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Correlating Acidities, Electron Affinities, and Bond Dissociation Energies. Measure One, Get All Three!

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Bond energies, acidities, and electron affinities are related in a thermodynamic cycle, and by measuring two of these quantities one can derive the third. This procedure is most often used to determine bond dissociation energies. In this work, we show that $\Delta H^\circ_{\mathrm{acid}}(\mathrm{HX})$, $\mathrm{EA}(\mathrm{X}^\bullet)$, and BDE(HX) are all linearly related for specific classes of compounds (e.g., alcohols and carboxylic acids), and therefore, only one of these quantities is needed to determine the others. This should simplify thermodynamic determinations and enable hundreds of new values to be obtained from already existing data in the literature. The intercepts obtained from plots of $\Delta H^\circ_{\mathrm{acid}}(\mathrm{HX})$ vs $\mathrm{EA}(\mathrm{X}^\bullet)$ provide bond energies which correspond to BDE(HX) when $\mathrm{EA}(\mathrm{X}^\bullet) = 0$. The results for eight different types of compounds are provided and some of these values are discussed. Sensitivity factors are obtained from the slopes of these plots, and their sign (+ vs −) can be predicted by considering physical effects such as hybridization and resonance.

Introduction

Thermochemical data play an essential role in the foundation of chemistry and enable critical insights into reaction processes to be obtained. For reactions involving radical intermediates, no quantity is more important than the homolytic bond dissociation energy (BDE). A variety of methods have been developed to measure them but no approach is more versatile or reliable than gas-phase negative-ion techniques which make use of the thermodynamic cycle shown in eq 1.[1] In principle, this relationship can be used to provide any of the three thermodynamic quantities (BDE(HX), $\Delta H^\circ_{\mathrm{acid}}(\mathrm{HX})$, and $\mathrm{EA}(\mathrm{X}^\bullet)$) by measuring the other two, given that the ionization potential of hydrogen is well-known to be 313.58 kcal mol^{-1}. This was first recognized at least as far back as

$$\mathrm{BDE(HX)} = \Delta H^\circ_{\mathrm{acid}}(\mathrm{HX}) - \mathrm{IP}(\mathrm{H}^\cdot) + \mathrm{EA}(\mathrm{X}^\cdot) \tag{1}$$

1938[2] and was used to establish the absolute gas-phase acidity scale.[3] These days, however, it is most commonly employed to provide bond energies by measuring acidities and electron affinities. Unfortunately, the accurate and precise determination of these quantities typically requires considerable effort. This situation would be greatly simplified if one could obtain bond energies or either of the other two parameters by measuring just one of the three terms and deriving the other two. This would facilitate such measurements and would provide hundreds of new bond energies, acidities, and electron affinities from data already reported in the literature. In this paper we demonstrate that for many classes of compounds this can be accomplished and the subsequent results are discussed.

Methodology

Experimentally determined gas-phase acidities, electron affinities, and bond dissociation energies were obtained from the NIST web site (www.nist.gov) and a few additional sources.[1,3−5] One of these quantities, usually the bond energy, was derived using eq 1. In principle, a small temperature correction should be included in eq 1 since acidities typically are determined at 298 K while the ionization potential of hydrogen and spectroscopically determined electron affinities are 0 K values. Many electron affinities have been measured by high-pressure equilibrium methods at 423 K,[6] however, and the thermal corrections invariably are small (<0.5 kcal mol^{-1})[1a,7] so they were omitted in this work. Computational

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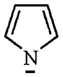
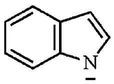
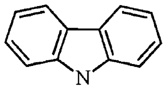
TABLE 1. Literature Acidities, Electron Affinities, and Bond Energies for Alkoxides (RO^-) and Their Derived Values Using the Observed Linear Correlation in Figure 1[a]

RO^{-b}	$\Delta H^\circ_{acid}(ROH)$		$EA(RO\cdot)$		$BDE(ROH)$	
	expt	plot[c]	expt	plot[d]	expt	plot[e]
CH_3O^{-f}	381.9 ± 0.5	381.5	36.3 ± 0.1	35.8	104.6 ± 0.7	104.1 (104.1)
$CH_3CH_2O^{-f}$	378.7 ± 0.8	378.6	39.5 ± 0.1	39.3	104.7 ± 0.8	104.4 (104.4)
$(CH_3)_2CHO^{-f}$	376.6 ± 0.7	375.7	42.6 ± 0.1	41.6	105.7 ± 0.7	104.6 (104.7)
$(CH_3)_3CO^{-f}$	375.8 ± 0.7	374.5	44.0 ± 0.1	42.5	106.3 ± 0.7	104.7 (104.9)
$(CH_3)_3CCH_2O^-$	372.6 ± 2.1	374.0	44.5 ± 1.2	46.1	103.5 ± 2.4	105.1 (104.9)
$(CH_3)_3CCH(Me)O^-$	371.9 ± 2.0	372.9	45.7 ± 0.1	46.8	104.0 ± 2.0	105.1 (105.0)
$C_6H_5CH_2O^-$	370.0 ± 2.1	369.6	49.4 ± 0.3	49.0	105.8 ± 2.1	105.4 (105.4)
$(CH_3)_3CCH(Et)O^-$	369.8 ± 2.0	371.0	47.8 ± 0.3	49.2	104.0 ± 2.0	105.4 (105.2)
$CF_3CH_2O^-$	361.7 ± 2.5	361.0	58.9 ± 0.1	58.1	107.0 ± 2.5	106.2 (106.3)

[a] All values in kcal mol^{-1}. [b] R = alkyl but not H or aryl. [c] Values obtained by using the experimental EA and the linear least-squares line shown in Figure 1. [d] Values obtained by using the experimental acidity and the linear least-squares line shown in Figure 1. [e] Both values were obtained by using eq 1. In the former case, the experimental acidity was combined with the predicted EA while the parenthetical quantity was obtained by using the literature EA and the predicted acidity. [f] See refs 4 and 11.

TABLE 2. Literature Acidities, Electron Affinities, and Bond Energies for Amides (R_2N^-) and Their Derived Values Using the Observed Linear Correlation in Figure 2[a]

R_2N^{-b}	$\Delta H^\circ_{acid}(R_2NH)$		$EA(R_2N\cdot)$		$BDE(R_2NH)$	
	expt	plot[c]	expt	plot[d]	expt	plot[e]
$MeNH^-$	403.2 ± 0.8	396.3	11.6 ± 0.7	5.2	101.2 ± 1.1	94.8 (94.3)
$(Me)_2N^-$	396.4 ± 0.9	398.0	10.0 ± 0.3	11.5	92.8 ± 0.9	94.3 (94.4)
p-$MeC_6H_4NH^-$	367.3 ± 2.1	372.3	33.8 ± 2.6	38.5	87.5 ± 1.5	92.2 (92.5)
$PhNH^-$	366.4 ± 2.1	366.4	39.3 ± 0.7	39.3	92.1 ± 2.2	92.1 (92.1)
$PhNMe^-$	364.8 ± 2.1	369.7	36.2 ± 2.9	40.8	87.4 ± 2.0	92.0 (92.3)
	358.6 ± 2.2	353.0	51.7 ± 3.0	46.5	96.7 ± 3.7	91.5 (91.1)
Ph_2N^-	350.8 ± 2.1	354.9	50.0 ± 2.6	53.8	87.2 ± 1.5	91.0 (91.3)
	349.2 ± 2.1	349.2	55.2 ± 2.3	55.2	90.8 ± 1.0	90.8 (90.8)
	345.1 ± 2.1	341.8	62.1 ± 2.3	59.0	93.6 ± 1.0	90.5 (90.3)

[a] All values in kcal mol^{-1}. [b] R = alkyl and aryl but not H. [c] Values obtained by using the experimental EA and the linear least-squares line shown in Figure 2. [d] Values obtained by using the experimental acidity and the linear least-squares line shown in Figure 2. [e] Both values were obtained by using eq 1. In the former case, the experimental acidity was combined with the predicted EA while the parenthetical quantity was obtained by using the literature EA and the predicted acidity.

results could be profitably used to extend this study, but we have chosen to employ only experimentally determined energetics at this time.

Results

Previous studies from our laboratories on the acidities and bond dissociation energies of 3,3-dimethylcyclopropene[8] and bridgehead hydrocarbons (HX)[9] suggested that $\Delta H^\circ_{acid}(HX)$, $EA(X^\bullet)$, and BDE(HX) are all linearly related to each other for simple hydrocarbons which give localized carbanions upon deprotonation. To probe this further, we plotted $\Delta H^\circ_{acid}(HX)$ vs $EA(X^\bullet)$ for different classes of compounds with experimentally known acidities and electron affinities. The results for alkoxides, amides, delocalized and localized carbanions, carboxylates, hetero-substituted oxy anions, silyl anions, and thiolates are given in Tables 1−8 and Figures 1−8;[10] no compounds were intentionally omitted from these data sets. Linear master equations with correlation coefficients (r^2) spanning from 0.95 to 1.00 and having an average value of 0.98 were obtained for all eight types of compounds by carrying out least-squares analyses.

To assess the quality of these linear correlations further and to provide a quantitative measure of their predicted accuracy, the average unsigned errors of $\Delta H^\circ_{acid}(HX)$, $EA(X^\bullet)$, and BDE(HX) were compared to the derived values obtained from the master equations (Table 9). More specifically, the predicted values for $\Delta H^\circ_{acid}(HX)$ and $EA(X^\bullet)$ were obtained using the equations for the

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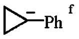
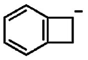
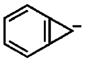
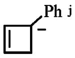
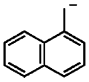
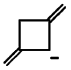
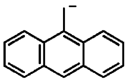
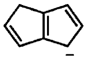
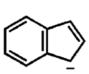
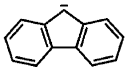
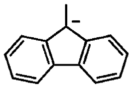
(10) Standard errors for the slope and the intercept are reported. These quantities were computed using Microsoft Excel 2001 on a Macintosh computer.

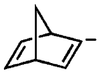
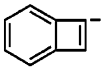
TABLE 3. Literature Acidities, Electron Affinities, and Bond Energies for Delocalized Carbanions (R^-) and Their Derived Values Using the Observed Linear Correlation in Figure 3[a]

R^-	ΔH°_{acid}(RH)		EA($R^\cdot$)		BDE(RH)	
	expt	plot[b]	expt	plot[c]	expt	plot[d]
$C_{20}H_{19}^-$ (dodecahedryl)[e]	402.0 ± 2.0	400.9	3.9 ± 2.3	3.1	92.3 ± 3.0	91.5 (91.2)
$CH_2{=}CHCH_2^-$	390.2 ± 0.7	391.8	11.1 ± 0.2	12.3	87.7 ± 0.7	88.9 (89.3)
$C_6H_5C^-{=}CH_2$ [f]	389.9 ± 0.9	-	22.1 ± 3.0	-	98.4 ± 3.1	-
 [f]	388.2 ± 1.6	383.6	17.5 ± 3.4	13.9	92.1 ± 3.8	88.5 (87.5)
$CH_2{=}C(CH_3)C(CH_2^-){=}CH_2$	388.1 ± 3.1	386.7	15.1 ± 0.2	14.0	89.6 ± 3.1	88.5 (88.2)
$CH_2{=}C(CH_3)CH_2^-$	387.0 ± 2.0	391.1	11.7 ± 0.1	14.8	85.1 ± 2.0	88.2 (89.1)
 [g]	386.2 ± 3.0	381.2	19.4 ± 2.5	15.5	92.0 ± 3.9	88.1 (87.0)
 [h]	386.0 ± 3.0	382.1	18.7 ± 6.9	15.6	91.1 ± 7.5	88.0 (87.2)
$C_6H_5CH_2^-$	382.3 ± 0.3	379.1	21.0 ± 0.1	18.5	89.7 ± 0.3	87.2 (86.5)
$CH_2{=}C{=}CH^-$ [i]	381.1 ± 3.0	378.9	21.2 ± 0.2	19.5	88.7 ± 3.0	87.0 (86.5)
	[382.7 ± 3.0]	[378.9]		[18.2]		[87.3(86.5)]
$C_6H_5CHCH_3^-$	379.7 ± 2.1	381.3	19.3 ± 2.6	20.6	85.4 ± 1.5	86.7 (87.0)
$C_6H_5C(CH_3)_2^-$	378.9 ± 2.1	381.6	19.1 ± 2.6	21.2	84.4 ± 1.5	86.5 (87.1)
 [j]	377.5 ± 0.7	378.3	21.7 ± 2.5	22.3	85.6 ± 2.6	86.2 (86.4)
$CH_2{=}CHCH{=}CHCH_2^-$	375.6 ± 3.1	379.2	21.0 ± 0.7	23.8	83.0 ± 3.0	85.8 (86.6)
	374.1 ± 2.1	374.6	24.6 ± 2.6	25.0	85.1 ± 1.5	85.5 (85.6)
$C_6H_5CH{=}CHCH_2^{-1}$	368.1 ± 2.1	374.8	24.4 ± 1.6	29.7	78.9 ± 2.6	84.2 (85.6)
	366.6 ± 3.1	372.4	26.3 ± 0.2	30.8	79.3 ± 3.1	83.8 (85.1)
$(C_6H_5)_2CH^-$	363.6 ± 2.1	361.9	34.5 ± 2.2	33.2	84.5 ± 0.5	83.2 (82.8)
	362.2 ± 2.4	363.6	33.2 ± 2.8	34.3	81.8 ± 1.5	82.9 (83.2)
$(C_6H_5)_3C^-$	358.7 ± 2.2	360.2	35.9 ± 3.0	37.0	81.0 ± 2.0	82.1 (82.5)
	354.7 ± 4.3	351.9	42.4 ± 9.9	40.2	83.5 ± 10.8	81.3 (80.7)
	353.6 ± 1.3	353.4	41.2 ± 0.5	41.1	81.2 ± 1.4	81.1 (81.0)
	351.9 ± 2.1	351.5	42.7 ± 0.3	42.4	81.0 ± 2.1	80.7 (80.6)
	351.7 ± 2.1	351.0	43.1 ± 0.3	42.5	81.2 ± 2.1	80.6 (80.5)
	350.8 ± 2.1	351.8	42.5 ± 2.9	43.2	79.7 ± 2.0	80.4 (80.7)

[a] All values in kcal mol^{-1}. [b] Values obtained by using the experimental EA and the linear least-squares line shown in Figure 3. [c] Values obtained by using the experimental acidity and the linear least-squares line shown in Figure 3. [d] Both values were obtained by using eq 1. In the former case, the experimental acidity was combined with the predicted EA while the parenthetical quantity was obtained by using the literature EA and the predicted acidity. [e] See ref 12. [f] See ref 13. [g] See ref 14. [h] See ref 15. [i] The first energy corresponds to the C−H acidity or bond energy for allene, whereas the values in parentheses are for $HC{\equiv}CCH_2{-}H$. See ref 16. [j] See ref 17.

straight lines and the literature electron affinities or acidities. Bond energies were derived using eq 1, the experimental value for ΔH°_{acid}(HX), and the predicted value for EA($X^\cdot$) or vice versa. The average errors in the computed values using the linear equations are smaller than the reported experimental uncertainties except for amides, localized carbanions, and hetero-substituted oxy anions where the additional errors range from 0.2 to 2.8 kcal mol^{-1}. These findings support our use of linear equations for fitting the experimental data but also reflect, in part, that the uncertainties in absolute acidities are usually 1 order of magnitude greater than the relative

TABLE 4. Literature Acidities, Electron Affinities, and Bond Energies for Localized Carbanions (R^-) and Their Derived Values Using the Observed Linear Correlation in Figure 4[a]

R^-	ΔH°_{acid} (RH)		EA ($R^\cdot$)		BDE (RH)	
	expt	plot[b]	expt	plot[c]	expt	plot[d]
$CH_3CH_2^-$	420.1 ± 2.0	418.4	-6.0 ± 2.0	-8.8	100.5 ± 0.3	97.7 (98.8)
$(CH_3)_2CH^-$	419.4 ± 2.0	419.4	-7.7 ± 2.1	-7.7	98.1 ± 0.7	98.1 (98.1)
c-$C_4H_7^-$ (cyclobutyl)	417.4 ± 2.0	418.4	-6.0 ± 2.0	-4.4	97.8 ± 0.3	99.4 (98.8)
CH_3^-	416.8 ± 0.7	413.6	1.8 ± 0.7	-3.4	105.0 ± 0.1	99.8 (101.8)
c-$C_5H_9^-$ (cyclopentyl)	416.1 ± 2.0	418.7	-6.5 ± 2.0	-2.3	96.0 ± 0.2	100.2 (98.6)
$CH_3CH_2CH^-CH_3$	415.7 ± 2.0	417.0	-3.8 ± 2.1	-1.6	98.3 ± 0.5	100.5 (99.6)
$CH_3CH_2CH_2^-$	415.6 ± 2.0	415.4	-1.1 ± 2.1	-1.5	100.9 ± 0.5	100.5 (100.7)
$(CH_3)_3C^-$	413.1 ± 2.0	417.1	-3.9 ± 2.1	2.6	95.6 ± 0.7	102.1 (99.6)
$(CH_3)_2CHCH_2^-$	412.9 ± 2.0	414.1	0.9 ± 2.2	2.9	100.2 ± 1.0	102.2 (101.4)
c-$C_3H_5^-$	411.5 ± 2.0	409.6	8.4 ± 2.0	5.2	106.3 ± 0.3	103.1 (104.4)
c-$C_3H_5CH_2^-$ (cyclopropylcarbinyl)	410.5 ± 2.0	414.4	0.5 ± 2.6	6.9	97.4 ± 1.6	103.8 (101.3)
$CH_2{=}CH^-$	409.4 ± 0.6	405.3	15.4 ± 0.6	8.6	111.2 ± 0.4	104.4 (107.1)
$(CH_3)_3CCH_2^-$	408.9 ± 2.0	411.6	5.0 ± 2.3	9.5	100.3 ± 1.0	104.8 (103.0)
 [e]	408.5 ± 0.9	405.6	14.8 ± 3.2	10.1	109.7 ± 3.3	105.0 (106.8)
$^-CH{=}CHCH_3$	404.7 ± 0.9	402.6	19.8 ± 4.2	16.3	110.9 ± 4.3	107.4 (108.8)
$C_8H_7^-$ (cubyl)[f]	404.0 ± 3.0	407.7	11.5 ± 2.3	17.5	101.9 ± 3.8	107.9 (105.6)
c-$C_7H_7^-$ (1-quadricylide)	403.0 ± 1.1	402.4	20.0 ± 0.1	19.1	109.4 ± 1.1	108.5 (108.8)
c-$C_7H_7^-$ (2-quadricylide)	402.9 ± 1.1	401.1	22.2 ± 0.1	19.2	111.5 ± 1.1	108.5 (109.7)
$C_{20}H_{19}^-$ (dodecahedryl)[g]	402.0 ± 2.0	-	3.9 ± 2.3		92.3 ± 3.0	-
$C_6H_5^-$	401.7 ± 0.5	399.2	25.3 ± 0.1	21.2	113.4 ± 0.5	109.3 (110.9)
	399.5 ± 1.7	396.5	29.7 ± 0.1	24.8	115.6 ± 1.7	110.7 (112.6)
 [h]	398.0 ± 2.0	-	17.8 ± 7.6	-	102.2 ± 7.9	-
2-$C_{10}H_7^-$ (2-naphthyl)[i]	395.5 ± 1.3	396.0	30.5 ± 0.5	31.3	112.4 ± 1.4	113.2 (112.9)
1-$C_{10}H_7^-$ (1-naphthyl)[i]	394.2 ± 1.2	395.3	31.6 ± 0.5	33.4	112.2 ± 1.3	114.0 (113.3)
 [j]	386.0 ± 3.0	389.3	41.5 ± 2.3	46.8	113.9 ± 3.8	119.2 (117.2)
c-$C_5H_7^-$ (3,3-dimethylcyclopropenyl)[k]	382.7 ± 1.1	-	37.6 ± 3.5	-	106.7 ± 3.7	-
$CH_3C{\equiv}C^-$	381.1 ± 2.1	376.3	62.7 ± 0.2	54.8	130.2 ± 2.1	122.3 (125.4)
$HC{\equiv}C^-$	377.9 ± 0.7	372.7	68.5 ± 0.1	60.0	132.8 ± 0.7	124.3 (127.6)
$HC{\equiv}C{-}C{\equiv}C^-$	360.4 ± 2.9	364.4	82.0 ± 0.2	88.6	128.8 ± 2.9	135.4 (132.8)
$HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C^-$	355.2 ± 3.1	361.4	87.5 ± 0.1	97.1	129.1 ± 3.1	138.7 (135.0)

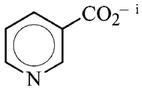
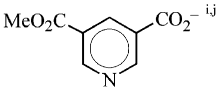
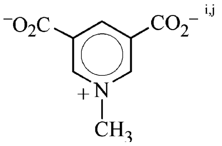
[a] All values in kcal mol^{-1}. [b] Values obtained by using the experimental EA and the linear least-squares line shown in Figure 4. [c] Values obtained by using the experimental acidity and the linear least-squares line shown in Figure 4. [d] Both values were obtained by using eq 1. In the former case, the experimental acidity was combined with the predicted EA while the parenthetical quantity was obtained by using the literature EA and the predicted acidity. [e] See ref 18. [f] See ref 19. [g] See ref 12. [h] See ref 20. [i] See ref 21. [j] See ref 22. [k] See ref 8.

errors. Predicted acidities, electron affinities, and bond energies, consequently, should generally be reliable to within 1–4 kcal mol^{-1}; the exact value depends on the type of compound and the quantity of interest. As with all correlations, this assumes that there is no systematic reason for a given molecule to deviate from the given lines.

Discussion

Over the past 40 years or so, the thermodynamic cycle summarized in eq 1 has been used to derive bond energies and to a lesser extent acidities and electron affinities.[2] As a consequence of this relationship, the sum of $\Delta H^\circ_{acid}(HX)$ and $EA(X^\cdot)$ must be constant for a series

TABLE 5. Literature Acidities, Electron Affinities, and Bond Energies for Carboxylates (RCO_2^-) and Their Derived Values Using the Observed Linear Correlation in Figure 5[a]

RCO_2^-	$\Delta H^\circ_{acid}(RCO_2H)$		$EA(RCO_2^\cdot)$		$BDE(RCO_2H)$	
	expt	plot[c]	expt	plot[d]	expt	plot[e]
$CH_3CO_2^-$ [f]	348.1 ± 2.2	348.8	77.3 ± 1.8	78.0	111.8 ± 2.8	112.5 (112.5)
HCO_2^- [g]	345.3 ± 2.2	345.1	80.7 ± 0.3	80.5	112.4 ± 2.2	112.2 (112.2)
$C_6H_5CO_2^-$ [h]	340.2 ± 2.2	339.9	85.3 ± 2.3	85.1	111.9 ± 3.2	111.7 (111.6)
 [i]	333.4 ± 2.8	333.5	91.1 ± 2.3	91.1	110.9 ± 3.6	110.9 (111.0)
 [i,j]	328.4 ± 5.2	327.8	96.2 ± 1.6	95.6	111.0 ± 5.4	110.4 (110.4)
 [i,j]	309.9 ± 5.0	310.4	111.8 ± 1.2	112.2	108.1 ± 5.1	108.5 (108.6)

[a] All values in kcal mol⁻¹. [b] R = H, alkyl, and aryl. [c] Values obtained by using the experimental EA and the linear least-squares line shown in Figure 5. [d] Values obtained by using the experimental acidity and the linear least-squares line shown in Figure 5. [e] Both values were obtained by using eq 1. In the former case, the experimental acidity was combined with the predicted EA while the parenthetical quantity was obtained by using the literature EA and the predicted acidity. [f] See ref 23. [g] See ref 24. [h] See ref 25. [i] See ref 26. [j] See refs 27 and 28.

TABLE 6. Literature Acidities, Electron Affinities, and Bond Energies for Hetero-Substituted Oxy Anions (XO^-) and Their Derived Values Using the Observed Linear Correlation in Figure 6[a]

	$\Delta H^\circ_{acid}(XOH)$		$EA(XO^\cdot)$		BDE(XOH)	
XO^-	expt	plot[b]	expt	plot[c]	expt	plot[d]
HOO^- [e]	376.5 ± 0.4	375.7	24.9 ± 0.1	23.8	87.8 ± 0.4	86.7 (87.0)
CH_3OO^- [f]	374.6 ± 1.0	374.3	26.8 ± 0.1	26.4	87.8 ± 1.0	87.4 (87.5)
$CH_3CH_2OO^-$ [f]	371.0 ± 2.2	373.8	27.4 ± 0.1	31.2	84.7 ± 2.1	88.6 (87.6)
$(CH_3)_3COO^-$ [f]	370.2 ± 2.1	373.7	27.6 ± 0.3	32.3	84.2 ± 2.1	88.9 (87.7)
FO^-	362.5 ± 3.3	355.2	52.4 ± 0.1	42.6	101.3 ± 3.3	91.5 (94.0)
ClO^-	355.7 ± 2.0	355.2	52.5 ± 0.03	51.7	94.5 ± 2.0	93.8 (94.0)
BrO^-	353.5 ± 2.4	353.7	54.3 ± 0.1	54.6	94.2 ± 2.4	94.5 (94.4)
NO_3^-	324.5 ± 0.2	326.5	90.8 ± 0.3	93.4	101.7 ± 0.4	104.3 (103.7)
HSO_4^-	309.6 ± 2.6	312.5	109.5 ± 2.3	113.4	105.5 ± 3.5	109.4 (108.4)
PO_3^-	310.8 ± 2.6	309.1	114.1 ± 1.4	111.8	111.3 ± 3.0	109.0 (109.6)

[a] All values in kcal mol⁻¹. [b] Values obtained by using the experimental EA and the linear least-squares line shown in Figure 6. [c] Values obtained by using the experimental acidity and the linear least-squares line shown in Figure 6. [d] Both values were obtained by using eq 1. In the former case, the experimental acidity was combined with the predicted EA while the parenthetical quantity was obtained by using the literature EA and the predicted acidity. [e] See ref 29. [f] See ref 30.

TABLE 7. Literature Acidities, Electron Affinities, and Bond Energies for Silyl Anions (R_3Si^-) and Their Derived Values Using the Observed Linear Correlation in Figure 7[a]

	$\Delta H^\circ_{acid}(R_3SiH)$		$EA(R_3Si^\cdot)$		$BDE(R_3SiH)$	
R_3Si^-	expt	plot[c]	expt	plot[d]	expt	plot[e]
Me_3Si^-	386.2 ± 0.8	385.8	22.4 ± 0.6	22.1	95.0 ± 0.5	94.7 (94.6)
Me_2SiH^-	382.4 ± 1.3	382.5	24.7 ± 0.5	24.7	93.5 ± 1.2	93.5 (93.6)
$MeSiH_2^-$	378.8 ± 1.4	378.4	27.5 ± 0.8	27.2	92.7 ± 1.2	92.4 (92.3)
$PhSi(Me)H^-$	372.6 ± 2.1	373.7	30.7 ± 0.9	31.4	89.7 ± 2.3	90.4 (90.8)
SiH_3^-	372.9 ± 0.6	371.2	32.4 ± 0.3	31.2	91.7 ± 0.5	90.5 (90.0)
$PhSiH_2^-$	368.2 ± 2.1	370.2	33.1 ± 0.1	34.4	87.7 ± 2.1	89.0 (89.7)
$(Me_3Si)_3Si^-$	350.5 ± 2.2	350.1	46.8 ± 2.0	46.5	83.7 ± 1.0	83.4 (83.3)

[a] All values in kcal mol⁻¹. [b] R = H, alkyl, and aryl. [c] Values obtained by using the experimental EA and the linear least-squares line shown in Figure 7. [d] Values obtained by using the experimental acidity and the linear least-squares line shown in Figure 7. [e] Both values were obtained by using eq 1. In the former case, the experimental acidity was combined with the predicted EA while the parenthetical quantity was obtained by using the literature EA and the predicted acidity.

of compounds with the same H−X bond energy and a plot of $\Delta H^\circ_{acid}(HX)$ vs $EA(X^\bullet)$ will be linear with a slope (m) of −1.00 and an intercept (b) of BDE(HX) +313.6 kcal mol⁻¹. If the bond energies vary then two of the three thermodynamic quantities ($\Delta H^\circ_{acid}(HX)$, $EA(X^\bullet)$, and BDE(HX)) are independent of each other and there is no

TABLE 8. Literature Acidities, Electron Affinities, and Bond Energies for Thiolates (RS^-) and Their Derived Values Using the Observed Linear Correlation in Figure 8[a]

R_3S^-	$\Delta H°_{acid}(RSH)$ expt	$\Delta H°_{acid}(RSH)$ plot[c]	$EA(RS\cdot)$ expt	$EA(RS\cdot)$ plot[d]	BDE(RSH) expt	BDE(RSH) plot[e]
CH_3S^-	356.9 ± 2.2	357.7	43.1 ± 0.1	43.8	86.4 ± 2.2	87.1 (87.2)
$CH_3CH_2S^-$	355.2 ± 2.2	355.4	45.0 ± 0.1	45.1	86.6 ± 2.2	86.7 (86.8)
$CH_3CH_2CH_2S^-$	354.2 ± 2.2	354.0	46.1 ± 0.5	45.9	86.7 ± 2.3	86.5 (86.5)
$(CH_3)_2CHS^-$	353.4 ± 2.2	353.4	46.6 ± 0.5	46.6	86.4 ± 2.3	86.4 (86.4)
$CH_3CH_2CH_2CH_2S^-$	353.7 ± 2.2	352.9	47.0 ± 0.5	46.3	87.1 ± 2.3	86.4 (86.3)
$(CH_3)_3CS^-$	352.5 ± 2.2	352.0	47.7 ± 0.5	47.3	86.6 ± 2.3	86.2 (86.1)
$C_6H_5S^-$	340.4 ± 2.1	340.8	56.7 ± 2.4	57.0	83.5 ± 1.1	83.8 (83.9)

[a] All values in kcal mol^{-1}. [b] R = alkyl and aryl but not H. [c] Values obtained by using the experimental EA and the linear least-squares line shown in Figure 8. [d] Values obtained by using the experimental acidity and the linear least-squares line shown in Figure 8. [e] Both values were obtained by using eq 1. In the former case, the experimental acidity was combined with the predicted EA while the parenthetical quantity was obtained by using the literature EA and the predicted acidity.

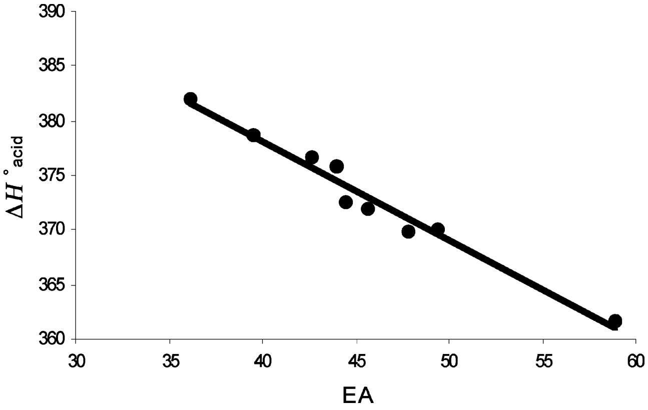


FIGURE 1. Alkoxide (RO^-) proton affinity versus electron affinity of the corresponding radical ($\Delta H°_{acid} = (-0.903 \pm 0.058) \times EA + (414.2 \pm 2.7)$, $r^2 = 0.97$).

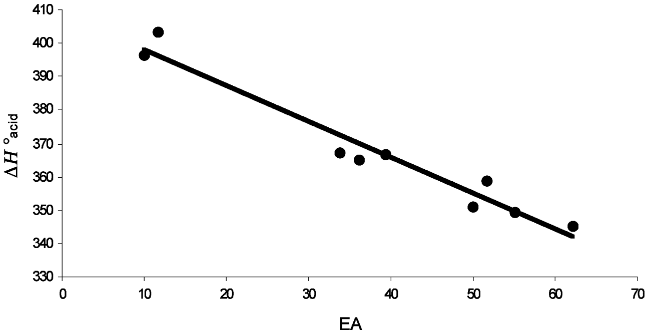


FIGURE 2. Amide (R_2N^-) proton affinity versus electron affinity of the corresponding radical ($\Delta H°_{acid} = (-1.079 \pm 0.092) \times EA + (408.8 \pm 3.9)$, $r^2 = 0.95$).

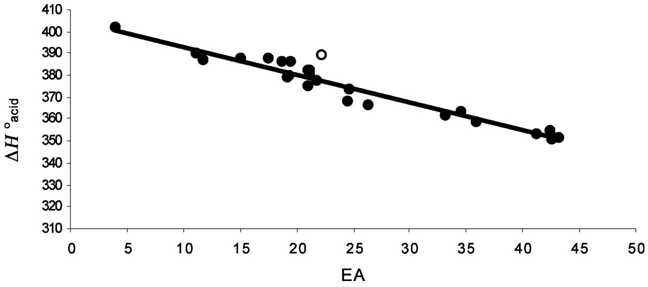


FIGURE 3. Carbanion (R^-, delocalized) proton affinity versus electron affinity of the corresponding radical. Compounds used to derive the indicated least-squares line are indicated by filled circles ($\Delta H°_{acid} = (-1.274 \pm 0.058) \times EA + (405.9 \pm 1.6)$, $r^2 = 0.95$), while the omitted point (styrene) is represented by an open circle.[31]

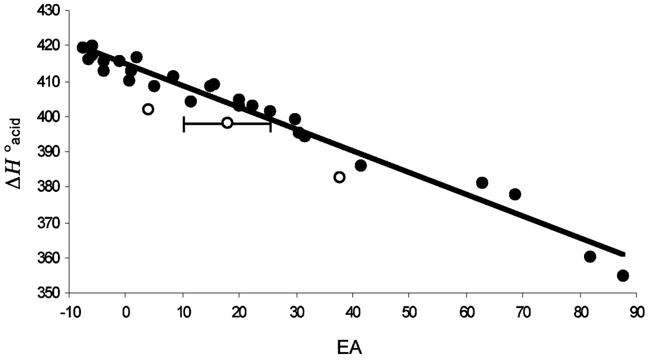


FIGURE 4. Carbanion (R^-, localized) proton affinity versus electron affinity of the corresponding radical. Compounds used to derive the indicated least-squares line are indicated by filled circles ($\Delta H°_{acid} = (-0.613 \pm 0.022) \times EA + (414.7 \pm 0.7)$, $r^2 = 0.97$), while those that were omitted from the correlation (bicyclo[1.1.0]butane, 3,3-dimethylcyclopropene, and dodecahedrane) are represented by open circles.[32]

apparent correlation between them. Nevertheless, we have found that $\Delta H°_{acid}(HX)$ and $EA(X^\bullet)$ are linearly correlated for a variety of classes of compounds even when the bond energies vary. There is no a priori reason this should be the case, but to the extent that it is, the electron affinity also must be linearly related to BDE(HX) (eq 2). This is qualitatively understandable given that HX and X^- are isoelectronic species which both afford $X^\bullet$ upon homolytic cleavage and electron detachment, respectively (eqs 3 and 4). In other words, for similar compounds it is not unreasonable that substituents affect bond energies and electron affinities in a related way.

$$BDE(HX) = \alpha EA(X^\bullet) + \beta \qquad (2)$$

$$HS \xrightarrow{BDE} X^\bullet + H^\bullet \qquad (3)$$

$$X^- \xrightarrow{EA} X^\bullet + e^- \qquad (4)$$

Upon substitution of eq 2 into eq 1, one can derive eq 5 where $m = \alpha - 1$ and $b = 313.6 + \beta$ kcal mol^{-1}. The intercept thus provides β ($\beta = b - 313.6$), which is the

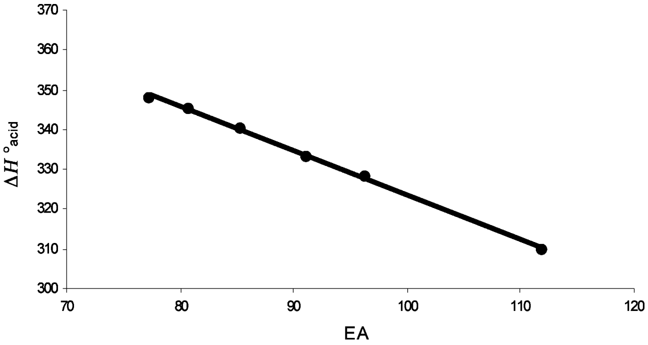


FIGURE 5. Carboxylate (RCO_2^-) proton affinity versus electron affinity of the corresponding radical ($\Delta H°_{acid} = (-1.116 \pm 0.020) \times EA + (435.1 \pm 1.9)$, $r^2 = 1.00$).

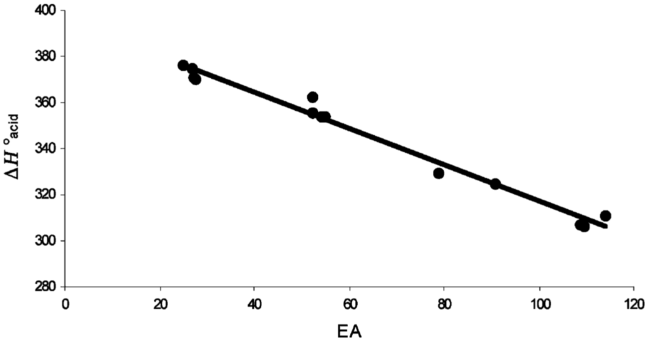


FIGURE 6. Hetero-substituted oxy anion (XO^-) proton affinity versus electron affinity of the corresponding radical ($\Delta H°_{acid} = (-0.747 \pm 0.032) \times EA + (394.3 \pm 2.2)$, $r^2 = 0.99$).

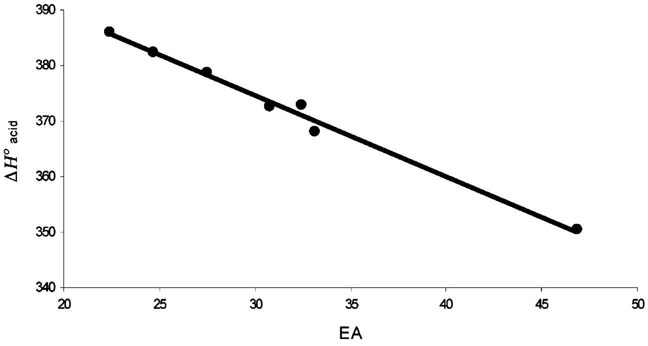


FIGURE 7. Silyl anion (R_3Si^-) proton affinity versus electron affinity of the corresponding radical ($\Delta H°_{acid} = (-1.463 \pm 0.066) \times EA + (418.6 \pm 2.1)$, $r^2 = 0.99$).

bond energy when $EA(X^\bullet) = 0$.

$$\Delta H°_{acid}(HX) = (\alpha - 1)\, EA(X^\bullet) + 313.6 + \beta \qquad (5)$$

This quantity can be viewed as an intrinsic bond energy (BDE_i), since there is no driving force for $X^\bullet$ to pick up an additional electron and the open- and closed-shell species are equally stable (i.e., $\Delta H°_f(X^\bullet) = \Delta H°_f(X^-)$). These values are provided in Table 9, and interestingly, the intrinsic bond strengths of ROH, RH (localized), R_3SiH, RSH, and probably R_2NH are all about the same (~100 kcal mol^{-1}). This suggests that the effect of electronegativity and size on H−X bond energies is mitigated when one accounts for the electron affinity of $X^\bullet$. Carboxylic acids, on the other hand, have a much larger intrinsic bond strength (122 kcal mol^{-1}) while RH (delocalized) and XOH have smaller BDE_is. The former result presumably is related to the localized nature of the odd electron in the σ plane of carboxyl ($RCO_2^\bullet$) radicals and is consistent with BDE (RCO_2−H) > BDE (RO−H).[33] The latter observations can be attributed to electron delocalization in the $R^\bullet$ and $XO^\bullet$ radicals.

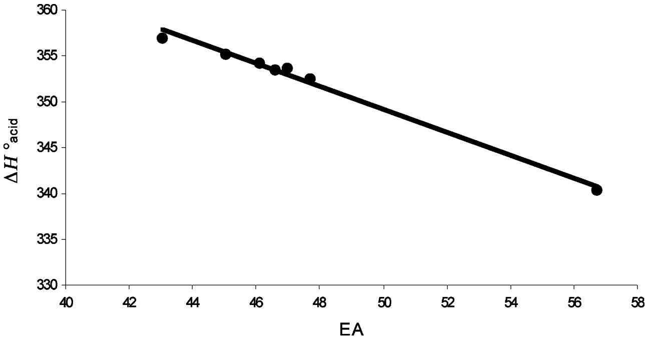


FIGURE 8. Thiolate (RS^-) proton affinity versus electron affinity of the corresponding radical ($\Delta H°_{acid} = (-1.245 \pm 0.057) \times EA + (411.4 \pm 2.7)$, $r^2 = 0.99$).

TABLE 9. Comparison of the Experimental Uncertainties and Those Obtained Using the Reported Correlations[a]

	average unsigned errors[b]						
	$\Delta H°_{acid}$		EA		BDE		
anions	lit.	plot	lit.	plot	lit.	plot	BDE_i
RO^- [a]	1.5	0.8	0.3	0.9	1.6	1.0 (0.9)	101 ± 3
R_2N^-	1.8	3.5	1.9	3.2	1.7	3.2 (3.5)	95 ± 4
R^- (delocalized)	2.2	2.5	2.1	1.9	2.7	1.9 (2.4)	92 ± 2
R^- (localized)	1.7	2.6	1.4	4.2	1.4	4.2 (2.6)	101 ± 1
RCO_2^-	3.3	0.4	1.6	0.4	3.7	0.4 (0.4)	122 ± 2
XO^-	1.9	2.2	0.5	3.0	2.0	3.0 (2.2)	81 ± 2
R_3Si^-	1.5	0.9	0.7	0.6	1.3	0.6 (0.9)	104 ± 2
RS^-	2.2	0.4	0.7	0.3	2.1	0.3 (0.4)	98 ± 3

[a] All values in kcal mol^{-1}. [b] The differences between each individual literature and predicted value (see Tables 1−8) were used to derive the average unsigned errors given in the columns labeled plot.

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α is obtained from the slope of a plot of ΔH°_{acid}(HX) vs EA(X$^\bullet$) (α = $m + 1$) and is a sensitivity factor. It is a positive number when BDE(HX) is directly proportional to EA(X$^\bullet$) and a negative number when they are inversely proportional. α is 0 when $m = -1$ and the bond energy is constant, but this does not appear to be the case for any of these compounds nor is there any reason it should be. Measured bond energies span only a small range for some types of compounds and often are assumed to be constant. This is reasonable for a limited range of substituents and the NIST website[3] employs such approximations, but unfortunately, it is not readily apparent when derived values are based upon assumed BDEs. As for the sign of α, it can be predicted by considering effects such as hybridization (α > 0) and resonance stabilization (α < 0) but the magnitude needs to be empirically determined at this time. Our data shows that α spans from −0.45 to +0.40, but there is no reason to suppose that these are theoretical limits.

The eight classes of compounds reported in this work were empirically determined. Additional groups undoubtedly can be found and we suspect that when more data becomes available the amides will need to be broken into localized and delocalized ions as was done for carbanions. Likewise, phenoxides and enolates should comprise their own group(s), but there is not enough gas-phase data available to reliably address this at present. As for the two second-row anion groups (i.e., RS^- and R_3Si^-), aryl substituents are included and do not need to be treated separately. This is a result of the large difference in size between a carbon and a sulfur or silicon 2p orbital, which results in weaker π bonds and less effective delocalization.[34]

Conclusions

Bond dissociation energies are often determined by combining an acidity and an electron affinity in a thermodynamic cycle which relates these quantities (eq 1). More generally, if one knows any two of the preceding terms, one can derive the third. In this study, we have shown that for specific classes of compounds ΔH°_{acid}(HX) is linearly related to EA(X$^\bullet$), and consequently, ΔH°_{acid}(HX), EA(X$^\bullet$), and BDE(HX) are all linearly dependent on each other. From a practical standpoint this means that by measuring any one of these quantities one can estimate the other two for many types of compounds. This will simplify the determination of bond energies (and electron affinities), and hundreds of new values can be obtained from data already reported in the literature. From these quantities, the heats of formation of many radicals can be predicted and used to estimate additional X−Y bond energies. As for the accuracy of this approach, it generally is as good or better than the experimental uncertainties for related compounds. In part, this is due to the fact that the relative errors for ΔH°_{acid}(HX) are about 1 order of magnitude smaller than the absolute uncertainties (~0.2 vs 2 kcal mol^{-1}). It also is a testament to the reliability of gas-phase data coming out of many different laboratories.

The results described herein can be applied to additional categories of compounds and are not necessarily confined to a negative-ion thermodynamic cycle. Aue and co-workers previously reported that the proton affinities and vertical ionization potentials of primary, secondary, and tertiary amines are linearly related.[35] Further inspection of the amine data and additional functional groups suggests that the adiabatic ionization potential can be used.[36] If this initial analysis is born out then positive ion bond energies and radical cation heats of formation also will become more readily available. This possibility is currently being explored.

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(31) Styrene was omitted from the least-squares analysis because its conjugate base is structurally different from the other ions. $PhC^-{=}CH_2$ is partially localized and partially delocalized, and the aromatic ring is conjugated to the double bond in the acid but to the charge center in the anion. Phenylcyclopropane could be viewed similarly, but conjugation is more important in the anion and less important in the acid as indicated by the B3LYP/6-31+G(d) rotational barriers. The inversion barrier in the anion also is smaller, so phenylcyclopropane was retained in the statistical analysis. Benzocyclopropene and dihydropentadiene also are included in the data analysis despite large experimental uncertainties because excluding them does not change the results.

(32) Bicyclo[1.1.0]butane, 3,3-dimethylcyclopropene, and dodecahedrane were omitted from the least-squares analysis because of the large uncertainty in the electron affinity of bicyclo[1.1.0]but-1-yl (± 7.6 kcal mol^{-1}), a stabilizing orbital interaction in 3,3-dimethylcyclopropen-1-yl radical which delocalizes the radical center (ref 8), and the inclusion of the $C_{20}H_{19}$ anion in the delocalized carbanion data set.

(33) It is interesting to note that acetic acid is 34.3 kcal mol^{-1} more acidic than methanol whereas EA ($CH_3CO_2^\bullet$ − $CH_3O^\bullet$) = 41.0 kcal mol^{-1}. This accounts for the 6.7 kcal mol^{-1} greater bond strength of CH_3CO_2−H and suggests that $CH_3CO_2^\bullet$ is not stabilized by delocalization of the odd electron. Instead, it appears that acetic acid is stabilized relative to methanol, presumably because of electrostatics and electron delocalization.

(34) Currently, it is unclear why R = H fits in some cases (CH_3^-, HCO_2^-, and SiH_3^-) but not in others (OH^-, NH_2^-, and SH^-).

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