J. Phys. Chem. A **1999,** *103,* 7087−7093

Protonation and Deprotonation Effects on the Chemistry of the Third-Row Elements: Homolytic versus Heterolytic Cleavage

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Received: March 30, 1999; In Final Form: June 23, 1999

Ab initio MO calculations indicate that the effect of protonation of third-row X (X = Ge, As, Se, Br) in CH_3XH_n, $C_2H_5XH_n$, $C_2H_3XH_n$, and C_2HXH_n is similar to that of first- and second-row X; specifically, both the CX homolytic bond dissociation energies (BDEs) and (except for As and the ethynyl compounds) the CX bond lengths (BLs) increase. Deprotonation decreases the CX BDE for saturated compounds, an electronegativity effect, but increases it for unsaturated ones (except Ge), a resonance effect; correspondingly, the CX BLs increase in saturated and decrease in unsaturated compounds (except Ge). Heterolytic CX dissociation of third-row $RCXH_{n+1}^+$ to RC^+ and XH_{n+1} is often favored over the homolytic process when XH_{n+1} is electronegative relative to the hydrocarbon moiety (XH_{n+1} = AsH_3, SeH_2, BrH); the corresponding dissociation of $RCXH_{n-1}^-$ to RC^- and XH_{n-1} similarly may be favored for RC = ethynyl and X_{n-1} low in electronegativity (XH_{n-1} = GeH_2^-, AsH^-, Se^-). The CC BDEs are also affected by protonation of X; protonation increases the CC BDEs and usually shortens the CC bond, while deprotonation does the opposite.

Introduction

The strength of a chemical bond, expressed in terms of its bond dissociation energy (BDE), is of fundamental importance in any consideration of chemical reactivity. Standard textbook tabulations[1,2] of average or representative BDEs are often used to estimate thermochemical data for processes for which direct experimental data are unavailable. In such calculations it is generally assumed that average BDEs can be used to predict the strengths of similar bonds irrespective of the nature of the substituents. This assumption can be misleading, especially for charged species. For example, protonation of the amine group has been shown to lead to a large increase in the homolytic BDE of the CN bond in methylamine and ethylamine. For methylamine the calculated 114 kJ/mol increase in the CN BDE due to protonation is in excellent agreement with the experimental value of 111 kJ/mol;[3] similarly, for ethylamine the calculated increase, 126 kJ/mol, agrees with the experimental value, 124 kJ/mol.[4] The increase in homolytic BDE that accompanies protonation of amines also holds for alcohols and other heteroatomic bonds and has been explained in terms of electronegativity trends.[3,4]

Perhaps even more interesting is the observation that as a consequence of protonation, the heterolytic process may be favored over the homolytic one.[4] Thus, it has been shown that the BDE for the heterolytic process

$$CH_3NH_3^+ \rightarrow CH_3^+ + NH_3$$

is favored over the homolytic process

$$CH_3NH_3^+ \rightarrow CH_3^{\bullet} + {}^{\bullet}NH_3^+$$

by 28 kJ/mol (experimental) and 26 kJ/mol (calculated).[4] The effects are even greater for more electronegative heteroatoms. For example, for protonated methanol the heterolytic process is favored over the homolytic process by 265 kJ/mol (experimental) and 274 kJ/mol (calculated). This observation has important implications for the well-known competitions between heterolytic cleavage and homolytic cleavage in organic photochemistry.[5]

There is, however, a paucity of thermochemical data from which accurate BDEs in the presence of various substituents can be determined. Fortunately, ab initio methods have been developed that make it feasible to obtain reliable thermochemical data by purely theoretical methods. The quantum chemical methods are especially helpful for short-lived and highly reactive intermediates.

The effects of both protonation and deprotonation on bond lengths (BLs) and BDEs have been studied theoretically in recent years by a number of groups.[6−10] We ourselves have investigated these effects on both first-[4] and second-row[11] elements. The earlier tabulations for the effects of protonation and deprotonation on bond dissociation energies have provided insight into topics as diverse as the synthesis of charged phenyl radicals in the gas phase,[12] the positive ion chemistry of elemental fluorine,[13] the structures of oxime/oximatoplatinum(II) complexes,[14] the photodissociation of *N*-(triphenylmethyl)anilines,[15] and the rearrangement reactions of *N*-(triarylmethyl)anilines.[16] The results of our previous studies are also relevant to a semiquantitative model for polar ground-state effects on bond dissociation energies[17] and the validity of additivity schemes for the estimation of the heats of formation of distonic radical cations.[18]

The present paper, which reports the completion of the series, examines the effects of protonation and deprotonation on BLs and BDEs of the third-row elements. Motivation for our additional computations is provided by recent experimental studies of the gas-phase basicities and acidities of small arsines,[19] closely related experimental measurements on germane and methyl germane,[20] and accurate theoretical studies[21] of the

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10.1021/jp991096q CCC: $18.00

thermochemical properties of the third-row binary hydrides, GeH_4, AsH_3, SeH_2, and HBr.

Thus, we have determined the homolytic CX BDEs for the species RXH_{n+1}^+, RXH_n, and RXH_{n-1}^-, i.e.,

$$RXH_{n+1}^+ \rightarrow R^\bullet + {}^\bullet XH_{n+1}^+$$

$$RXH_n \rightarrow R^\bullet + {}^\bullet XH_n$$

$$RXH_{n-1}^- \rightarrow R^\bullet + {}^\bullet XH_{n-1}^-$$

where R = CH_3, CH_3CH_2, $H_2C{=}CH$, and $HC{\equiv}C$, while X = Ge, As, Se, and Br. For comparison, we have calculated the corresponding heterolytic CX BDEs, i.e.,

$$RXH_{n+1}^+ \rightarrow R{:}^- + XH_{n+1}^{2+}$$

$$RXH_n \rightarrow R{:}^- + XH_n^+$$

$$RXH_{n-1}^- \rightarrow R{:}^- + XH_{n-1}$$

and

$$RXH_{n+1}^+ \rightarrow R^+ + {:}XH_{n+1}$$

$$RXH_n \rightarrow R^+ + {:}XH_n^-$$

$$RXH_{n-1}^- \rightarrow R^+ + {:}XH_{n-1}^{2-}$$

Finally, we have also computed the CC BDEs for RXH_{n+1}^+, RXH_n, and RXH_{n-1}^- where R = CH_3CH_2, $H_2C{=}CH$, and $HC{\equiv}C$, while X = Ge, As, Se, and Br. Results for a total of 80 homolytic and 104 heterolytic processes involving 40 parent species are reported in the present paper. In all cases, the BDEs were computed with respect to the most stable fragments, irrespective of whether the latter species have classical or nonclassical structures, e.g. bridging hydrogens, or whether they are unbound (as is the case of the dications and dianions.)

Computational Methods

To allow direct comparison with our earlier work,[4,11] all energies and geometries were determined by use of the GAUSSIAN 94 program[22] at the MP2/6-31+G(d,p)//MP2/6-31+G(d,p) level (including all electrons in the post-Hartree–Fock calculations). All open-shell species have been treated with unrestricted wave functions, which are known to yield a better description of bond dissociation.[23] Frequency analyses were done at the HF/6-31+G(d,p)//HF/6-31+G(d,p) level to confirm that the geometries were local minima, as well as to obtain zero-point and thermal energies; the zero-point energies were scaled (by 0.9).[23,24] Spin contamination was relatively low in the majority of the species considered herein; $\langle S^2\rangle$ was typically in the range 0.75–0.77 for the doublet states (except for the $C{-}XH_n$ dissociation products from the ethynyl compounds) and 2.00–2.03 for the triplet states. For the methyl series of compounds and ions, the standard G2 level of theory[25] (rather than any of the proposed modifications for third-row species[26,27]) was also used to ascertain whether the trends observed at the MP2/6-31+G(d,p) level of theory parallel those at the higher level; they do. All BDEs have been corrected to 298 K to facilitate comparison with experimental data. Full details on the calculation of the BDEs are given elsewhere.[4]

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 = Ge, As, Se, Br

	CX bond		CC bond	
	ΔH_{298}(CX bond cleavage)[a] (kJ/mol)	CX bond length (Å)	ΔH_{298}(CC bond cleavage)[b] (kJ/mol)	CC bond length (Å)
Germanium Series				
CH_3GeH_3	355 (334)	1.926		
$CH_3GeH_2^-$	268 (255)	2.019		
$C_2H_5GeH_3$	353	1.927	378	1.527
$C_2H_5GeH_2^-$	272	2.013	348	1.525
$C_2H_3GeH_3$	430	1.913	881/779/803/*701*	1.342
$C_2H_3GeH_2^-$	363	1.986	661/747/*583*/669	1.347
C_2HGeH_3	608	1.879	1087	1.227
$C_2HGeH_2^-$	577	1.956	943	1.237
Arsenic Series				
$CH_3AsH_3^+$	420 (400)	1.891		
CH_3AsH_2	286 (270)	1.954		
CH_3AsH^-	250 (250)	2.001		
$C_2H_5AsH_3^+$	435	1.899	412	1.528
$C_2H_5AsH_2$	290	1.958	377	1.524
$C_2H_5AsH^-$	250	1.984	319	1.527
$C_2H_3AsH_3^+$	483	1.871	911/816/833/*738*	1.334
$C_2H_3AsH_2$	362	1.922	773/775/*695*/697	1.340
$C_2H_3AsH^-$	384	1.882	642/757/*564*/678	1.361
$C_2HAsH_3^+$	608	1.800	1084	1.222
C_2HAsH_2	523	1.868	992	1.225
C_2HAsH^-	569	1.866	849	1.239
Selenium Series				
$CH_3SeH_2^+$	367 (354)	1.944		
CH_3SeH	288 (281)	1.943		
CH_3Se^-	256 (255)	1.970		
$C_2H_5SeH_2^+$	390	1.964	426	1.519
C_2H_5SeH	301	1.947	374	1.518
$C_2H_5Se^-$	278	1.962	341	1.532
$C_2H_3SeH_2^+$	438	1.900	882/869/803/*791*	1.335
C_2H_3SeH	372	1.879	726/780/*648*/702	1.339
$C_2H_3Se^-$	387	1.865	707/949/*629*/871	1.355
$C_2HSeH_2^+$	522	1.806	1005	1.219
C_2HSeH	514	1.818	882	1.222
C_2HSe^-	584	1.799	853	1.240
Bromine Series				
CH_3BrH^+	409 (414)	1.993		
CH_3Br	301 (308)	1.944		
$C_2H_5BrH^+$	445	2.047	449	1.499
C_2H_5Br	317	1.958	390	1.512
$C_2H_3BrH^+$	517	1.953	880/886/*801*/808	1.325
C_2H_3Br	377	1.890	789/785/711/*707*	1.333
C_2HBrH^+	508	1.793	894	1.216
C_2HBr	489	1.787	876	1.220

[a] Data in parentheses are BDEs determined by using G2 calculations. [b] The products of homolytic dissociation of the double bonds in $H_2C{=}CHXH_n$ 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 H_2C is in a singlet state and the $CHXH_n$ is in a triplet one, etc. The lowest BDE for each dissociation is italicized and is used for comparative purposes.

Results and Discussion

The homolytic CX and CC BDEs and BLs for the third-row RXH_n (i.e., X = Ge, As, Se, Br), together with those for their protonated and deprotonated species, are listed in Table 1. A graphical representation of the changes in homolytic CX BDEs and BLs with protonation and deprotonation is presented in Figure 1, with the corresponding changes for first-row[4] and

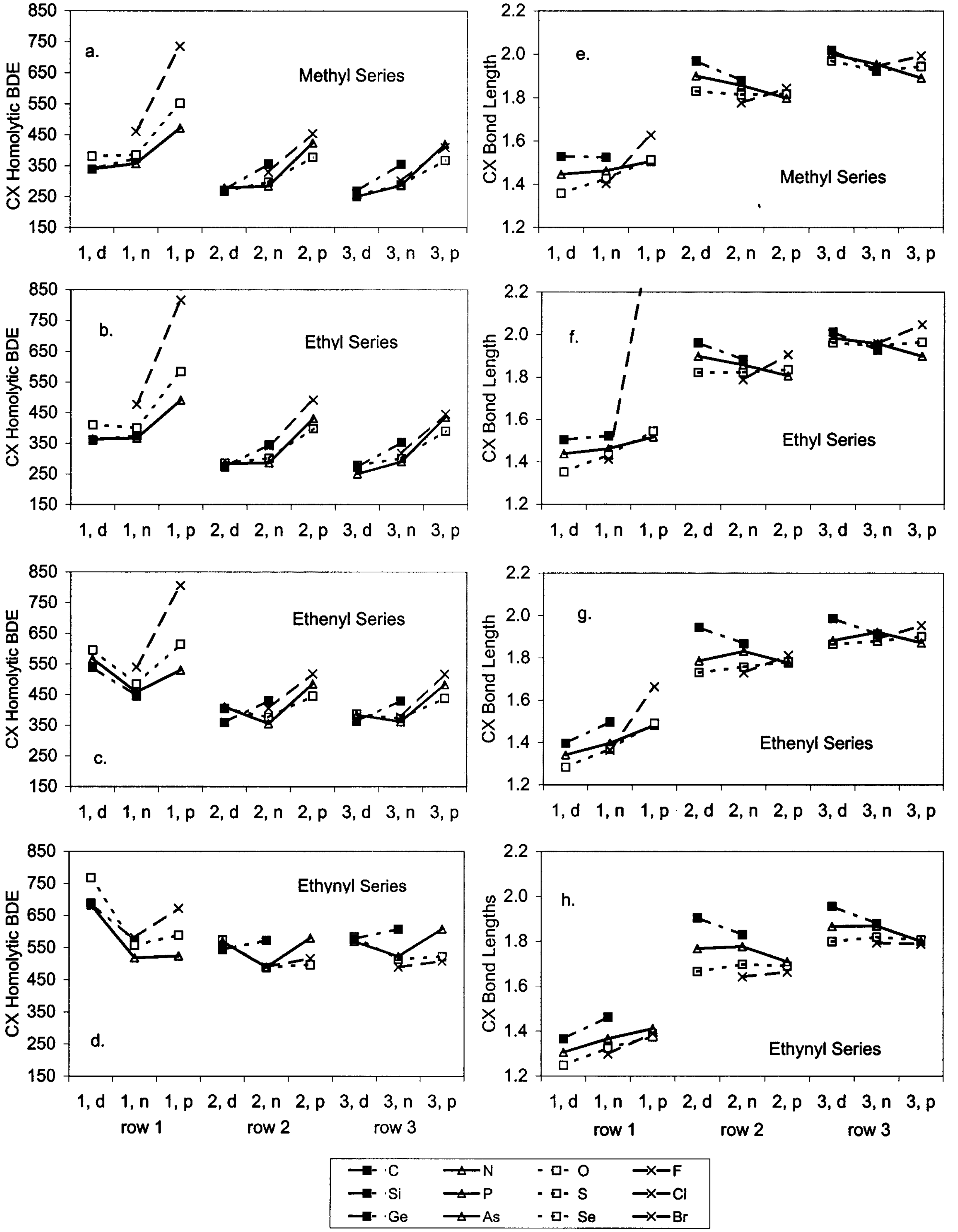

Figure 1. Effect of protonation and deprotonation of X on CX homolytic BDEs (kJ/mol) (a–d) and BLs (Å) (e–h) for the methyl, ethyl, ethenyl, and ethynyl series. 1,d = deprotonated row 1 ions; 1,n = neutral row 1 compounds; 1,p = protonated row 1 ions; etc.

second-row[11] elements included for comparison; Figure 2 illustrates the analogous changes in the CC BDEs and BLs. Table 2 lists the heterolytic RX BDEs for both processes (i.e., those producing R^+ and R^-), and Figure 3 gives the corresponding graphical representation.

Effect of Protonation and Deprotonation on Homolytic CX BDEs. Parts a–d of Figure 1 summarize the trends associated with 120 CX homolytic bond cleavages: the 40 heteroatomic bonds involving Ge, As, Se, and Br reported in this paper, together with the corresponding data for the first-row

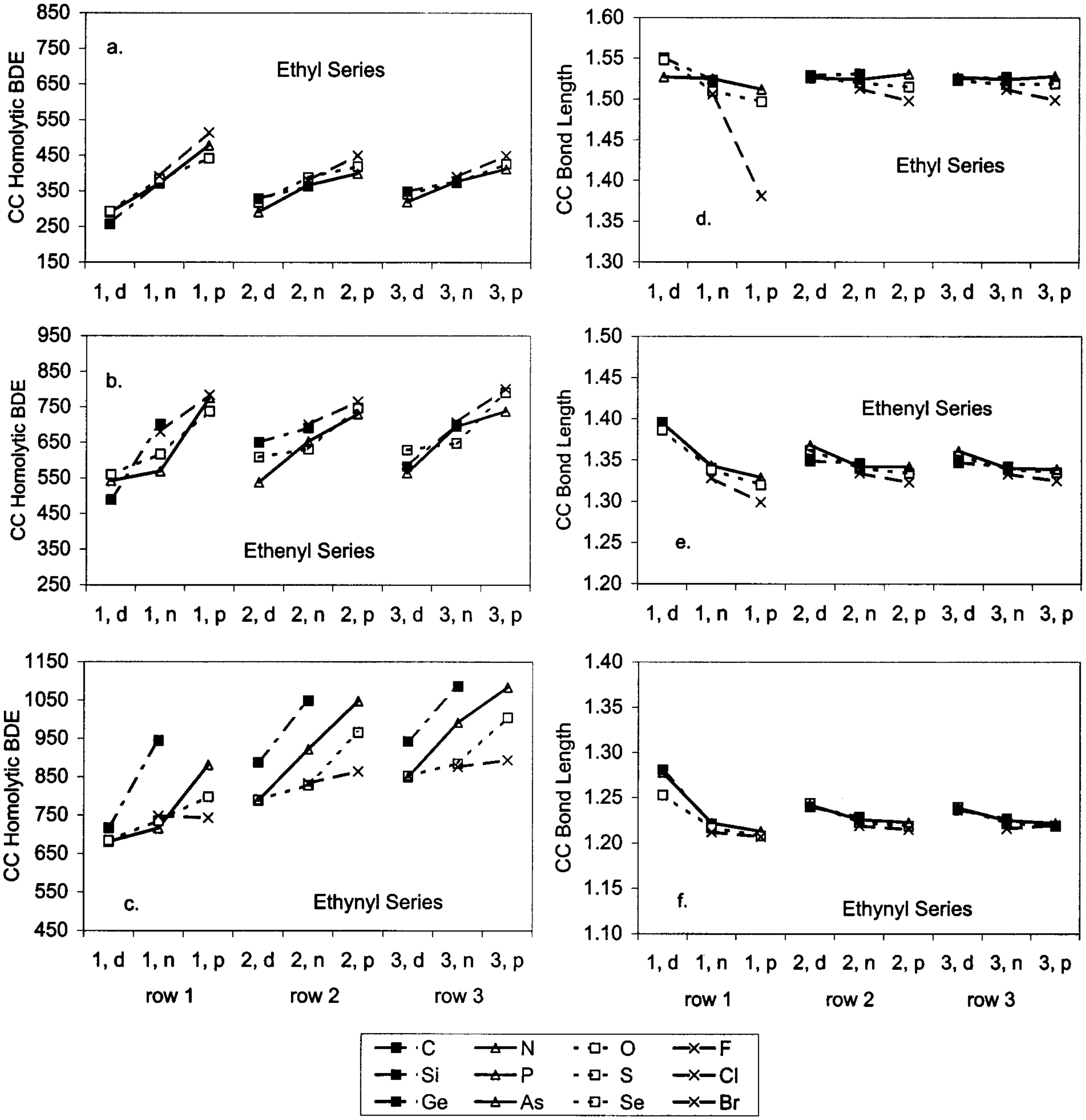

Figure 2. Effect of protonation and deprotonation of X on α-CC homolytic BDEs (kJ/mol) (a−c) and BLs (Å) (d−f) for the ethyl, ethenyl, and ethynyl series. 1,d = deprotonated row 1 ions; 1,n = neutral row 1 compounds; 1,p = protonated row 1 ions; etc.

and second-row elements. Generally speaking, the BDE decreases as one descends a given group; for the ethynyl compounds, however, the third-row species have higher BDEs than the second-row ones.

The most striking feature, which emerges clearly in Figure 1, is the similarity between the trends in BDEs of the second- and third-row elements, both of which differ distinctly from those of the first-row elements. Thus, for a given group of the periodic table, the changes between the second- and third-row BDEs are smaller than the corresponding changes between the first- and second-row BDEs. This trend is not surprising. On the basis of many experimental properties and chemical concepts, it has long been known that larger differences exist between first- and second-row elements than between second- and third-row ones.[28−31] An example comes from accurate spectroscopic data[32] for the hydrogen halides: the equilibrium bond lengths are 0.917, 1.275, 1.414, and 1.609 Å for HF, HCl, HBr, and HI, respectively, and the corresponding BDEs are 5.87, 4.43, 3.76, and 3.05 eV.

For all third-row RXH_n compounds, protonation of X increases the CX BDE, as observed previously for the analogous first- and second-row compounds. This increase can be rationalized by the fact that protonation increases the electronegativity of the X group, which leads to an increase in homolytic bond strength.[3,4,6,11]

In the *saturated* third-row compounds, deprotonation in all cases decreases the BDEs, although the effect is less dramatic than the increase in BDE upon protonation. It is interesting that deprotonation decreases the BDE for the third-row saturated compounds to a greater extent than it does for the second-row ones. (For example, for CH_3PH_2 and CH_3PH^-, it is 284 and 278 kJ/mol, respectively, a change of 6 kJ/mol, while for CH_3AsH_2 and CH_3AsH^- it is 286 and 250 kJ/mol, respectively, a change of 36 kJ/mol.)

Deprotonation increases the BDE in *unsaturated* third-row compounds (except Ge) because of a resonance effect, e.g., $H_2C{=}CH{-}X^- \leftrightarrow H_2C^-{-}CH{=}X$, as previously noted for first- and second-row compounds.[4,11] Ge, like Si,[11] is an exception

TABLE 2: Heterolytic CX Bond Dissociation Energies in CXH_n and $CCXH_n$: Effect of Protonation and Deprotonation of XH_n, X = Ge, As, Se, Br[a]

	ΔH_{298} (kJ/mol)	
	$RCXH_n \rightarrow RC^+ + XH_n^-$	$RCXH_n \rightarrow RC^- + XH_n^{+\,c}$
	Germanium Series	
CH_3GeH_3	1170 (1122)	1139 (1090)
$CH_3GeH_2^-$	1618 (1573)	*392*/464 (*350*/459)
$C_2H_5GeH_3$	1003	1158
$C_2H_5GeH_2^-$	1458	*418*/490
$C_2H_3GeH_3$	1124	1124
$C_2H_3GeH_2^-$	1593	*398*/470
C_2HGeH_3	1649	1050
$C_2HGeH_2^-$	2153	*360*/432[b]
	Arsenic Series	
$CH_3AsH_3^+$	443 (406)	2115 (2063)
CH_3AsH_2	1123 (1086)	*1216*/1282 (*1165*/1265)
CH_3AsH^-	1568 (1543)	503/*366* (440/*343*)
$C_2H_5AsH_3^+$	294[b]	2152
$C_2H_5AsH_2$	963	*1243*/1308
$C_2H_5AsH^-$	1293	414/*278*
$C_2H_3AsH_3^+$	386[b]	2089
$C_2H_3AsH_2$	1078	*1202*/1267
$C_2H_3AsH^-$	1580	546/*410*
$C_2HAsH_3^+$	857	1962
C_2HAsH_2	1585	*1112*/1177
C_2HAsH^-	2112	480/*344*[b]
	Selenium Series	
$CH_3SeH_2^+$	371 (346)	*2301*/2323 (*2248*/2301)
CH_3SeH	1018 (999)	1409/*1219* (1332/*1210*)
CH_3Se^-	1537 (1530)	623/*450* (553/*446*)
$C_2H_5SeH_2^+$	231[b]	*2346*/2368
C_2H_5SeH	748	1325/*1135*
$C_2H_5Se^-$	1395	668/*495*
$C_2H_3SeH_2^+$	322[b]	*2282*/2304
C_2H_3SeH	982	1403/*1214*
$C_2H_3Se^-$	1547	664/*491*
$C_2HSeH_2^+$	752	*2114*/2137
C_2HSeH	1470	1294/*1104*
C_2HSe^-	2090	610/*437*[b]
	Bromine Series	
CH_3BrH^+	220 (223)[b]	2625/*2406* (2547/*2406*)
CH_3Br	907 (915)	1646/*1441* (1565/*1436*)
$C_2H_5BrH^+$	−11[b]	2581/*2361*
C_2H_5Br	759	1684/*1479*
$C_2H_3BrH^+$	208[b]	2624/*2424*
C_2H_3Br	862	1632/*1427*
C_2HBrH^+	545	2384/*2164*
C_2HBr	1321	1494/*1288*

[a] Values in parentheses are G2 BDEs. [b] Heterolytic cleavage is lower in energy than the corresponding homolytic clevage. [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 italicized and used for comparative purposes.

in that deprotonation decreases the CX BDE in unsaturated species as it does in saturated ones. The weakening of the CSi and CGe multiple bonds associated with deprotonation is consistent with the extensive literature[33] that indicates that Si (and presumably Ge) does not participate in π-bonding to the same extent as carbon and some of the other main group elements. A referee has suggested the following rationalization for this effect. The lack of π-bonding to Ge and Si in $H_2C{=}CHGeH_2^-$ and $H_2C{=}CHSiH_2^-$ may be in part due to the fact that these species are not planar, unlike $H_2C{=}CHAsH^-$, $H_2C{=}CHPH^-$, $H_2C{=}CHSe^-$, and $H_2C{=}CHS^-$, all of which have orbitals with the right π symmetry to conjugate with the vinyl group. The planar forms of the Ge and Si derivatives are further destabilized because of the planarization/inversion energy barrier of the germyl and silyl anions.[34]

Effect of Protonation and Deprotonation on CX Bond Lengths. CX BLs where X is a third-row element are, of course, longer than those where X is a second-row one. The relative difference between the BLs is greater than that for the corresponding BDEs of the third-row versus second-row elements (parts e−h of Figure 1); that is, the CX bonds containing third-row elements are longer than, but about equally as strong as, the CX bonds containing second-row X.

As observed for all first-row and most second-row elements (except P),[4,11] protonation of the third-row species (except As) generally leads to increases in BLs. The exception is in the ethynyl compounds, where protonation decreases all BLs of third-row elements, correlating with the increase in BDE experienced by these compounds upon protonation. The increases in BLs of the methyl, ethyl, and ethenyl compounds on the other hand occur concomitantly with increases in homolytic BDEs, an apparent anomaly; however, as before,[4,11] protonation often leads to an ion−dipole structure, favoring heterolytic bond dissociation, which will be discussed below.

Deprotonation of the *saturated* compounds generally produces an increase in the CX BLs for the second-row and third-row compounds, contrary to the decrease observed for the first-row species. For the second- and third-row species, the increase in BL correlates with the decrease in homolytic BDEs upon deprotonation, the normal trend;[35] the decreased electronegativity of the deprotonated X group results in a weakening and lengthening of the bond.

In the case of the *unsaturated* compounds, deprotonation shortens the CX bonds in compounds in all three rows, with the exception of compounds of Si and Ge. This is a resonance effect, as discussed above.

Effect of Protonation and Deprotonation on Heterolytic CX BDEs. BDEs for the heterolytic cleavage of CX bonds in CXH_n and $CCXH_n$ compounds are presented in Table 2 and Figure 3; the latter again contains data for the corresponding first- and second-row species, with parts a−d of Figure 3 illustrating cleavage to RC^+ and parts e−h of Figure 3 showing the cleavage to RC^-.

A low heterolytic BDE for the protonated compounds is due to the carbocation/dipole character of the $RCXH_{n+1}^+$ ($RC^+\cdots XH_{n+1}$). That is, contributions from a "no bond" resonance structure (RC^+XH_{n+1})[7,18] result in a lengthening of the CX bond, an increase in the homolytic BDE, and a lowering of the heterolytic CX BDE. The heterolytic cleavage (even in the gas phase) becomes the preferred route in $C_2H_5AsH_3^+$, $C_2H_3AsH_3^+$, $C_2H_5SeH_2^+$, $C_2H_3SeH_2^+$, $C_2H_5BrH^+$, $C_2H_3BrH^+$, and CH_3BrH^+, as footnoted in Table 2. As observed for the second-row elements, the third-row elements favor heterolytic dissociation to a lesser extent than first-row elements. Thus, heterolytic bond dissociation for protonated species (i.e., $RCXH_{n+1}^+ \rightarrow RC^+ + XH_{n+1}$) is energetically favored over the homolytic dissociation (i.e., $RCXH_{n+1}^+ \rightarrow RC^\bullet + {}^\bullet XH_{n+1}$) for 11 of the possible 12 dissociations of the first-row compounds, 9 of the second-row ones, and 7 of the third-row species. Heterolytic dissociation is almost always favored for the protonated species when X is highly electronegative relative to the hydrocarbon moiety, as in X = F, O, Cl, and Br (except protonated ethynyl bromide.) As the electronegativity of X decreases, there are fewer instances in which heterolytic cleavage to RC^+ is favored; for example, for X = N, S, and Br, it is no longer favored for the ethynyl species, and for P, As, and Se it is favored for neither the ethynyl nor the methyl species. In the case of the ethynyl compounds, the ethynyl group is more electronegative than the ethenyl or ethyl groups (2.65 compared to 2.58 and 2.55, respectively[36])

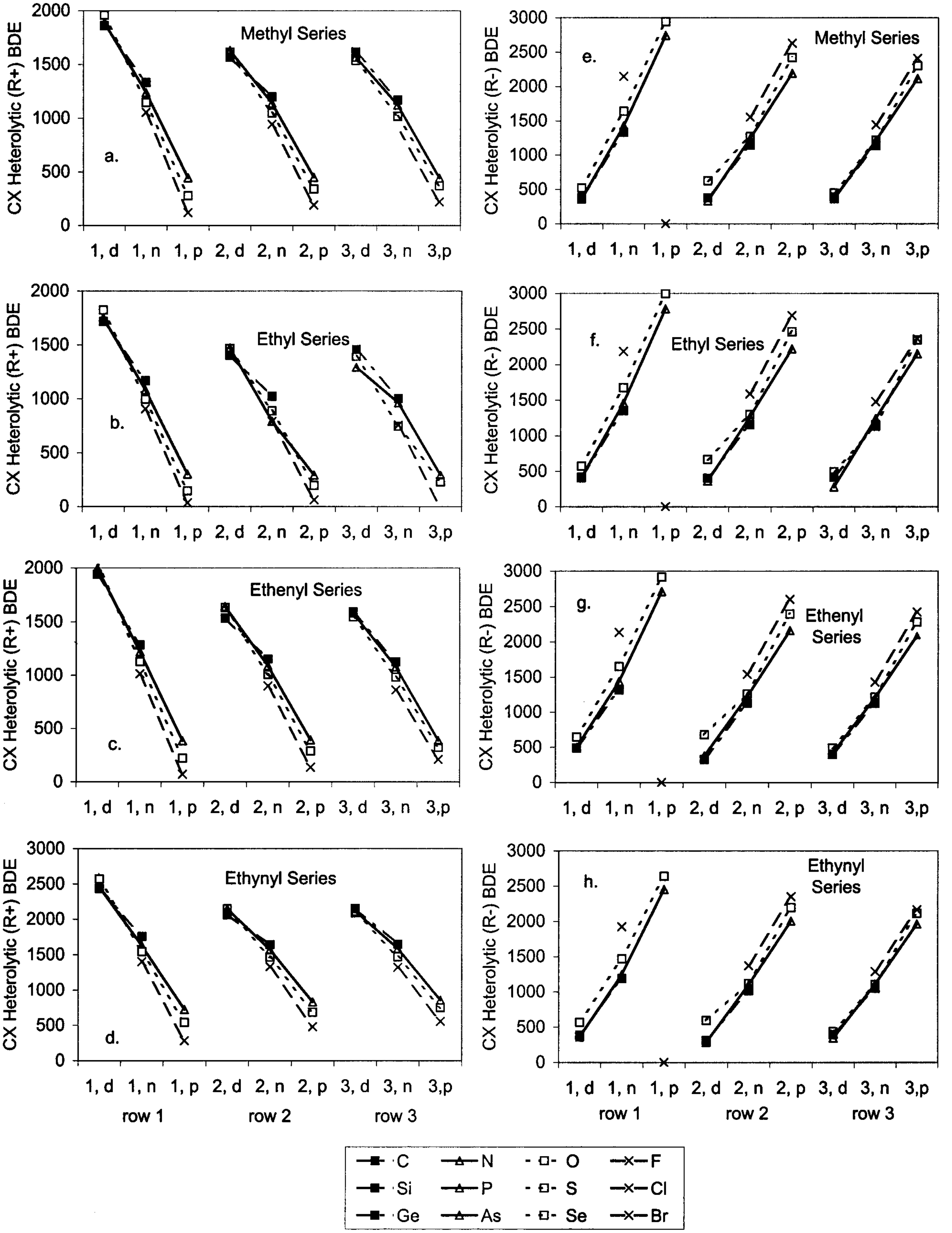

Figure 3. Effect of protonation and deprotonation of X on CX heterolytic BDEs (kJ/mol) for the methyl, ethyl, ethenyl, and ethynyl series. Parts a–d illustrate the BDEs for heterolytic cleavage to R^+, and parts e–h show the BDEs for cleavage to R^-. 1,d = deprotonated row 1 ions; 1,n = neutral row 1 compounds; 1,p = protonated row 1 ions; etc.

so that protonation of X does not increase its electronegativity sufficiently to allow heterolytic over homolytic dissociation. For the situation with the methyl compounds, the methyl carbocation product is less stable than the ethyl or unsaturated carbocations ($H_2C{=}CH^+$ and $HC{\equiv}C^+$), since the latter form bridging structures.

The corresponding heterolytic cleavage of the deprotonated $RCXH_{n-1}^-$ species (i.e., $RCXH_{n-1}^- \rightarrow RC^- + XH_{n-1}$) is also relatively low in energy, even in the gas phase, but is favored less often over the homolytic process (i.e., $RCXH_{n-1}^- \rightarrow RC^\bullet + {}^\bullet XH_{n-1}^-$) than the protonated cases. Only for the deprotonated ethynyl Ge, As, and Se species are the heterolytic BDEs lower than the homolytic ones. Again, the relatively high electronegativity of the ethynyl group, together with the low electronegativity of the deprotonated GeH_2^-, AsH^-, and Se^- groups, allows a significant "no bond" resonance contributor, RC^-XH_{n-1}, with the result that the heterolytic BDE is lower than the homolytic one.

Effect of Protonation and Deprotonation on Homolytic CC BDEs and BLs. The CC BDEs and BLs listed in Table 1 for the $CCXH_n$ species, where X is a third-row element, closely resemble those where X is a second-row element, and both undergo less dramatic, though parallel, changes upon protonation and deprotonation relative to the first-row species. Protonation in all cases (except ethynyl fluoride) increases the homolytic CC BDE. In species containing the first-row elements, as well as those with S, Cl, and Br, this produces a shortening of the CC bond length, owing to the increase in electronegativity of the X group. For P, Se, and As, however, despite the increase in homolytic BDE upon protonation, there is a slight lengthening of the CC bond, i.e., an increase in homolytic bond strength together with an increase in bond length.

Deprotonation for species in all three rows decreases the homolytic CC BDE. For all ethyl compounds but those of Si and Ge, the BL correspondingly increases, but the change is very small. All unsaturated compounds experience an increase in CC BL upon deprotonation, a resonance effect.

Conclusions

1. Homolytic CX BDEs for compounds containing third-row elements are generally slightly lower than those of the second-row (except for the ethynyl compounds), and both are considerably lower than those of the first-row elements. Protonation increases the CX homolytic BDEs for all third-row species. Deprotonation decreases the CX BDEs for saturated third-row compounds but increases it for unsaturated ones (except Ge).

2. Not surprisingly, CX BLs are longer for third-row compounds than for second- or first-row ones. Protonation of X increases the CX BL (except for X = As) for the methyl, ethyl, and ethenyl compounds; for the ethynyl compounds, protonation shortens the BL. Deprotonation increase the CX BLs for all saturated third-row species and decreases it in unsaturated compounds except those of Ge.

3. Heterolytic $RCXH_{n+1}^+$ dissociation to RC^+ and XH_{n+1} becomes favored when an electronegative X is protonated. Similarly, dissociation of $RCXH_{n-1}^-$ to RC^- and XH_{n-1} is competitive in cases when X is low in electronegativity and is favored for the ethynyl compounds.

4. Protonation of X in $CCXH_n$ increases the homolytic CC BDEs for all third-row species and increases the CC BLs slightly for the Se and As species but decreases it for the Br ones. Deprotonation decreases the CC BDEs and generally increases the CC BLs.

Acknowledgment. We are delighted to acknowledge the hospitality of Professor Leo Radom and his colleagues in the Research School of Chemistry at the Australian National University where the present manuscript was written. 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.

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