A Theoretical Study of the Effects of Protonation and Deprotonation on Bond Dissociation Energies

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Abstract: *Ab initio* molecular orbital calculations indicate that the bond dissociation energies (BDE) for homolytic cleavage of CX bonds (X = C, N, O, F) are increased by protonation of the corresponding alkyl, amine, alcohol, or fluoride functional groups; the effect of deprotonation of these groups is rather small for saturated species, whereas for unsaturated ones deprotonation leads to large increases in the CX BDEs. The effects on the CC BDEs in CCX compounds are quite systematic: protonation of X increases the CC BDE, while the converse holds for deprotonation. Two types of correlation between bond lengths and homolytic bond dissociation energies are observed. Firstly, protonation and deprotonation lead to a normal correlation for the adjacent CC bonds: the bond length decreases as the BDE increases. Protonation, however, results in an anomalous correlation for the CX bonds: the bond length increases as the BDE increases. These observations are rationalized in terms of electronegativity, resonance stabilization, and competing heterolytic dissociation.

Introduction

The strength of a chemical bond, expressed in terms of the bond dissociation energy (BDE), is one of the fundamental quantities of chemistry. Textbook compilations of BDEs for the common bonds of organic chemistry are averages of experimental values, while the BDE for a given bond in an inorganic species is usually based on thermochemical data for a single compound. Tabulations 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 mislead, especially for charged groups. 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.[1] The striking effect of protonation of X on the BDEs of CX bonds, where X = N, O and F, has been explained in terms of electronegativity arguments.[1] Given that protonation has such a large effect and that reactions involving charged species (radical cations, radical anions and closed-shell ions) are common, it is natural to ask what the effect of a charged substituent is on the BDE of an adjacent bond, and whether deprotonation has the opposite effect.

Ab initio methods have been developed to the extent that it is now possible to obtain reliable thermochemical data by purely theoretical methods. Moreover theoretical methods can be applied to a large number of systems which are not amenable to experiment. The effect of substituents on BDEs can be investigated by considering a series of related molecules in which the charge on the substituent and the bond order of the adjacent bond are varied systematically. Starting with ethylamine, for example, nine species can be generated by protonation and deprotonation of the amine group and by introducing successive degrees of unsaturation into the CC bond:

$CH_3{-}CH_2{-}NH_3^+$ $CH_2{=}CH{-}NH_3^+$ $CH{\equiv}C{-}NH_3^+$

$CH_3{-}CH_2{-}NH_2$ $CH_2{=}CH{-}NH_2$ $CH{\equiv}C{-}NH_2$

$CH_3{-}CH_2{-}NH^-$ $CH_2{=}CH{-}NH^-$ $CH{\equiv}C{-}NH^-$

An analogous nine are based on ethanol as the parent molecule. In addition six species exist in each of the propane and ethyl fluoride series:

$CH_3{-}CH_2{-}CH_3$ $CH_2{=}CH{-}CH_3$ $CH{\equiv}C{-}CH_3$

$CH_3{-}CH_2{-}CH_2^-$ $CH_2{=}CH{-}CH_2^-$ $CH{\equiv}C{-}CH_2^-$

and

$CH_3{-}CH_2{-}FH^+$ $CH_2{=}CH{-}FH^+$ $CH{\equiv}C{-}FH^+$

$CH_3{-}CH_2{-}F$ $CH_2{=}CH{-}F$ $CH{\equiv}C{-}F$

The products of homolytic cleavage of the double bonds are carbenes which may be formed in singlet and triplet states. Thus, for each C=C species we can list four BDE values corresponding to the four possible dissociation products. Homolytic cleavage of all other bonds yields radicals with doublet ground states.

This paper describes the results of a systematic *ab initio* molecular orbital study of the effects of protonation and deprotonation of X (X = C, N, O, and F) on the bond dissociation energies of the CX bonds and of adjacent C−CX, C=CX, and C≡CX bonds in hydrocarbons, amines, alcohols, and alkyl fluorides. Results for a further 10 molecules in the methyl series are included for comparison; the methyl series

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(1) Boyd, R. J.; Glover, J. N. M.; Pincock, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 5152.

was also used to ascertain the appropriate level of theory and basis set to be used in the study. Therefore 40 species, with 100 homolytic dissociation reactions, were examined. In addition, heterolytic dissociation of the 40 systems was investigated, requiring a further 108 processes.

Choice of the Computational Level

In order to calculate accurate bond dissociation energies it is desirable to use a level of theory comparable to the Gaussian-1 and Gaussian-2 procedures[2,3] (denoted by G1 and G2, respectively) which have been shown to yield total atomization energies that reproduce experimental thermochemical data to an accuracy better than 8 kJ mol^{-1} for most molecules involving only first-row atoms and hydrogen. Given that the treatment of electron correlation is less demanding for the BDEs of individual bonds than for total atomization energies and that the systems of interest here are too large to compute at the G1 and G2 levels with our facilities, we have opted for a lower level of theory. In an earlier paper[1] we calculated energies to third-order in Møller−Plesset (MP3) perturbation theory by use of the 6-31G(d,p) basis set at the Hartree−Fock 6-31G(d) optimized geometries. This level of molecular orbital theory is denoted by MP3/6-31G(d,p)//HF/6-31G(d). We noted that the MP3/6-31G(d,p) calculations give results very similar to those obtained via fourth-order Møller−Plesset perturbation theory; moreover Hehre *et al.*[4] have suggested that any residual errors (typically 20−40 kJ mol^{-1}) are due largely to the limitation of the 6-31G(d,p) basis set and not to truncation of the perturbation series expansion. We noted further that unpublished calculations by Pople[5] indicate that the MP3/6-31G(d,p) method accurately predicts the trends associated with protonation.

The present study involves anions, and therefore diffuse functions must be included in the basis set. A systematic study of several basis sets (6-31G(d), 6-31+G(d,p), 6-31++G(d,p)) and levels (SCF, MP2, MP3, MP4(SDTQ)) was undertaken to compare calculated homolytic BDEs to experimental ones; on the basis of the results listed in Table S1, we have concluded that 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, leads to reliable results. (In our test series, for example, the experimental energies were reproduced with a mean error of −3 (±8) kJ mol^{-1} as compared to the most complete set of experimental thermochemical data available.[6] We note, however, that many of the experimental quantities are themselves uncertain.)

All energies were consequently determined at the MP2/6-31+G(d,p)//MP2/6-31+G(d,p) level. Frequency calculations were done at the HF/6-31+G(d,p) optimized geometry to obtain thermal energies and to confirm that the structure was at a minimum on the potential energy surface; in cases where the MP2/6-31+G(d,p) optimized geometry differed considerably from the HF/6-31+G(d,p) optimized geometry, frequency analyses were also done at the former level. Bond lengths were obtained from the MP2/6-31+G(d,p) optimized geometries. All calculations were performed with the GAUSSIAN 90[7] and GAUSSIAN 92[8] packages of programs.

Experimental bond lengths were obtained from Harmony *et al.*[9] or Calloman *et al.*[10] Experimental BDEs were determined from thermodynamic data (ΔH_f^{298}), where available.[6,11] Thus, for the process

$$\mathrm{A{-}B} \rightarrow \mathrm{A} + \mathrm{B}$$

the experimental bond dissociation energy for the A−B bond was obtained as follows:

$$\mathrm{BDE}_{\mathrm{exp}}(\mathrm{A{-}B}) = \Delta H^{289}_{\mathrm{exp}} = \Delta H_f^{298}(\mathrm{A}) + \Delta H_f^{298}(\mathrm{B}) - \Delta H_f^{298}(\mathrm{A{-}B})$$

In order to facilitate comparison with these experimental data, theoretical BDE were calculated at 298 K by the method of Foresman and Frisch,[12] except that the zero point vibrational energies were scaled by a factor of 0.9.[13] Thus,

$$\mathrm{BDE}_{\mathrm{calc}}(\mathrm{A{-}B}) = \Delta H^{298}_{\mathrm{calc}} = \Delta E^{298}_{\mathrm{calc}} + \Delta(PV)$$

$$\Delta E^{298}_{\mathrm{calc}} = \Delta E^0_e + \Delta(E_{\mathrm{Thermal}})^{\mathrm{corr}}$$

$$\Delta(E_{\mathrm{Thermal}})^{\mathrm{corr}} = \Delta(\Delta E_e)^{298} + 0.9\Delta E^0_v + \Delta(\Delta E_v)^{298} + \Delta E_r^{298} + \Delta E_t^{298} = \Delta(E_{\mathrm{Thermal}}) - 0.1\Delta E^0_v$$

where ΔE^0_e = total energy difference between products and reactants at 0 K as obtained from total energies computed at MP2/6-31+G(d,p)//MP2/6-31+G(d,p). $\Delta(\Delta E_e)^{298}$ = change in the electronic energy difference between 0 and 298 K. This term is negligible for the species involved and was ignored. ΔE^0_v = difference between the zero-point energies of products and reactants at 0 K. $\Delta(\Delta E_v)^{298}$ = change in the vibrational energy difference between 0 and 298 K. ΔE_r^{298} = difference in the rotational energies of products and reactants. ΔE_t^{298} = translational energy change between products and reactants. $\Delta(E_{\mathrm{Thermal}})^{\mathrm{corr}}$ = the corrected thermal energy difference between products and reactants. The thermal energy, E_{Thermal}, was obtained directly from the HF/6-31+G(d,p) frequency analysis and includes all of the *E* terms except the ΔE^0_e; $\Delta(E_{\mathrm{Thermal}})$ is the difference in thermal energies of reactants and products, and $\Delta(E_{\mathrm{Thermal}})^{\mathrm{corr}} = \Delta(E_{\mathrm{Thermal}}) - 0.1\Delta E^0_v$. $\Delta(PV)$ = PV work term = $+RT$ since there is a net increase of 1 mol of gas formed in each dissociation reaction.

Results and Discussion

Tables 1 and 2 list the homolytic bond dissociation energies at 298 K and the corresponding equilibrium bond lengths for

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(13) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; p 260.

Table 1. CC Bonds in CCX: Homolytic C−C, C=C, and C≡C Bond Dissociation Energies (BDE, kJ mol^{-1}) and Bond Lengths (BL, Å)[a]

$$CCX \rightarrow C^{\bullet} + {}^{\bullet}CX$$

X		hydrocarbon moiety (CC)		
		CH_3−CH_2	H_2C=CH	HC≡C
CH_3	BDE	374(368)	$\underline{702}$/745/780/823[b]	945
	BL	1.523(1.526)	1.340(1.339)	1.221(1.206)
CH_2^-	BDE	257	686/$\underline{489}$/764/567(486)	717
	BL	1.551	1.396	1.281
NH_3^+	BDE	448(413)	$\underline{776}$/828/854/907	914
	BL	1.512	1.327	1.213
NH_2	BDE	371(352)	717/$\underline{562}$/797/642	716
	BL	1.525	1.343	1.222
NH^-	BDE	290	713/$\underline{542}$/791/620	681
	BL	1.527	1.395	1.278
OH_2^+	BDE	442	765/$\underline{738}$/842/816	797
	BL	1.497	1.320	1.208
OH	BDE	383(355)	708/$\underline{618}$/787/695	735
	BL	1.510(1.512)	1.338	1.217
O^-	BDE	291	667/$\underline{560}$/745/638	684
	BL	1.548	1.386	1.253
FH^+	BDE	513(477)	818/$\underline{784}$/897/863	743
	BL	1.381	1.299	1.207
F	BDE	390(376)	715/$\underline{680}$/795/758(638)	748(744)
	BL	1.506(1.505)	1.328(1.329)	1.212(1.198)

[a] Calculated BDEs are based on MP2/6-31+G(d,p)//MP2/6-31+G(d,p) energies; BLs are from MP2/6-31+G(d,p) optimized geometries. Experimental data are in parentheses; the BDEs were calculated from the thermodynamic data in ref 6, and the BLs are from ref 9. [b] The products of homolytic dissociation of the double bonds in H_2C=CHX are carbenes which may be in singlet or triplet states; therefore, the BDEs calculated for the various combinations of products states are all presented. They are listed in the order of TT/TS/ST/SS, where TS means that the H_2C: is in a triplet state and the:CHX is in a singlet state, etc. The lowest BDE in each dissociation is underlined and is used for comparative purposes.

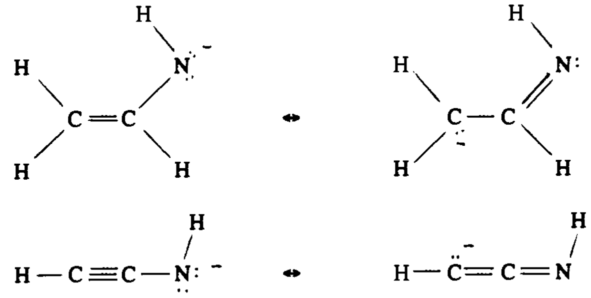
the 100 homolytic bond dissociation processes delineated in the Introduction. The results are represented graphically in Figures 1 and 2.

Effect of Protonation and Deprotonation of X on Homolytic Dissociation of CC Bonds in CCX. For the CC bonds which are adjacent to the X being protonated or deprotonated, there is a clear trend. The data in Table 1 and Figure 1 indicate that protonation of X increases the bond dissociation energy and decreases the bond length for the α-CC bonds, and the opposite is true for deprotonation. For example, in ethylamine, ethanol, and ethyl fluoride, protonation raises the C−C BDEs by 77 (from 371 to 448), 59 (from 383 to 442), and 123 (from 390 to 513) kJ mol^{-1}, respectively, while the C−C bond lengths are shortened by 0.013 (from 1.525 to 1.512), 0.013 (from 1.510 to 1.497), and 0.125 (from 1.506 to 1.381) Å, respectively. Deprotonation of propane, ethylamine, and ethanol has the opposite effect: it decreases the C−C BDEs by 117 (from 374 to 257), 81 (from 371 to 290), and 92 (from 383 to 291) kJ mol^{-1} and increases the C−C bond lengths by 0.028 (from 1.523 to 1.551), 0.002 (from 1.525 to 1.527), and 0.038 (from 1.510 to 1.548) Å, respectively. The same trends, with one exception, are evident for the corresponding C=C and C≡C BDEs and bond lengths: protonation increases the CC BDE and shortens the CC bond, while deprotonation decreases the BDE and lengthens the bond. The exception is HC≡CF. In this case although protonation does shorten the CC bond by 0.005 Å (from 1.212 to 1.207Å), the BDE decreases by 5 kJ mol^{-1} (from 748 to 743 kJ mol^{-1}); the anomalous behavior of protonated fluorides has been noted previously.[1]

The effect of protonation and deprotonation of X on homolytic bond dissociation energies of α-CC bonds can be rationalized in terms of Pauling's original ideas[14] about the connection between the bond energy and the electronegativity difference between two bonded atoms: bond strength increases with increasing differences in the electronegativity of the atoms in the bond. For example, the $CH_2NH_3^+$ group in protonated ethylamine, $CH_3CH_2NH_3^+$, is more electronegative than the corresponding CH_2NH_2 in the neutral ethylamine, $CH_3CH_2NH_2$, and consequently the BDE for the C−C bond in the protonated species is larger.[1]

Effect of Deprotonation of X on Homolytic Dissociation of CX Bonds in C=CX and C≡CX. Another general trend is observed in deprotonation of X adjacent to an unsaturated hydrocarbon (see Table 2 and Figure 2): deprotonation greatly increases the CX BDEs of the ethenyl and ethynyl species. For example, the BDEs of ethenol and ethynol increase by 111 (from 485 to 596) and 211 (from 557 to 768) kJ mol^{-1}, respectively. As shall be discussed shortly, BDEs of CX bonds in saturated compounds by comparison change only very slightly as a result of deprotonation.

The qualitative difference between the saturated and unsaturated cases is consistent with resonance stabilization. For H_2C=$CHNH^-$ and HC≡CNH^-, this can be illustrated as follows:



With the loss of a proton, the CN bonds of the anions should therefore gain substantial double bond character and their BDEs should increase, while the bond orders and BDEs of the CC multiple bonds should decrease by similar amounts. This interpretation of the BDE trends is supported quantitatively by the structural changes which accompany deprotonation (Figure 3). Thus, deprotonation of ethenylamine results in a shortening of the CN bond by 0.056 Å (from 1.397 to 1.341 Å), while the CC bond increases by 0.052 Å (from 1.343 to 1.395 Å). The results for ethynyl amine are very similar, with the CN bond decreasing by 0.061 and the CC triple bond increasing by 0.056 Å; deprotonation also has a distinct effect on the bond angles, with the HCC bond changing from 174.7° in ethynyl amine to 132.8° in the deprotonated species. The unsaturated hydrocarbon, amine, and fluoride analogues behave in a similar manner; i.e., resonance results in the shortening and strengthening of the C−X bonds and the lengthening and weakening of the C=C or C≡C bonds in the deprotonated species.

Effect of Protonation and Deprotonation of X on Homolytic Dissociation of CX Bonds. As can be seen from the data of Table 2, protonation of X increases the CX BDE of all compounds studied, with the effect being greater in the saturated molecules than in the unsaturated ones. For example, the increase is 114 (from 357 to 471) and 126 (from 365 to 491) kJ mol^{-1} for methylamine and ethylamine, and 72 (from 458 to 530) and 7 (from 518 to 525) kJ mol^{-1} for ethenylamine and ethynylamine, respectively. Again, electronegativity arguments can explain this trend. For example, protonation of the amine

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[14] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 3. See also ref 1.

Table 2. CX Bonds in RCX: Homolytic CX Bond Dissociation Energies (BDE, kJ mol^{-1}) and Bond Lengths (BL, Å)[a]

$RCX \rightarrow RC^{\bullet} + {}^{\bullet}X$

fragment X$^{\bullet}$		hydrocarbon fragment (RC$^{\bullet}$)			
		$H_3C^{\bullet}$	$CH_3{-}CH_2^{\bullet}$	$H_2C{=}CH^{\bullet}$	$HC{\equiv}C^{\bullet}$
$^{\bullet}CH_3$	C−C BDE	374(376, 368)	374(368)	446(391)	572(524, 490)
	C−C BL	1.524(1.533)	1.523(1.526)	1.497	1.462(1.459)
$^{\bullet}CH_2^-$	C−C BDE	340(326)	360	539(467)	689
	C−C BL	1.528	1.504	1.396	1.365
$^{\bullet}NH_3^+$	C−N BDE	471(469)	491(478)	530(556)[b]	525
	C−N BL	1.506	1.517	1.481	1.411
$^{\bullet}NH_2$	C−N BDE	357(358, 331)	365(354)	458(425)	518
	C−N BL	1.462(1.471)	1.462	1.397	1.366
$^{\bullet}NH^-$	C−N BDE	339(352)	365(365)	566	683
	C−N BL	1.446	1.438	1.341	1.305
$^{\bullet}OH_2^+$	C−O BDE	552(554)	584(586)	615(621)	589
	C−O BL	1.513	1.545	1.491	1.374
$^{\bullet}OH$	C−O BDE	385(386, 377)	400(392)	485(429)	557
	C−O BL	1.426(1.425)	1.433(1.431)	1.369	1.324
$^{\bullet}O^-$	C−O BDE	381(393)	412(412)	596(539)	768(724)
	C−O BL	1.358	1.353	1.283	1.248
$^{\bullet}FH^+$	C−F BDE	743(743)	816(817)	806	672
	C−F BL	1.627	2.521	1.663	1.389
$^{\bullet}F$	C−F BDE	461(472, 452)	479(461)	540(484)	581(537)
	C−F BL	1.403(1.383)	1.412(1.398)	1.363(1.347)	1.298(1.279)

[a] In cases where two values for the experimental BDEs appear, the second one utilizes data found in ref 11. [b] This experimental BDE is based on ΔH_f ($CH_2{=}CHNH_3^-$) from *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

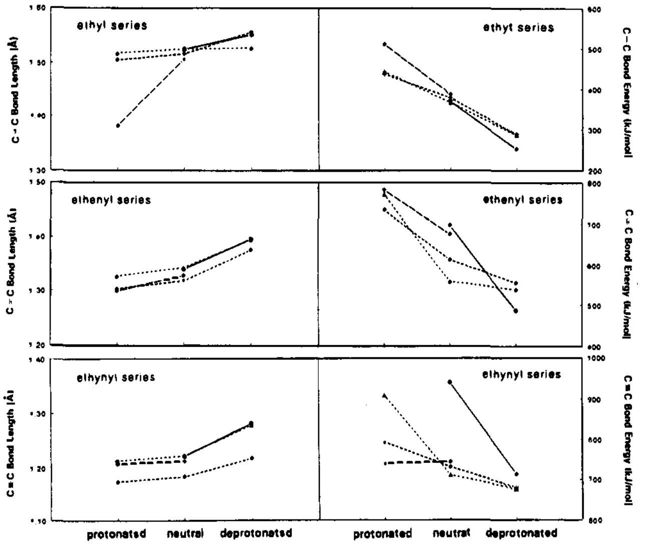

Figure 1. Effect of protonation and deprotonation of X on α-C−C, α-C=C, and α-C≡C bond lengths and homolytic bond dissociation energies for the ethyl series (CH_3CH_2X), the ethenyl series ($H_2C{=}CHX$), and the ethynyl series ($HC{\equiv}CX$): (●) X = CH_3; (▲) X = NH_2; (+) X = OH; (♦) X = F.

group in CH_3NH_2 to $CH_3NH_3^+$ increases the CN BDE because NH_3^+ is more electronegative than NH_2 (3.21 *vs* 3.12).[15] Electronegativity also accounts for the smaller increase in BDE as the CC becomes increasingly unsaturated, e.g., within the ethylamine, ethenylamine, and ethynylamine series. The electronegativities of the ethyl, ethenyl, and ethynyl groups increase with the degree of unsaturation, e.g., they are 2.55, 2.58, and 2.65, respectively.[15] Therefore the increase in the electronegativity of the hydrocarbon moiety opposes the effect of increasing the electronegativity of the alcohol group by protonation. In fact, the electronegativity of the ethynyl group is sufficiently high to nearly nullify the effect of protonation of the NH_2 on the CN BDE.

Remarkably, in addition to the increase in BDE of CX bonds with protonation of X, protonation also leads to an increase in the CX bond lengths. In the amine series for example, there is an increase of 0.044 (from 1.462 to 1.506), 0.055 (from 1.462 to 1.517), 0.084 (from 1.397 to 1.481), and 0.045 (1.366 to 1.411) Å for methylamine, ethylamine, ethenylamine, and ethynylamine,[16] respectively, which is parallelled in the other series. This concurrent increase in bond lengths and BDEs is contrary to the usual trend for neutral molecules: bond lengths generally decrease as bond strengths increase. Similar anomalies involving protonation have been reported previously.[1]

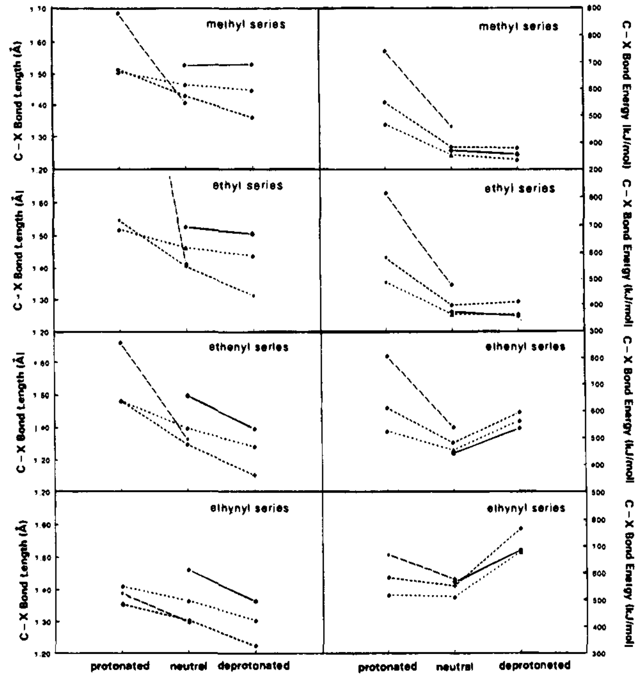

Figure 2. Effect of protonation and deprotonation of X on C−X bond lengths and homolytic bond dissociation energies for the methyl series (CH_3X), the ethyl series (CH_3CH_2X), the ethenyl series ($H_2C{=}CHX$), and the ethynyl series ($HC{\equiv}CX$): (●) X = CH_3; (▲) X = NH_2; (+) X = OH; and (♦) X = F.

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(15) Boyd, R. J.; Boyd, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652.

(16) For an interesting discussion relating to the effect of protonation on C=N stretching frequencies and related matters, see Bond, D. *J. Am. Chem. Soc.* **1991**, *113*, 385.

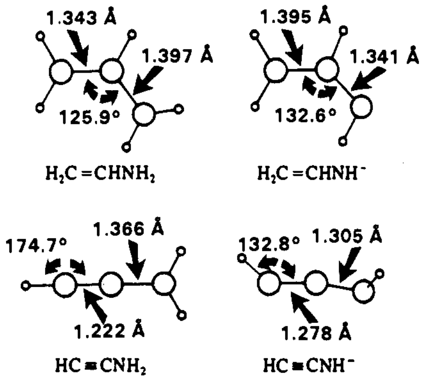

Figure 3. MP2/6-31+G(d,p) optimized geometries for ethenylamine, deprotonated ethenylamine, ethynylamine, and deprotonated ethynylamine.

By the reasoning which explains the increase in the CX BDEs due to protonation, deprotonation would be expected to reduce the electronegativity difference and lead to a decrease in the CX BDEs; however, the changes in BDEs resulting from deprotonation are almost negligible for saturated compounds. (The effects of deprotonation of X on the CX BDE for unsaturated compounds have been described above.) For example, deprotonation of methylamine leads to a decrease of 18 (from 357 to 339) kJ mol^{-1}, and that of ethylamine results in no change (the BDE is constant at 365 kJ mol^{-1}); the BDE for ethanol upon deprotonation actually increases by a small amount (12 kJ mol^{-1}, from 400 to 412 kJ mol^{-1}). The CX bond lengths, nonetheless, do contract with deprotonation, e.g., by 0.016 (from 1.462 to 1.446) and 0.024 (1.462 to 1.438) Å in methylamine and ethylamine, respectively, and by 0.080 Å (from 1.433 to 1.353 Å) in ethanol. Thus deprotonation has little effect on the homolytic BDE but decreases the bond length.

Effect of Protonation and Deprotonation on Heterolytic Dissociation of CX Bonds. In an attempt to explain the apparent anomaly between the increase in homolytic BDE and the concurrent increase in bond length, a study of heterolytic CX bond dissociation energies was undertaken; homolytic and heterolytic cleavage may be competitive even in the gas phase depending upon the structure.[17,18] Heterolytic dissociation would be likely if the protonated RCX (i.e., RCXH$^+$) had ion–dipole character; then the CX bond length, interpreted here as an "intermolecular" distance, RC$^{+}\cdots$XH, would be expected to be longer than the CX bond within the neutral RCX molecule.

Indeed, the optimized geometries of the protonated compounds do suggest that carbocation–dipole complexes are important resonance contributors to the structure of RCXH$^+$. The structures of the protonated fluorides are presented in Figure 4. Most dramatically illustrating the carbocation–dipole complex is the optimized structure for protonated ethyl fluoride which clearly resembles a protonated ethene cation[19] loosely bonded to the HF dipolar molecule. The protonated methyl fluoride also shows flattening of the CH_3 (the HCH bond angles are 110.7° in CH_3F and 117.5° in CH_3FH^+, while the FCH bond angles are 108.2° and 101.7°, respectively) so the structure approaches a complex between CH_3^+ and HF.

If the RCXH$^+$ species are indeed ion–dipole complexes, then heterolytic bond dissociation should proceed readily, producing RC$^+$ and XH. For heterolytic bond dissociation to be favored, the ionization energy (IE) of the hydrocarbon radical, RC$^\bullet$, should be less than that for neutral XH (the IE of XH is the negative of the electron affinity, EA, of the radical cation, $^\bullet$XH$^+$). Consider the CO bond dissociation process in protonated methanol (see Scheme 1). Certainly in this case heterolytic cleavage would be expected to be favored over homolytic cleavage since the (calculated) sum of IE($H_3C^\bullet$) + EA($^\bullet OH_2^+$) suggests a change in the ΔH^{298} by −274 kJ mol^{-1}, giving a heterolytic BDE of 278 kJ mol^{-1}.

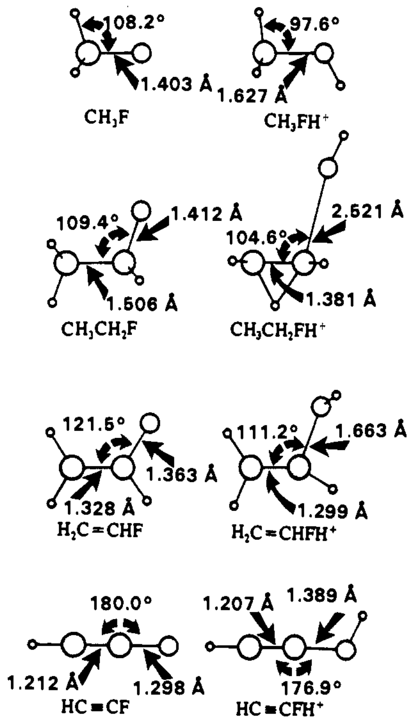

Figure 4. MP2/6-31+G(d,p) optimized geometries for neutral and protonated methyl fluoride, ethyl fluoride, ethenyl fluoride, and ethynyl fluoride.

Therefore, a full investigation was undertaken, and the heterolytic BDE for the CX bonds in the 40 molecules being studied are listed in Table 3 for processes of the type

$$RCX \rightarrow RC^+ + X^-$$

i.e., to a carbocation; those presented in Table 4 are for heterolytic dissociation to a carbanion,

$$RCX \rightarrow RC^- + X^+$$

Where available, experimental data are also presented and show good agreement with the calculated heterolytic BDEs. The calculated data are plotted in Figure 5, which also includes the corresponding homolytic BDE data for each species for direct visual comparison.

The data in Table 3 show that, even in the gas phase, protonation of X in RCX (i.e., to RCXH$^+$) results in a favoring of heterolytic over homolytic dissociation of the CX bond in cases when the carbocation (RC$^+$) and a neutral leaving group (XH) result; this is particularly true for highly electronegative X-groups (X = O or F). For example, as noted above, the homolytic and heterolytic BDEs for $CH_3OH_2^+$ are, respectively, 552 and 278 kJ mol^{-1}. The fluoride series even more convincingly demonstrates that heterolytic dissociation is favored, with CH_3FH^+ having a homolytic BDE of 743 kJ mol^{-1} and a heterolytic BDE of 120 kJ mol^{-1}.

Heterolytic dissociation of a protonated species (RCXH$^+$) to a carbocation and a neutral molecule is therefore favored: what appeared to be, anomalously, a longer but stronger CX covalent

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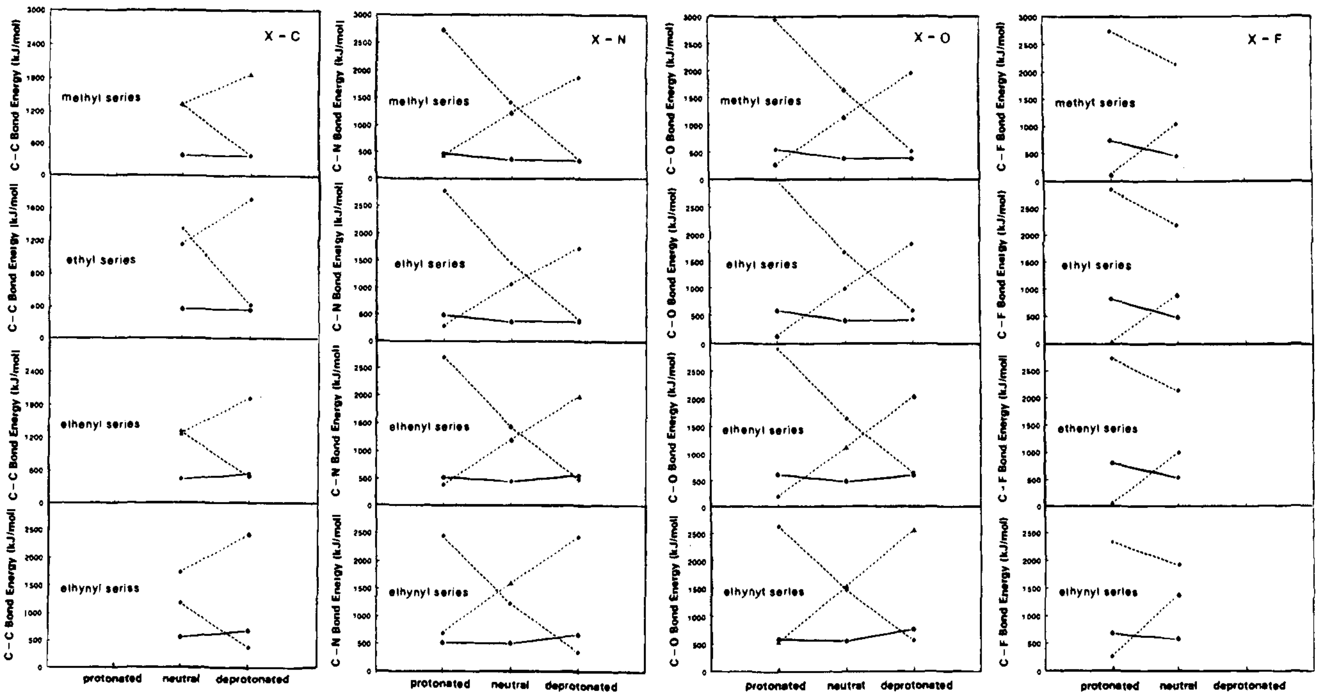
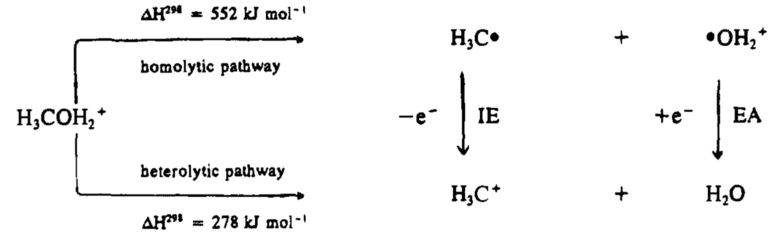


Figure 5. Effect of protonation and deprotonation of X on CX bond dissociation energies in RCXH: (●) homolytic BDE; (▲) heterolytic BDE as determined from RCX → $RC^+ + X^-$; (+) heterolytic BDE as determined from RCX → $RC^- + X^+$

Scheme 1



$$H_3C\bullet \rightarrow H_3C^+ + e^- \qquad \Delta H^{298} = IE(\bullet CH_3) = 922\ \text{kJ mol}^{-1}$$

$$e^- + H_2O\bullet^+ \rightarrow H_2O \qquad \Delta H^{298} = EA(H_2O\bullet^+)$$

$$= -IE(H_2O) = -1196\ \text{kJ mol}^{-1}$$

Table 3. CX Bonds in RCX: Heterolytic CX Bond Dissociation Energies (kJ mol^{-1}) for the Process

$$RCX \rightarrow RC^+ + X^-$$

	hydrocarbon fragment (RC^+)			
fragment X^-	H_3C^+	$CH_3{-}CH_2^+$	$H_2C{=}CH^+$	$HC{\equiv}C^+$
CH_3^-	1332(1321)	1169(1146)	1284(1232)	1756(1646)
CH_2^{2-}	1877	1718	1941	2437
NH_3	445[a](441)	302[a](282)	384[a]	724
NH_2^-	1238(1234)	1082(1063)	1218(1196)	1624
NH^{2-}	1889	1750	1996	2454
OH_2	278[a](289)	147[a](153)	220[a](251)	541[a]
OH^-	1147(1163)	998(1000)	1126(1100)	1544
O^{2-}	1957	1824	2052	2571
FH	120[a](148)	36[a](53)	70[a]	282[a]
F^-	1055(1096)	907(916)	1013(1002)	1400(1337)

[a] This heterolytic BDE is lower than the corresponding homolytic BDE in Table 2.

bond in $RCXH^+$ (compared to that in RCX) is actually a longer and weaker intermolecular bond. Heterolytic dissociation of a neutral molecule (to a carbocation and an anion) or a deprotonated species (to a carbocation and a divalent anion) is, by contrast, very unfavorable relative to homolytic dissociation (see Figure 5), as would be expected since large charge separation is being forced in the latter two cases.

Analogously, heterolytic dissociation of deprotonated species becomes energetically feasible when a carbanion and a neutral species are the products; the effect however is less marked than that for protonated species dissociating to a carbocation, because the neutral product of heterolytic dissociation of RCX^- to RC^- and X is an unstable diradical, unlike the stable neutral molecular species produced when $RCXH^+$ heterolytically dissociates to RC^+ and XH. As is evident from the data of Table 4, heterolytic BDEs for deprotonated RCXH (i.e., RCX^-) energetically approach homolytic BDEs when the RCX^- are saturated, i.e., when the products are the saturated carbanion (RC^-) and a neutral X; compare, for example, the heterolytic (to CH_3^- and CH_2^T) and homolytic (to $^\bullet CH_3$ and $^\bullet CH_2^-$) BDE of $CH_3CH_2^-$ which are 379 and 340 kJ mol^{-1}, respectively. The heterolytic BDEs are actually lower than the homolytic BDEs when the RCX^- are unsaturated, i.e. when the products are the unsaturated carbanions, $H_2C{=}CH^-$ or $HC{\equiv}C^-$, and neutral X; an example of this is the heterolytic BDE of $HC{\equiv}CCH_2^-$ (the products are $HC{\equiv}C^-$ and CH_2^T) which is 388 kJ mol^{-1}, compared to a homolytic BDE (when the products are $HC{\equiv}C^\bullet$ and $^\bullet CH_2^-$) of 689 kJ mol^{-1}. Heterolytic dissociation of deprotonated RCX^- tends to be favored more for X of low electronegativity; for example, in $H_2C{=}CHO^-$, $H_2C{=}CHNH^-$, and $H_2C{=}CHCH_2^-$,

Table 4. CX Bonds in RCX: Heterolytic CX Bond Dissociation Energies (kJ mol^{-1}) for the Process

$$RCX \rightarrow RC^- + X^+$$

	hydrocarbon fragment (RC^-)			
fragment X^+	H_3C^-	$CH_3{-}CH_2^-$	$H_2C{=}CH^-$	$HC{\equiv}C^-$
CH_3^+	1333(1321)	1355(1350)	1316(1299)	1189(1185)
CH_2	457/$\underline{379}$[a](382)	500/$\underline{422}$	567/$\underline{489}$[c](423)	466/$\underline{388}$[c]
NH_3^{2+}	2742	2784	2711	2454
NH_2^+	1589/$\underline{1426}$(1425)	1621/$\underline{1459}$(1458)	1601/$\underline{1437}$(1456)	1410/$\underline{1246}$
NH	595/$\underline{360}$(382)	642/$\underline{405}$(430)	733/$\underline{498}$[c]	598/$\underline{362}$[c]
OH_2^{2+}	3253/$\underline{2944}$	3308/$\underline{2999}$	3226/$\underline{2917}$	2949/$\underline{2640}$
OH^+	1955/$\underline{1640}$(1634)	1992/$\underline{1676}$(1675)	1965/$\underline{1649}$(1639)	1785/$\underline{1470}$
O	809/$\underline{523}$(527)	860/$\underline{574}$(582)	933/$\underline{647}$(635)	854/$\underline{568}$[c](574)
FH^{2+} [b]	3116/$\underline{2745}$	3218/$\underline{2848}$	3097/$\underline{2726}$	2712/$\underline{2341}$
F^+	2516/$\underline{2146}$(2146)	2555/$\underline{2184}$(2170)	2506/$\underline{2136}$(2120)	2295/$\underline{1924}$(1927)

[a] The product X^+ can exist in either singlet or triplet state; BDE for dissociation to both states is given in the form S/T, with the BDE for the lower energy products underlined and used for comparative purposes. [b] The FH^{2+} product is unstable with respect to F^+ and H^+; therefore the BDE for $CH_3FH^+ \rightarrow CH_3^- + FH^{2+}$ could not be determined. The quantities in this row of the table are for the process $CH_3FH^+ \rightarrow CH_3^- + F^+ + H^+$ and are included for completeness. [c] This heterolytic BDE is lower than the corresponding homolytic BDE in Table 2.

the heterolytic BDEs are respectively 647, 498, and 489 kJ mol^{-1} compared to 596, 566, and 539 kJ mol^{-1} for the corresponding homolytic BDEs.

Again, heterolytic dissociations of either neutral or protonated species to carbanions are highly unfavored in view of the charge separation involved.

In terms of optimized geometries, the carbanion–dipole complex is definitely less important as a resonance contributor than the corresponding carbocation–dipole complex in the protonated species. This can be seen in Figure 3: despite the fact that heterolytic dissociation of $HC{\equiv}CNH^-$ to $HC{\equiv}C^-$ and NH is energetically favored over homolytic dissociation to $HC{\equiv}C^{\bullet}$ and $^{\bullet}NH^-$ (362 kJ mol^{-1} compared to 683 kJ mol^{-1}), there is no indication from the optimized geometry of $HC{\equiv}CNH^-$ that an ion–dipole complex is a resonance contributor. Indeed the shortened CN bond, rationalized above using simple resonance arguments, would be expected to make heterolytic dissociation less favorable. This further accounts for the fact that heterolytic bond dissociation of RCX^- to RC^- and X occurs less readily than that of $RCXH^+$ to RC^+ and XH.

Conclusions

1. Effect of Protonation and Deprotonation on Homolytic BDE and Bond Lengths. a. CC Bonds. The effects of protonation and deprotonation of X in CCX on the homolytic BDEs of the α-CC bonds are quite systematic: protonation increases the BDE and decreases the length of the CC bond, while deprotonation does the opposite. These effects can be rationalized by electronegativity and resonance arguments.

b. CX Bonds. Protonation of X in RCX increases the CX homolytic BDE. The effect is greater in saturated molecules than in unsaturated ones. These increases in BDEs anomalously accompany increases in CX bond lengths; i.e., bond lengths increase as homolytic bond strengths increase. The effect of deprotonation of X is quite different. In saturated compounds, deprotonation has an essentially negligible effect on the CX BDEs but does result in a shortening of the CX bond length. In unsaturated compounds ($H_2C{=}CHX$ and $HC{\equiv}CX$) deprotonation causes the CX BDEs to increase dramatically; these large increases are accompanied by substantial geometric changes in the anions which are conveniently rationalized by resonance stabilization.

2. Heterolytic *vs* Homolytic Bond Dissociation Energies. a. Protonation. Heterolytic bond dissociation for the process $RCXH^+ \rightarrow RC^+ + XH$ is energetically favored over the homolytic process, $RCXH^+ \rightarrow RC^{\bullet} + {}^{\bullet}XH^+$, particularly when X is highly electronegative; indeed, the optimized geometries suggest that the $RCXH^+$ species have considerable carbocation-dipole character. Therefore, the apparent anomaly—that of increased bond length accompanying increased homolytic BDE upon protonation—can be explained by the fact that protonation of X in RCX produces an ion–dipole complex. Thus, the RC–XH^+ bond is not an intramolecular polar-covalent bond but is instead an intermolecular bond, $RC^{+}\cdots XH$; heterolytic dissociation consequently occurs readily, whereas homolytic dissociation requires an energetically expensive electron transfer from neutral XH to RC^+.

b. Deprotonation. When RCXH is deprotonated to RCX^-, heterolytic bond dissociation approaches homolytic dissociation for the process $RCX^- \rightarrow RC^- + X$, provided that X is low in electronegativity; in fact it is favored when the carbanion RC^- is unsaturated. However, because the product X is a reactive diradical, the effect is less striking than for protonation; this is supported by the fact that anion-dipole character is not apparent in the optimized geometry of RCX^-.

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Supporting Information Available: Table of basis sets and levels of theory for determination of homolytic bond dissociation energies (BDE) of substituted methanes (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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