Table I. Thermally corrected G4 total energies and differences for 31 H-R molecules and their associate D(H-R) bond enthalpies calculated using the AIIR method.

H-R	$E_{H\text{-}R}$	E_R	$E_{H\text{-}R}$-E_R	D_{AIIR}(H-Y)
	(Hartree)			(kcal/mol)
H-H	-1.165662	-0.500004	-0.665658	104.976
H-Cl	-460.676356	-460.013636	-0.662720	103.069
H-OH	-76.394411	-75.707113	-0.687298	118.466
H-F	-100.419992	-99.703566	-0.716426	136.818
H-CH$_3$	-40.462439	-39.796853	-0.665586	104.868
H-ONO	-205.640395	-205.016797	-0.623598	78.471
H-NO	-130.432227	-129.856237	-0.575990	48.677
H-NH$_2$	-56.514755	-55.845601	-0.669154	107.082
H-CHO	-114.450315	-113.810749	-0.639566	88.573
H-Br	-2574.221604	-2573.583929	-0.637675	87.354
H-OOH	-151.491313	-150.853981	-0.637332	87.120
H-CN	-93.390208	-92.688463	-0.701745	127.661
H-CCH	-77.287436	-76.578736	-0.708700	131.812
H-ONO$_2$	-280.800264	-280.138879	-0.661385	102.235
H-C$_2$H$_5$	-79.734607	-79.075099	-0.659508	101.058
H-CH$_2$OH	-115.648429	-114.996442	-0.651987	96.338
H-C$_2$H$_3$	-78.518820	-77.844548	-0.674272	110.322
H-OCH$_3$	-115.648429	-114.983063	-0.665366	104.734
H-SH	-399.255626	-398.611864	-0.643762	91.177
H-C(O)CH$_3$	-153.739882	-153.099430	-0.640452	89.100
H-OC$_2$H$_5$	-154.929862	-154.265842	-0.664020	103.889
H-C$_6$H$_5$	-232.089547	-231.411057	-0.678490	112.969
H-CH(CH$_3$)$_2$	-119.011199	-118.356197	-0.655002	98.230
H-C(CH$_3$)$_3$	-158.291216	-157.639171	-0.652045	96.374
H-CH$_2$CHCH$_2$	-117.799750	-117.161917	-0.637833	87.456
H-SiH$_3$	-291.723405	-291.078007	-0.645398	92.203
H-SCH$_3$	-438.525591	-437.889499	-0.636092	86.364
H-H(CH$_3$)C$_2$H$_5$	-158.288096	-157.633104	-0.654992	98.224
H-CH$_2$C$_6$H$_5$	-271.371095	-270.728925	-0.642170	90.178
H-OCH(CH$_3$)$_2$	-194.213258	-193.546402	-0.666856	105.669
H-OC(CH$_3$)$_3$	-233.497594	-232.830523	-0.667071	105.803

Values of Coefficients used in Equation (12)

Level of Theory	a (kcal mol^{-1} $hartree^{-1}$)	b (kcal mol-1)	Est. Uncertainty [1] (kcal/mol)
CBS-4M	-626.339	-314.790	1.78
CBS-QB3	-627.560	-312.910	0.73
G1	-627.699	-312.748	1.18
G2	-627.910	-313.534	0.93
G2MP2	-628.005	-313.872	0.90
G3	-628.085	-313.080	0.82
G3B3	-627.177	-312.395	0.69
G3MP2	-628.020	-313.648	0.90
G3MP2B3	-627.107	-313.050	0.80
G4	-627.501	-312.785	0.49
G4MP2	-627.414	-313.331	0.65

Table II. Coefficients for thermally corrected data calculated at the specified level of theory fit to equation (12). These data pertain to calculating D(H-R) at 298 K.

G3B3 Energies at 298.15 K

	$E_{H\text{-}R}$	E_R	difference	D(H-R) calc	Lit. [3]
		(hartree)		(kcal/mol)	
H-CF_3	-338.088497	-337.419072	-0.66942	107.41	106.58(61)
H-CHF_2	-238.863206	-238.202181	-0.66102	102.15	--
H-CH_2F	-139.649142	-138.989339	-0.65980	101.38	--
H-CH_3	-40.455412	-39.790499	-0.66491	104.58	104.916(13)

Table III. Results for D(H-R) (R = CF_3, CHF_2, CH_2F, and CH_3) calculated using the Simplified AIIR method at the G3B3 level of theory. The Mean Absolute Deviation (MAD) for D_{AIIR}(H-R) is 0.83 kcal/mol [1].