

Theoretical Study of the Effects of Protonation and Deprotonation on Bond Dissociation Energies of Second-Row Elements: Comparison with First-Row Elements

Susan L. Boyd* and Russell J. Boyd

Contribution from the Departments of Chemistry, Mount Saint Vincent University, Halifax, Nova Scotia, B3M 2J6, and Dalhousie University, Halifax, Nova Scotia, B3H 4J3

Received June 11, 1996. Revised Manuscript Received March 10, 1997[⊗]

Abstract: *Ab initio* MO calculations indicate that protonation of XH_n to XH_{n+1}^+ increases bond dissociation energies (BDEs) for homolytic cleavage of CX bonds in CH_3XH_n , $CH_3-CH_2-XH_n$, $CH_2=CH-XH_n$, and $CH\equiv C-XH_n$ compounds (X = N, O, F, P, S, and Cl). Deprotonation of XH_n to XH_{n-1}^- (X = C, N, O, Si, P, and S) in saturated species generally results in small decreases in CX BDEs; in unsaturated substances, as a result of resonance, deprotonation yields large increases in the CX BDEs, X = Si being the exception. For adjacent CC bonds, protonation of XH_n increases the CC BDEs because it produces larger electronegativity differences between bonded groups; deprotonation decreases the BDEs as a result of resonance effects. Two types of correlation between bond lengths and homolytic BDEs are observed, with second-row elements exhibiting bond length changes to a much lesser extent than first-row ones. Firstly, bond lengths of adjacent CC bonds increase as their BDEs decrease. Secondly, and apparently anomalously, CX bond lengths and homolytic BDEs both increase with protonation of XH_n , except with X = P. The increase in BDE together with the increase in bond length is, in part, a result of the focus on homolytic BDEs: heterolytic cleavage of most protonated, and many deprotonated, species is actually preferred, in which case bond lengths generally increase as bond strengths decrease in accordance with the normally accepted trend.

Introduction

Bond dissociation energies (BDEs) and bond lengths are fundamental quantities in chemistry. While most textbook compilations present average values for the common bonds, it is well recognized that the environment of a particular bond affects both its BDE and its bond length. But experimental BDEs and bond lengths, particularly of radicals and ions, are available only to a limited extent, so a detailed study of the degree to which different environments do affect BDEs and bond lengths is hampered. *Ab initio* methods for the calculation of BDEs and bond lengths are, however, now readily available, and indeed, have been applied to determine sequential BDEs, involving dissociation of radicals, with high accuracy.¹ To consider bond dissociation of charged species, we have undertaken an examination of the effect of protonation and deprotonation on bond dissociation energies and bond lengths. Our initial study² focussed on CX and CCX compounds containing first-row elements, X = C, N, O, and F; the present work continues that study to ascertain if the trends observed for the first-row elements are followed by the related second-row ones, i.e., X = Si, P, S, and Cl. Thus, this work examines the CC and CX bond dissociation energies and bond lengths in CH_3-XH_n , $CH_3-CH_2-XH_n$, $CH_2=CH-XH_n$, and $CH\equiv C-XH_n$ (i.e., RXH_n), for X = Si, P, S, and Cl, and compares these to the BDEs and bond lengths of the corresponding protonated RXH_{n+1}^+ and deprotonated RXH_{n-1}^- species; it thereby sheds more light on the differences between carbon bonds to first-row elements versus those to higher main-group elements.³

Computational Method

It would have been preferable to use the more accurate methods now available.⁴ But some of the species being studied are fairly large and computationally demanding; moreover, we wished to be consistent

with our study of the first-row elements.² Thus all energies and geometries were determined at the MP2/6-31+G(d,p)/MP2/6-31+G(d,p) level⁵ (including all electrons in the post-Hartree–Fock calculations) with GAUSSIAN 92⁶ and GAUSSIAN 94.⁷ (In our earlier study, a systematic analysis of several basis sets, namely 6-31G(d), 6-31G+(d,p), and 6-31++G(d,p), and levels, i.e., MP2, MP3, and MP4(SDTQ), was performed to compare calculated homolytic BDEs to experimental ones; the MP2/6-31+G(d,p)/MP2/6-31+G(d,p) level of theory, including all electrons in the post-Hartree–Fock calculations, led to reliable results, with experimental BDEs for the methyl compounds reproduced with a mean error and standard deviation of $-3 (\pm 8)$ kJ mol⁻¹. The BDEs for the compounds involving second-row elements are undoubtedly less accurate with this level of theory; however, the trends observed are valid, as indicated by a G2 study on the BDEs of the CH_3XH_n series: it is the trends that primarily interest us.) Frequency analyses were done at HF/6-31+G(d,p)/HF/6-31+G(d,p) to confirm that the geometries are local minima and to obtain zero point and thermal energies; the former were scaled (by 0.9)^{8,9} to correct for overestimation of vibrational frequencies. Full details on the calculation of the BDEs are given elsewhere.²

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(3) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

(4) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

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* Address correspondence to this author at Mount Saint Vincent University.

[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1997.

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Table 1. Homolytic CX and CC Bond Dissociation Energies and Bond Lengths in CXH_n and CCXH_n: Effect of Protonation and Deprotonation of XH_n, X = Si, P, S, Cl

	CX bond		CC bond	
	ΔH_{298} (CX bond cleavage) (kJ/mol)	CX bond length (Å)	ΔH_{298} (CC bond cleavage) (kJ/mol)	CC bond length (Å)
Silicon Series				
CH ₃ SiH ₃	356 (373, ^a 372 ^b)	1.879		
CH ₃ SiH ₂ ⁻	271 (283)	1.969		
C ₂ H ₅ SiH ₃	345	1.883	363	1.531
C ₂ H ₅ SiH ₂ ⁻	273	1.962	329	1.529
C ₂ H ₃ SiH ₃	430 (408)	1.868	881/769/803/691 ^c	1.346
C ₂ H ₃ SiH ₂ ⁻	359	1.944	732/729/654/650	1.349
C ₂ HSiH ₃	572 (541)	1.829	1046	1.229
C ₂ HSiH ₂ ⁻	544	1.904	888	1.240
Phosphorus Series				
CH ₃ PH ₃ ⁺	424 (450)	1.798		
CH ₃ PH ₂	284 (302, 300)	1.857		
CH ₃ PH ⁻	278 (278)	1.900		
C ₂ H ₅ PH ₃ ⁺	431	1.807	399	1.531
C ₂ H ₅ PH ₂	286	1.858	366	1.524
C ₂ H ₅ PH ⁻	283	1.899	291	1.526
C ₂ H ₃ PH ₃ ⁺	485	1.776	910/808/832/730	1.342
C ₂ H ₃ PH ₂	355 (345)	1.831	731/759/652/681	1.342
C ₂ H ₃ PH ⁻	410	1.786	616/738/538/660	1.368
C ₂ H ₂ PH ₃ ⁺	580	1.709	1043	1.223
C ₂ H ₂ PH ₂	489 (460)	1.776	922	1.226
C ₂ H ₂ PH ⁻	568	1.767	788	1.242
Sulfur Series				
CH ₃ SH ₂ ⁺	377 (401)	1.818		
CH ₃ SH	297 (313, 322)	1.814		
CH ₃ S ⁻	267 (285)	1.830		
C ₂ H ₅ SH ₂ ⁺	398	1.835	420	1.515
C ₂ H ₅ SH	301	1.823	388	1.520
C ₂ H ₅ S ⁻	285	1.822	318	1.527
C ₂ H ₃ SH ₂ ⁺	445	1.782	864/825/786/747	1.334
C ₂ H ₃ SH	376 (360)	1.757	700/767/631/688	1.340
C ₂ H ₃ S ⁻	405	1.730	687/729/609/651	1.362
C ₂ HSH ₂ ⁺	497	1.690	966	1.219
C ₂ HSH	488 (461)	1.697	828	1.223
C ₂ HS ⁻	574	1.665	790	1.244
Chlorine Series				
CH ₃ ClH ⁺	453 (483)	1.843		
CH ₃ Cl	329 (354, 364)	1.776		
C ₂ H ₅ ClH ⁺	491	1.906	450	1.498
C ₂ H ₅ Cl	341	1.788	379	1.513
C ₂ H ₃ ClH ⁺	519	1.812	844/847/765/769	1.323
C ₂ H ₃ Cl	405 (405)	1.729	784/778/706/700	1.334
C ₂ HClH ⁺	516	1.663	864	1.215
C ₂ HCl	490 (474)	1.642	833	1.219

^a Data in parentheses are BDEs determined by using G2 calculations. ^b Data that are italicized within parentheses are from ref 10. ^c The products of homolytic dissociation of the double bonds in H₂C=CHXH_n are carbenes, which may be in singlet or triplet states; therefore, the BDEs calculated for the various combinations of product states are all presented. They are listed in order of SS/ST/TS/TT, where ST means that the H₂C is in a singlet state and the CHXH_n is in a triplet one, etc. The lowest BDE in each dissociation is underlined and is used for comparative purposes.

Results and Discussion

Table 1 presents the homolytic CX and CC BDEs and bond lengths in the second-row CXH_n and CCXH_n compounds studied, i.e., X = Si, P, S, and Cl, together with the corresponding protonated and deprotonated species. Numbers in parentheses are the BDE calculated with the G2 method.⁴ This much higher level of calculation, with its established corrections, yields results for the methyl compounds with the same trends in BDEs as those at the level reported herein. Because of computing limitations, it was not possible to obtain all BDEs at the G2 level, but the limited study we could do suggests that the lower level trends are valid. Some G2 results for BDEs reported to have a root-mean-square deviation of 1.4 kcal/mol (6.0 kJ/mol) from experimental data¹⁰ are also included in Table 1 for comparison.

(8) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(9) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996.

Figure 1 graphically illustrates the changes in BDEs and bond lengths observed upon protonation and deprotonation of each X, and includes the analogous trends observed for the first-row compounds and ions,² i.e., X = C, N, O, and F, to allow visual comparison.

Figure 2 presents the bond length data from the perspective of periodic trends within the protonated, neutral, and deprotonated species for both first- and second-row species.

Effect of Protonation and Deprotonation on Homolytic BDEs and Bond Lengths. Not surprisingly, in view of the larger atoms and lower electronegativities involved, the BDEs for CX bonds where X is a second-row element are lower than those for the corresponding bonds where X is a first-row element; also the CX bond lengths for second-row X are longer. Protonation of RCXH_n increases the CX homolytic BDE in all compounds with second-row X, as it does for all species

(10) Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117*, 11299. (Data are from Table 5, G2 column, with 1.5 kcal/mol (6.3 kJ/mol) added for approximate correction to 298 K.)

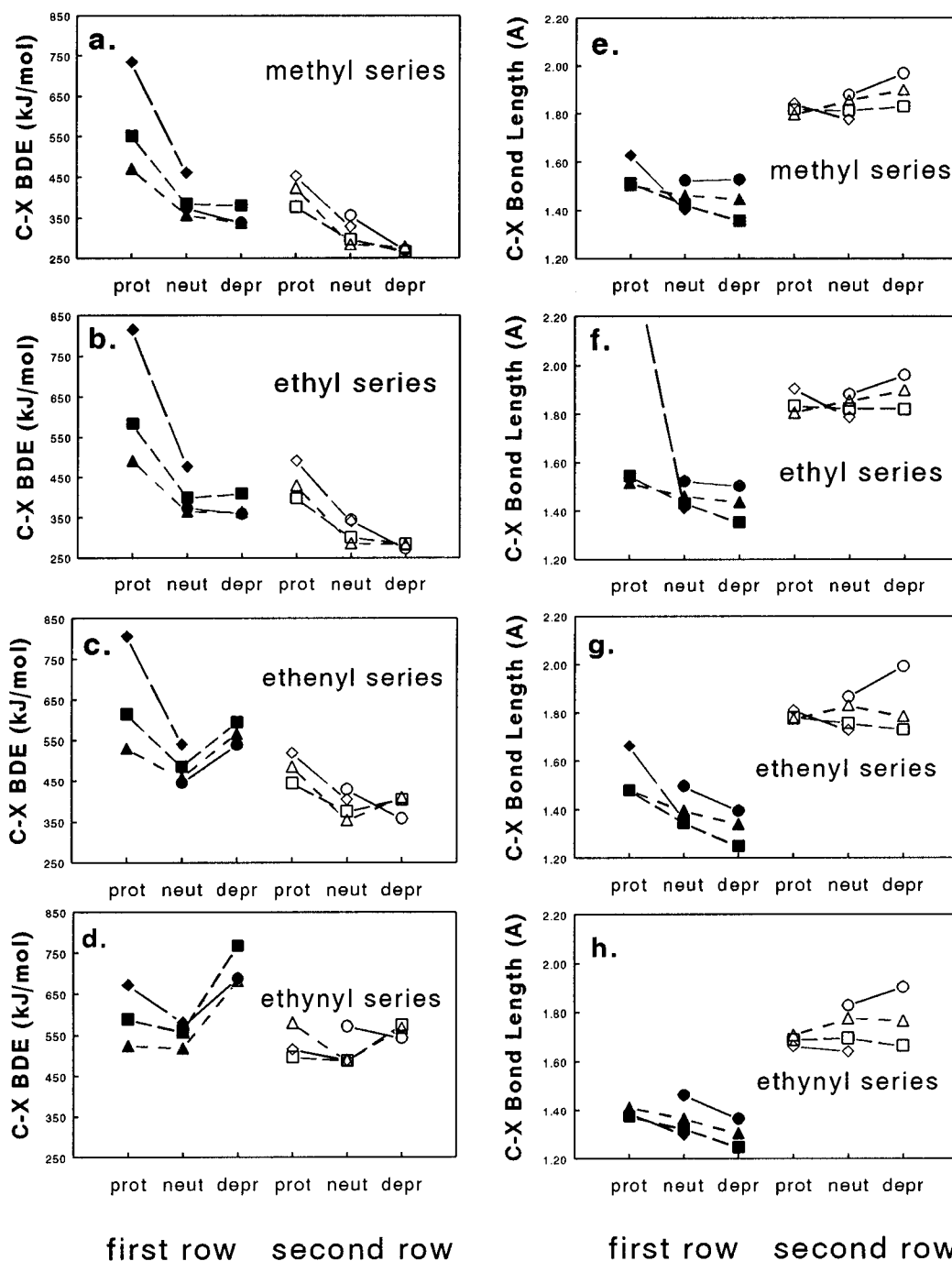


Figure 1. Effect of protonation and deprotonation of X on C–X homolytic bond dissociation energies and bond lengths for the methyl, ethyl, ethenyl, and ethynyl series: X = C, ●; N, ▲; O, ■; F, ◆; Si, ○; P, △; S, □; Cl, ◇.

containing first-row X (Figure 1a,b,c,d). The effect is somewhat greater in saturated molecules than in unsaturated ones, the increase being smallest for the ethynyl compounds, i.e., when $\text{HC}\equiv\text{CXH}_n$ is protonated to $\text{HC}\equiv\text{CXH}_{n+1}^+$. For example the increases in BDEs for the sulfur series are 80 kJ mol^{-1} (from 297 to 377 kJ mol^{-1}) for methyl thiol, 97 kJ mol^{-1} (from 301 to 398 kJ mol^{-1}) for ethyl thiol, 69 kJ mol^{-1} (from 376 to 445 kJ mol^{-1}) for ethenyl thiol, and 9 kJ mol^{-1} (from 488 to 497 kJ mol^{-1}) for ethynyl thiol. In general, the increases in BDE observed upon protonation can be rationalized by simple electronegativity arguments. According to Pauling's original ideas,¹¹ bond strength increases with increasing differences in the electronegativity of the atoms in the bond; protonation of CH_3SH to CH_3SH_2^+ therefore increases the CS BDE because the SH_2^+ group is more electronegative than the SH group. The increase in BDE is less in unsaturated compounds than in

saturated compounds because the ethynyl and ethenyl groups are correspondingly more electronegative than the ethyl or methyl groups ($\chi = 2.66, 2.58, 2.55,$ and 2.55 , respectively);¹² the higher electronegativity of the hydrocarbon moiety reduces the effect of increasing the electronegativity of the thiol group ($\chi = 2.65$) by protonation, such that the BDE is less affected by protonation for the unsaturated compounds, particularly the ethynyl ones.

Correlation of stronger bonds with shorter bonds is widely accepted among chemists,¹³ although exceptions have been

(11) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 3. See also ref 2.

(12) Boyd, R. J.; Boyd, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652. These group electronegativities are expressed in "Pauling units" ($\chi = 1.0$ for Li and 4.0 for F) and obtained from the bond critical point model, according to which the electronegativity of group X is calculated from the topological properties of the electron density at the bond critical point of HX.

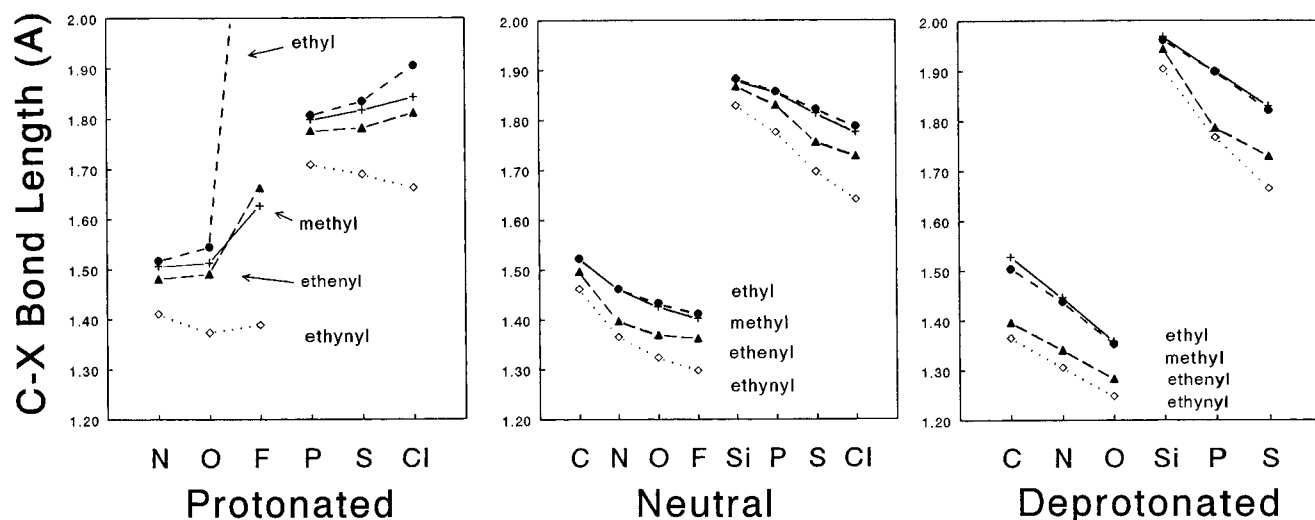


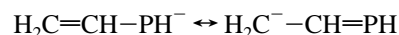
Figure 2. Periodic trends in CX bond lengths upon protonation and deprotonation of X: +, methyl compounds; ●, ethyl compounds; ▲, ethenyl compounds; ◇, ethynyl compounds.

reported.¹⁴ The $C-XH_{n+1}^+$ bonds, where X is a first-row element, therefore appear to exhibit anomalous behavior: the increases in CX BDEs upon protonation of compounds containing N, O, or F accompany substantial increases in CX bond lengths. In compounds with second-row X, the BDE increases are concurrent with much smaller increases (X = S and Cl), and for X = P there is a significant decrease in CX bond lengths (Figure 1e,f,g,h). Phosphorus is therefore the only element among the six that behaves as chemical intuition would suggest it should. Discussion of the change in bond length, which occurs when homolytic BDE increases upon protonation, will be continued below.

The effect of deprotonation of RXH_n is quite different, and there are two distinct trends depending on whether the hydrocarbon moiety is saturated or unsaturated. Consider saturated compounds first. Relative to protonation, deprotonation of compounds with X = P or S, like deprotonation when X = C, N, or O, causes only a small change in CX BDEs; for example, deprotonation of methyl- and ethylphosphine decreases the BDE by only 6 (from 284 to 278 kJ mol^{-1}) and 3 kJ mol^{-1} (from 286 to 283 kJ mol^{-1}), respectively. (The corresponding BDE increases with protonation are 140 and 145 kJ mol^{-1} .) The decrease in BDE with deprotonation is significant, however, when X = Si (i.e., 85 and 72 kJ mol^{-1} in methyl- and ethylsilane, respectively). For saturated compounds containing first-row X, deprotonation results in a shortening of the CX bond length, so again the anomalous correlation of weakening and shortening of bonds is observed. By contrast, for second-row X in saturated compounds, deprotonation increases the CX bond length; therefore, in saturated compounds containing second-row elements, a weakening of the bond is accompanied by a lengthening of the bond, which correlates with the usual trend for neutral molecules.

In unsaturated compounds ($H_2C=CHX_n$ and $HC\equiv CX_n$), the effects of deprotonation of XH_n are much more dramatic: deprotonation causes the CX BDEs to increase considerably for all first-row X, and moderately for X = P and S. These increases are accompanied by substantial geometric changes in the anions, namely both a shortening of the CX bond and an opening of the CXH bond angle, which can be rationalized by

resonance stabilization and π -bond formation.² For example,



Deprotonation of unsaturated SiH_3 compounds, on the other hand, does not lead to shortening and strengthening of the CSi bond; the bond is in fact weakened and lengthened in a parallel fashion to its behavior in saturated compounds, suggesting that Si does not participate in π -bonding to the same extent as the other atoms examined. This agrees with data in the extensive literature on multiple bonds of Si.¹⁵

The effects of protonation and deprotonation of CCX_n compounds on the α -CC bond strengths and lengths with second-row X are presented in Table 1 and illustrated in Figure 3; again, for visual comparison, the related changes for first-row X are included in Figure 3.

In general, protonation of XH_n increases the BDE and decreases the length of the adjacent CC bond, while deprotonation does the opposite. (The changes in the CC bond lengths, however, are very much smaller, indeed almost negligible, for the second-row elements, particularly for Si and P, compared to the first-row ones, despite considerable changes in BDEs.) Again, these effects can be rationalized by electronegativity and resonance arguments. For example, protonation of the CH_2SH group to $CH_2SH_2^+$ results in an increase in electronegativity, which in turn increases the homolytic CC bond strength by 36 kJ mol^{-1} when CH_3CH_2SH becomes $CH_3CH_2SH_2^+$ (i.e., from 384 to 420 kJ mol^{-1}); the CC bond length in the same protonation process decreases by 0.005 Å (from 1.520 to 1.515 Å). Interestingly, protonation of XH_n in unsaturated CCX compounds increases the CX BDEs to a greater extent than deprotonation decreases them, while the effect on the CC BDEs is of similar magnitude for protonation and deprotonation; for example, in ethylphosphine, protonation increases the CP BDE by 145 kJ mol^{-1} and the CC BDE by 33 kJ mol^{-1} , while deprotonation decreases the CP BDE by only 3 kJ mol^{-1} and the CC BDE by 75 kJ mol^{-1} .

Heterolytic vs Homolytic Bond Dissociation Energies.

Data for the heterolytic cleavage of CX bonds in CXH_n and CCX_n compounds are presented in Table 2. The cases for which heterolytic cleavage is lower in energy than the corresponding homolytic cleavage are footnoted.

(13) Shriver, D. F.; Atkins, P. W.; Langford, C. H. In *Inorganic Chemistry*, 2nd ed.; Freeman: New York, 1994; pp 75 and 76.

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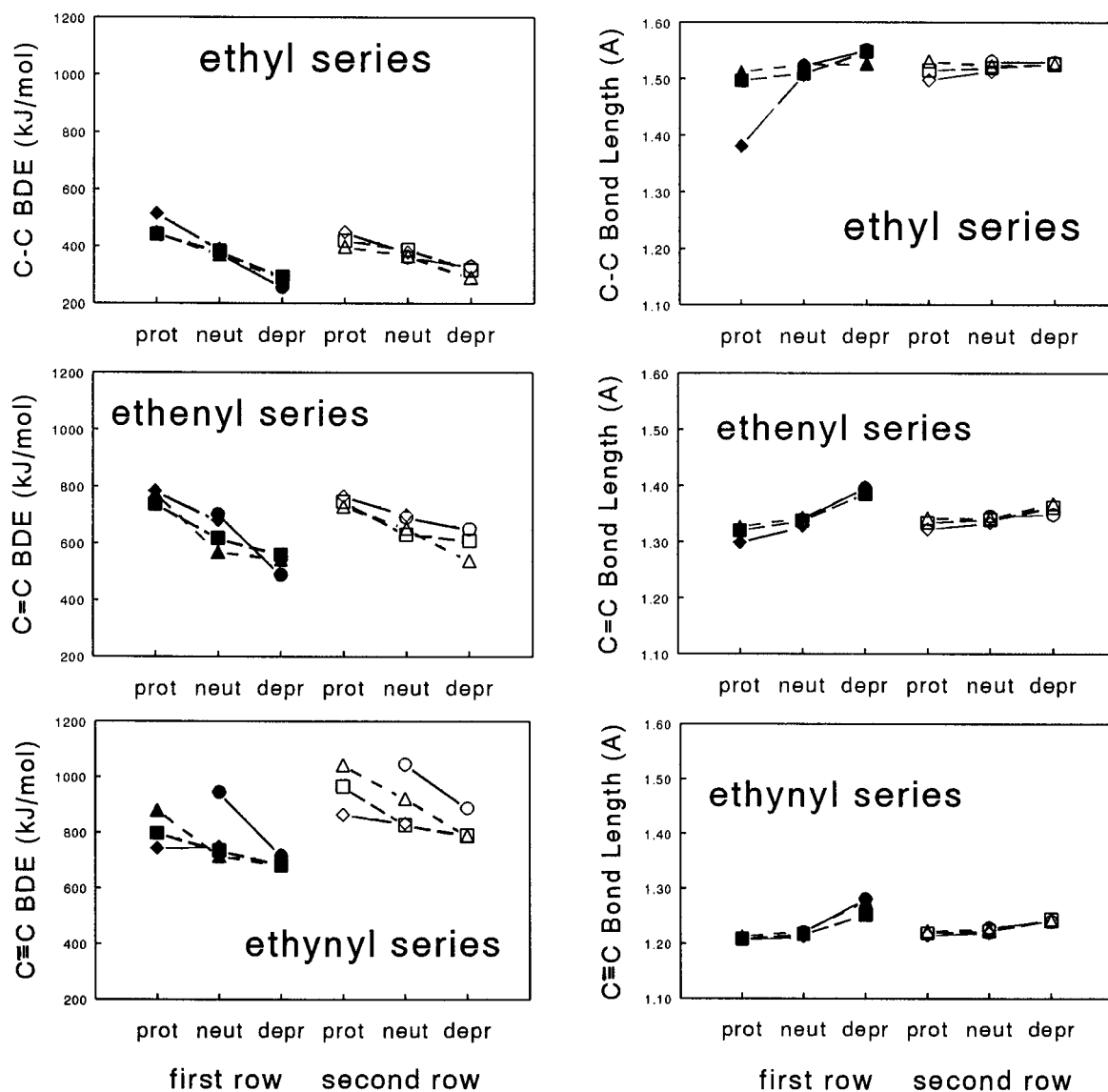


Figure 3. Effect of protonation and deprotonation of X on CC homolytic bond dissociation energies and bond lengths for the ethyl, ethenyl, and ethynyl series of CCX compounds. X = C, ●; N, ▲; O, ■; F, ◆; Si, ○; P, △; S, □; Cl, ◇.

Second-row elements favor heterolytic dissociation to a lesser extent than first-row elements. Thus, heterolytic bond dissociation for protonated species, i.e., $\text{RCXH}_{n+1}^+ \rightarrow \text{RC}^+ + \text{XH}_n$, is energetically favored over the homolytic dissociation for the same species, i.e., $\text{RCXH}_{n+1}^+ \rightarrow \text{RC}^\bullet + \bullet\text{XH}_{n+1}^+$, for 11 of the possible 12 dissociations of first-row compounds but only 9 of the 12 second-row compounds. Heterolytic dissociation is always favored when X is highly electronegative relative to the hydrocarbon moiety, as in X = F, O, and Cl. As the electronegativity of X decreases, there are fewer instances in which heterolytic cleavage is favored. For example, for X = N or S, it is no longer favored for the ethynyl compounds; and for X = P it is favored for neither ethynyl- nor methylphosphine.

It is not surprising that heterolytic cleavage is favored for protonated compounds containing highly electronegative atoms, since the optimized geometries of the protonated compounds suggest that the RCXH_{n+1}^+ species, particularly those for X = F, O, and Cl, have considerable carbocation-dipole character, $\text{RC}^+\cdots\text{XH}_{n+1}$, as illustrated previously.² While bond lengths decrease for neutral species as one proceeds from left to right in a given row, the trend is reversed for protonated species (Figure 2); electronegative Xs result in particularly long C-XH_{n+1}⁺ bonds. The exception to this is the protonated ethynyl species, whose bond lengths generally decrease left to

right like the neutral compounds; but recall that the protonated ethynyl species favor heterolytic dissociation only for the most electronegative elements (X = F, O, and Cl).

Essentially the opposite situation prevails when RCXH_n is deprotonated to RCXH_{n-1}^- . Now the heterolytic BDE approaches the homolytic one for $\text{RCX}_{n-1}^- \rightarrow \text{RC}^- + \text{XH}_{n-1}$, provided that X is low in electronegativity; in fact, it is often favored when the carbanion product RC^- is unsaturated, e.g., as with $\text{HC}\equiv\text{CX}_{n-1}^-$ (X = C, N, O, Si, and P) and $\text{H}_2\text{C}=\text{CHX}_{n-1}^-$ (X = C, N, and P). However, the reactivity of the product XH_{n-1} means that heterolytic cleavage is favored less often with the deprotonated starting material than with the protonated one. Carbanion-dipole character ($\text{RC}^-\cdots\text{XN}_{n-1}$) is also less apparent in the optimized geometry of RCXH_{n-1}^- ; nor is there as dramatic a change in the CX bond lengths upon deprotonation as occurs with protonation, particularly for the saturated species (Figure 1).

Thus, for F, O, and Cl, and to a lesser extent for S and N, the apparently anomalous behavior of increasing BDE together with increasing bond length upon protonation is a result of the focus on homolytic bond cleavage. In fact, heterolytic cleavage is the preferred route. The C-XH_{n+1}⁺ bond lengthens relative to the C-XH_n bond, and it weakens heterolytically, despite its

Table 2: Heterolytic CX Bond Dissociation Energies in CXH_n and CCXH_n: Effect of Protonation and Deprotonation of XH_n, X = Si, P, S, Cl^a

	CX bond	
	ΔH_{298} (RCXH _n → RC ⁺ + XH _n ⁻) (kJ/mol)	ΔH_{298} (RCXH _n → RC ⁻ + XH _n ⁺) (kJ/mol)
Silicon Series		
CH ₃ SiH ₃	1199 (1179) ^b	1144 (1145)
CH ₃ SiH ₂ ⁻	1566 (1648)	379/439 ^c (374/471)
C ₂ H ₅ SiH ₃	1024	1155
C ₂ H ₅ SiH ₂ ⁻	1404	403/462
C ₂ H ₅ SiH ₃	1152	1128
C ₂ H ₅ SiH ₂ ⁻	1534	378/437
C ₂ H ₅ SiH ₃	1641	1019
C ₂ H ₅ SiH ₂ ⁻	2065	311/371 ^a
Phosphorus Series		
CH ₃ PH ₃ ⁺	450 (440) ^a	2191 (2197)
CH ₃ PH ₂	1138 (1125)	1242/1284 (1235/1320)
CH ₃ PH ⁻	1629 (1619)	497/334 (467/365)
C ₂ H ₅ PH ₃ ⁺	293 ^a	2220
C ₂ H ₅ PH ₂	975	1265/1308
C ₂ H ₅ PH ⁻	1471	524/362
C ₂ H ₅ PH ₃ ⁺	390 ^a	2161
C ₂ H ₅ PH ₂	1087	1222/1265
C ₂ H ₅ PH ⁻	1641	539/376
C ₂ H ₅ PH ₃ ⁺	832	2005
C ₂ H ₅ PH ₂	1568	1105/1148
C ₂ H ₅ PH ⁻	2146	446/284 ^a
Sulfur Series		
CH ₃ SH ₂ ⁺	341 ^a (338)	2737/2418 (2436/2458)
CH ₃ SH	1049 (1034)	1476/1271 (1436/1304)
CH ₃ S ⁻	1615 (1611)	629/672 (590/473)
C ₂ H ₅ SH ₂ ⁺	198 ^a	2780/2462
C ₂ H ₅ SH	889	1502/1297
C ₂ H ₅ S ⁻	1468	669/712
C ₂ H ₅ SH ₂ ⁺	288 ^a	2715/2396
C ₂ H ₅ SH	1007	1465/1260
C ₂ H ₅ S ⁻	1632	677/720
C ₂ H ₅ SH ₂ ⁺	686	2526/2197
C ₂ H ₅ SH	1466	1326/1121
C ₂ H ₅ S ⁻	2148	595/638
Chlorine Series		
CH ₃ ClH ⁺	191 ^a (199)	2871/2628 (2830/2670)
CH ₃ Cl	943 (949)	1781/1553 (1733/1588)
C ₂ H ₅ ClH ⁺	64 ^a	2931/2688
C ₂ H ₅ Cl	792	1815/1587
C ₂ H ₅ ClH ⁺	135 ^a	2846/2604
C ₂ H ₅ Cl	899	1767/1539
C ₂ HClH ⁺	479 ^a	2592/2350
C ₂ HCl	1330	1601/1373

^a Heterolytic cleavage is lower in energy than the corresponding homolytic cleavage. ^b Where values in parentheses appear, these are the G2 BDEs. ^c Most of the XH_n⁺ products can exist in either singlet or triplet state; in these cases, BDEs for dissociation to both states are given in the form S/T, with the BDE for the lower energy product underlined and used for comparative purposes.

homolytic strengthening. The universal tenet of chemistry, that longer bonds are weaker, is therefore supported.

There remains, however, some discrepancy with the methylamine, methylphosphine, and methyl thiol series: there is an increase in both homolytic and heterolytic CX BDEs, concurrent with increases in CX bond lengths, with protonation of these compounds.

Second-row elements behave in a "similar, but different," manner to first-row ones: bond length changes upon protonation and deprotonation are less dramatic, and clearly Si, as well as P to a lesser extent, is fundamentally different from C and N.

Conclusions

1. Effect of Protonation and Deprotonation on Homolytic BDEs and Bond Lengths. a. CX Bonds. BDEs for second-

row elements are lower than those for first-row elements, and bond lengths are correspondingly longer. **Protonation** of XH_n in RCXH_n increases the CX homolytic BDE in all first- and second-row elements. The effect is greater in saturated molecules than in unsaturated ones, and can be rationalized by simple electronegativity arguments, supported by group electronegativities. These increases in BDEs anomalously accompany substantial increases in CX bond lengths in the first-row elements (N, O, F), but in the second-row elements either much smaller increases (S, Cl) in bond length or significant decreases (P) result upon protonation. Relative to protonation, **deprotonation** of XH_n within **saturated** compounds causes only a small change (generally a decrease) in CX BDEs, although the effect becomes significant in Si. Deprotonation concurrently results in a shortening of the CX bond length (thus the anomalous decrease in BDE and decrease in bond length is apparent again) for compounds containing first-row X, but an increase in CX bond length for those with second-row X. In **unsaturated** compounds (H₂C=CHXH_n and HC≡CXH_n) deprotonation causes the CX BDEs to increase considerably in all cases but Si. These large increases are accompanied by bond length decrease and bond angle opening resulting from increased CX π-bonding in the anions due to resonance stabilization.

b. CC Bonds. Protonation of XH_n increases the BDE and decreases the bond length of the adjacent CC bond for all first- and second-row CCXH_n compounds; deprotonation does the reverse. (The effect on the CC bond lengths, however, is very much smaller for the second-row elements than for the first-row ones, despite considerable changes in BDEs.) These effects can be rationalized by electronegativity and resonance arguments.

2. Heterolytic vs Homolytic Bond Dissociation Energies. Second-row elements favor heterolytic dissociation less than first-row elements.

a. Protonation. Heterolytic bond dissociation for the process RCXH_{n+1}⁺ → RC⁺ + XH_{n+1} is energetically favored over the homolytic process RCXH_{n+1}⁺ → RC[•] + •XH_{n+1}⁺ when X is highly electronegative. The protonated starting materials, RCXH_{n+1}⁺, in fact have geometries that show definite carbocation-dipole character, i.e., positive charge on the C and long C–X bonds.

b. Deprotonation. When RCXH_n is deprotonated to RCXH_{n-1}⁻, heterolytic bond dissociation for the process RCXH_{n-1}⁻ → RC⁻ + XH_{n-1} is also occasionally favored, particularly when X is low in electronegativity and when the carbanion, RC⁻, is unsaturated.² The product XH_{n-1} is a reactive diradical, however, so the favoring of heterolytic cleavage over the homolytic process occurs less often than in the protonated series; carbanion-dipole character is also not evident in the optimized geometry of RCXH_{n-1}⁻.

The apparently anomalous behavior of CX bond length increase occurring together with CX bond strength increase during protonation and deprotonation of XH_n in CX_n and CCXH_n compounds may therefore be an artifact of focussing on bond cleavage as a homolytic process; protonation and deprotonation of both first- and second-row elements within these compounds often make heterolytic cleavage the favored route, and bond lengthening is accompanied by bond weakening in most of these cases.

Acknowledgment. The financial support of the Mount Saint Vincent University Research Fund (to S.L.B.) and the Natural Sciences and Engineering Research Council of Canada (to R.J.B.) is gratefully acknowledged.