Substituent Effects. 5. Vinyl and Ethynyl Derivatives. An Examination of the Interaction of Amino and Hydroxy Groups with C–C Double and Triple Bonds

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Abstract: The effect of substituents on the energies of vinyl derivatives was examined with the use of group separation reactions with ethane to give propene and a substituted methane. The energy changes for these reactions were much smaller than those found for a corresponding set of acetyl derivatives. The bond dissociation energies (BDEs) for the vinyl derivatives were found to be linearly related to those of the related methyl derivatives with a slope close to unity. The average difference between BDEs in the two series was 12.1 ± 1.5 kcal/mol, with the larger values found in the vinyl series. This is in accord with the difference in hybridization between vinyl and methyl. The results for the vinyl series stand in marked contrast to the acetyl series previously studied. Here, the effect of electronegativity on the BDEs was much larger than for the methyl compounds, and the correlation for changes in electronegativity was different from that for changes in hybridization in the substituent. The results of the present study confirm our conclusion that the effects in the acetyl series are dominated by the strong polarization of the carbonyl group and the resultant Coulombic interactions. The effect of substituents on acetylene also was studied. An unusual trend in group separation reactions was found to result from the atypically high C–C bond dissociation energy of propyne combined with the smaller effect of electronegative substituents on bond dissociation energies for ethynyl derivatives as compared to methyl derivatives.

1. Introduction

We have recently reported a study of the effect of substituents on acetyl derivatives.[1] Making use of the group separation reactions,

$$CH_3COX + C_2H_6 \rightarrow CH_3COCH_3 + CH_3X$$

it was found that substituents such as NH_2, OH, and F gave markedly endothermic reactions (about +20 kcal/mol), whereas other substituents such as SiH_3, CF_3, and CN gave markedly exothermic reactions (about −10 kcal/mol). Although the energy change with acetamide was comparable to its rotational barrier, and thus might reasonably be ascribed to amide resonance, it was larger for acetic acid, whereas the rotational barrier[2] is smaller than that for amides, indicating that some other factor must be involved. Then, with acetyl fluoride, the energy change for the above reaction was about the same as for acetamide, despite the much lower energy of the lone pairs of fluorine as compared to the amino group and the smaller expected π-donor interaction.

It was possible to determine the reasons for the differences in reaction energies by comparing the bond dissociation energies (BDEs) in the CH_3COX and CH_3X series.[1] The CH_3–X bonds were used as the reference since it seems generally agreed that these bonds are good models for normal C–X bonds.[3] Thus, we wished to see if the C–X bonds in other compounds are different from the "normal" bonds. In this connection, it should be noted that even with methyl derivatives there are both σ- and π-components to the C–X bonds. Thus, the covalent C–C π-bond order for ethane is 0.04 and for the C–F bond of methyl fluoride it is 0.09.[4]

The comparison with the acetyl derivatives showed that four factors were involved in the differences with respect to the methyl derivatives. The first was a π-electron interaction with the carbonyl group that was found with NH_2 and OH, and to a smaller extent with SH. No such interaction was found with PH_2, Cl, or F. If this factor were eliminated by a 90° rotation about the C–X bond, there was a linear relationship between the CH_3COX and CH_3X bond dissociation energies for a series of substituents which have relatively constant hybridization, and increasing electronegativity (PH_2, rotated SH, Cl, rotated NH_2, rotated OH, and F) with a slope of 1.6. The third factor was hybridization, which affected the CH_3COX and CH_3X series about equally (X = CH_3, $H_2C{=}CH$, and $HC{\equiv}C$). The fourth factor was the charge at the atom attached to the carbonyl carbon; with X = SiH_3, CF_3, or CN where the atom has a positive charge, the bond dissociation energy in the CH_3COX series was reduced because of the Coulombic repulsion between the positively charged carbonyl carbon and the substituent.

The magnitude of the group separation energy change for acetamide is then largely determined by the interaction of the nitrogen lone pair with the carbonyl group, and that for acetyl fluoride is largely determined by the greater effect of electronegative substituents on the acetyl group. The origin of the considerably enhanced effect of electronegativity in the CH_3COX series as compared to the CH_3X cases was of special interest. Increasing electronegativity increases the BDE in both cases, so that the C–X BDE of methyl fluoride is 20 kcal/mol greater than that of ethane and the C–X BDE of acetyl fluoride is 39 kcal/mol greater than that of acetone. The difference in the methyl series is a result of the increasing polarization of the C–X bond with increasing difference in electronegativity of CH_3 and X. The

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[1] Wiberg, K. B.; Hadad, C. M.; Rablen, P. R.; Cioslowski, J. *J. Am. Chem. Soc.* **1992**, *114*, 8644.

[2] Blom, C. E.; Günthard, Hs. H. *Chem. Phys. Lett.* **1981**, *84*, 267. Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935.

[3] It has been found that substituents affect methyl, ethyl, and isopropyl groups in essentially the same way so that all of them may be considered to have "normal" C–X bonds: Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1990**, *112*, 8765. Wiberg, K. B. *J. Org. Chem.* **1991**, *56*, 544.

[4] The covalent bond orders were calculated using the method of Cioslowski and Mixon: Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1991**, *113*, 4142.

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Table I. Calculated Energies, hartrees

compound	MP2/6-31G*	ZPE[a]	MP3/6-311++G**[b]	G2[c]
propene	−117.469 66	47.9	−117.583 17	−117.645 02
vinyllithium	−85.135 58	24.0	−85.207 78	−84.265 14
vinylamine (gs)	−133.491 28	41.6	−133.607 95	−133.691 29
vinylamine (ts)	−133.482 03	41.3	−133.600 21	−133.683 17
vinyl alcohol (gs)	−153.332 16	34.2	−153.453 01	−153.558 99
vinyl alcohol (ts)	−153.323 13	33.5	−153.446 19	−153.552 67
vinyl fluoride	−177.315 16	26.7	−177.446 87	−177.572 08
vinylsilane	−368.463 11	40.2	−368.591 58	−368.666 47
vinylphosphine (gs)	−419.701 92	36.3	−419.824 32	−419.918 20
vinylphosphine (ts)	−419.699 13	36.4	−419.820 85	−419.915 61
ethylenethiol (gs)	−475.935 93	31.0	−476.048 84	−476.161 72
ethylenethiol (ts)	−475.932 09	30.8	−476.045 78	−476.160 63
vinyl chloride	−537.336 06	25.9	−537.436 41	−537.568 25
acrylonitrile	−170.316 11	30.8	−170.398 13	−170.533 96
butadiene	−155.441 71	51.3	−155.566 99	−155.664 26
vinylacetylene	−154.224 92	37.1	−154.318 62	−154.430 82
nitroethylene	−282.311 31	33.8	−282.450 46	
3,3,3-trifluoropropene	−414.563 41	35.0	−414.831 36	
propyne	−116.256 24	33.7	−116.339 02	−116.419 41
ethynyllithium	−83.959 63	10.8	−84.001 99	−84.075 45
ethynylamine	−132.267 21	27.1	−132.353 52	−132.455 12
hydroxyacetylene	−152.098 15	19.5	−152.189 81	−152.313 62
fluoroacetylene	−176.072 69	12.7	−176.173 53	−176.314 99
ethynylsilane	−367.260 69	26.4	−367.357 29	−367.450 11
ethynylphosphine	−418.491 38	22.2	−418.582 46	−418.695 09
acetylenethiol	−474.716 31	16.7	−474.799 33	−474.933 20
chloroacetylene	−536.106 65	11.8	−536.176 26	−536.327 54
cyanoacetylene	−169.097 59	16.8	−169.144 74	−169.299 61
nitroacetylene	−281.066 83	19.4	−281.172 14	
3,3,3-trifluoropropyne	−413.336 01	20.8	−413.572 58	

[a] Calculated at the HF/6-31G* level and scaled by 0.8934 (in kcal/mol). [b] Calculated at the MP2 geometries. The frozen core option and six Cartesian d functions were used. [c] The G2 energies include the zero-point energies.

more ionic character a covalent bond has, the greater the coulombic attraction between C and X and the greater the BDE.[5] The fact that the difference in electronegativity is the important factor is shown by the unusually large C–Si BDE of methylsilane (87 kcal/mol), which is greater than that for methyl chloride (82 kcal/mol) and considerably greater than for methylphosphine (69 kcal/mol). Here, the silicon is electropositive with respect to carbon, leading to ionic character in the bond, but with a different polarization than for methyl chloride.

The same factor will be important with the CH_3COX series so that in changing X from CH_3 to F there will be an increase in the polarity of the C–X bond, leading to an increased strength of the C–F bond. However, the carbonyl group is strongly polarized in the sense C^+–O^-. When the carbonyl carbon becomes even more positively charged as a result of an increase in electronegativity of the substituent, the C–O group will be further Coulombically stabilized. Thus, *both* the C–X and C–O bonds are strengthened by the introduction of a more electronegative substituent, leading to the observed larger effect in the CH_3COX series as compared to CH_3X. It is this factor that leads to the larger group separation energy change for acetic acid *vs* acetamide and for the similarity in the energy changes for acetyl fluoride and acetamide.

2. Interaction of Substituents with Vinyl Groups

It seemed important to check these conclusions by examining the effect of substituents on a nonpolarized double bond. Here, the group separation reactions of the type described above should lead to small energy changes, and the effect of substituents on the bond dissociation energies should be similar to those found with the CH_3X derivatives. Some vinyl compounds have been studied via these reactions by us[6] and by Schleyer,[7] but for a detailed comparison with the carbonyl compounds it appeared desirable to use a higher level of theory than was employed in the earlier studies. An examination of these compounds also would allow a study of π-interactions between lone pairs on N and O and the C–C double bond. Some calculations for vinyl derivatives at higher theoretical levels using MP2/6-31G* geometries were recently reported by Head-Gordon and Pople.[8]

The MP2/6-31G* energies are given in Table I, and the calculated geometries[9] are compared with the observed structures[10] in Table II. They are in generally good agreement with the experimental structures. The MP2 geometries were then used to calculate the energies at the G2 level of theory. The G2 model has been developed by Pople and his co-workers and is effectively QCISD(T)/6-311+G(3df,2p)//MP2/6-31G* plus a higher level correction and a correction for the zero-point energy.[11] It is able to predict atomization energies with an average error of only $\sim$1 kcal/mol, but is computationally fairly demanding. In other cases, we have found the computationally less demanding MP3/6-311++G** level to yield satisfactory relative energies,[12] and these energies also have been obtained using the MP2/6-31G* geometries.

The energies for group separation reactions of the vinyl derivatives with ethane are summarized in Table III. It can be seen that the energies calculated at the MP3 and G2 levels are in very good agreement, but the MP2 energies are somewhat different. With the vinyl derivatives there are few reliable experimental data with which the calculations may be compared. In the cases of vinyl alcohol, vinyl fluoride, acrylonitrile, and acrolein, there is good agreement between theory and experiment.

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(5) Pauling, L. *The Nature of the Chemical Bond*, 2nd ed.; Cornell Univ. Press: Ithaca, NY, 1944.

(6) Wiberg, K. B.; Laidig, K. E. *J. Org. Chem.* **1992**, *57*, 5092.

(7) Schleyer, P. v. R. *Pure Appl. Chem.* **1987**, *59*, 1647.

(8) Head-Gordon, M.; Pople, J. A. *J. Phys. Chem.* **1993**, *97*, 1147.

(9) The full structural data are available as supplementary material.

(10) The experimental structural data were taken from the following: *Landolt-Bornstein*, New Series, II/17, Springer-Verlag: Berlin, 1987.

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

(12) Wiberg, K. B.; Murcko, M. A. *J. Phys. Chem.* **1987**, *91*, 3616. Wiberg, K. B.; Breneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61.

Table II. Calculated (MP2/6-31G*) Structures of Vinyl and Ethynyl Derivatives[a]

A. Vinyl Derivatives

X	$r_{C=C}$	r_{CX}	∠CCX	r_{XY}	∠CXY
CH_3	1.336	1.498	124.64		
	(1.336)	(1.501)	(124.3)		
NH_2	1.340	1.400	126.06		
	(1.335)	(1.397)	(125.2)		
OH	1.336	1.367	126.81		
	(1.326)	(1.372)	(126.2)		
F	1.327	1.353	122.04		
	(1.330)	(1.351)	(121.5)		
SiH_3	1.343	1.865	122.79		
	(1.347)	(1.853)	(122.7)		
PH_2	1.339	1.829	120.64		
SH	1.337	1.760	127.68		
	(1.332)	(1.766)	(127)		
Cl	1.331	1.731	122.20		
	(1.342)	(1.730)	(122.5)		
NO_2	1.329	1.461	120.72	1.240, 1.244	115.51, 119.02
	(1.325)	(1.458)	(120.9)	(1.227, 1.228)	(116.0, 119.1)
CF_3	1.333	1.488	122.61	1.349, 1.354	112.88, 111.02
	(1.312)	(1.489)	(124.8)	(1.345)	
CN	1.341	1.432	122.06	1.182	
	(1.339)	(1.426)	(122.6)	(1.164)	
$CH=CH_2$	1.343	1.456	123.71		
	(1.348)	(1.468)	(124.3)		
Li	1.354	1.967	116.54		

B. Ethynyl Derivatives

X	r_{CC}	r_{CH}	r_{CX}	r_{XY}	∠CXY
CH_3	1.218	1.066	1.461	1.093	110.88
	(1.207)	(1.060)	(1.459)	(1.112)	(110.5)
NH_2	1.218	1.064	1.376	1.015	112.79
OH	1.215	1.064	1.324	0.975	108.92
F	1.210	1.064	1.294		
	(1.198)	(1.053)	(1.279)		
SiH_3	1.226	1.068	1.483	1.483	109.58
	(1.208)	(1.056)	(1.826)	(1.455)	(110.2)
PH_2	1.224	1.067	1.773	1.416	97.62
SH	1.220	1.066	1.699	1.342	96.60
Cl	1.217	1.066	1.646		
	(1.203)	(1.055)	(1.637)		
NO_2	1.215	1.067	1.404	1.242	116.64
CF_3	1.216	1.067	1.458	1.348	111.16
	(1.201)	(1.058)	(1.464)	(1.335)	(111.3)
CN	1.222	1.068	1.375	1.186	180.00
	(1.205)	(1.058)	(1.378)	(1.159)	
Li	1.242	1.069	1.906		

[a] The observed structures[10] are given in parentheses.

It is surprising that a large difference between experiment and theory is found with vinyl chloride.[13] It is difficult to determine the origin of the difference, but in view of the ability of the G2 level of theory to reproduce experimental thermochemical data, it is tempting to think that the experimental ΔH_f for vinyl chloride might be in error.

It can be seen that the group separation energies are relatively small. Vinylamine, vinyl alcohol, and vinyl fluoride all give endothermic reactions, indicating that these substituents prefer vinyl to methyl. The energy changes are much smaller than those found for the acetyl derivatives, and that for vinyl fluoride is especially small. Similarly, the calculated G2 rotational barriers are smaller than for the acetyl derivatives, being 5.1 kcal/mol for vinylamine and 4.0 kcal/mol for vinyl alcohol as compared to 13.9 for acetamide and 11.5 for acetic acid. Unlike the acetyl compounds, with the vinyl derivatives, the rotational barriers are in close agreement with the group separation energies. This suggests that the π-interaction of the lone pairs with the C=C π-bond may be the primary energetic factor involved in the group separation energies.

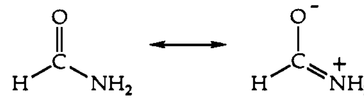
As in the case of the acetyl derivatives, it is not readily possible to determine the reasons for the differences in group separation reactions without additional data. Since ethane and propene are common to all of the reactions of the vinyl compounds, it is possible to concentrate on just the bonds being exchanged via the calculation of bond dissociation energies (BDEs Table IV). They were obtained using the G2 energies (Table I). Some of the needed energies have been given previously.[11] The calculated BDEs are generally in good agreement with the available experimental data, except for vinyl chloride where as noted above the experimental heat of formation might be in error. In the cases of vinylamine, vinyl alcohol, and ethylenethiol, we have tried to eliminate possible π-electron interactions by calculating the energies of the transition state for rotation about the C–X bond. This was not necessary with vinylphosphine since the unconjugated rotamer had the lower energy.[14] The relationship between the two sets of energies is shown in Figure 1, and for X = OH, NH_2, and SH, the BDEs calculated for both the ground state and the rotational transition state are given.

It can be seen that the data are reasonably well fit by a straight line with a slope close to unity (1.1). In addition, the points for X = CH_3, $CH_2=CH$, and $HC\equiv C$ fall close to the line. Thus, there is little difference in the effect of substituents on the BDEs of vinyl and methyl derivatives. The main difference between the two is an average increase of 12.1 ± 1.5 kcal/mol for vinyl derivatives with respect to the methyl BDEs. This is in good accord with the difference in hybridization between vinyl and methyl groups.

For a comparison at the same level of theory, we have now calculated the G2 energies for a series of carbonyl compounds, and these data are given in Table V. The relationship between the bond dissociation energies and those for methyl derivatives is shown in Figure 2. It can be seen that the changes in BDE are similar to those for the vinyl compounds, except for the slope of the line.

3. π-Electron Interactions of Substituents

There does appear to be a small π-electron interaction of the vinyl group with OH and NH_2. However, it must be different from that found with the acetyl derivatives. To take acetamide as an example, the preference for planarity in amides has usually been explained in terms of either resonance interactions[15] or frontier molecular orbital (FMO) arguments.[16] In the resonance description, the stabilization is ascribed to the participation of the dipolar resonance structure in addition to the ordinary structure which has no separation of formal charge.



The dipolar structure is not unreasonable insofar as it invokes a transfer of charge from a less electronegative element (nitrogen) to a more electronegative element (oxygen). In past studies, we have, however, found little evidence for *net* charge transfer from nitrogen to oxygen.[17] The C=O bond is highly polarized in both the σ and π systems, and consequently the nitrogen lone pair can donate electron density to the carbon without needing to further displace much charge density from the carbon to the oxygen. For these reasons, we might choose to depict the interaction using

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[13] The experimental ΔH_f values were taken from the following: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.

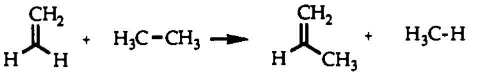
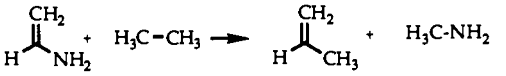
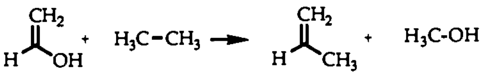
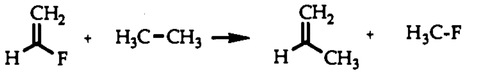
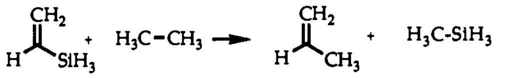
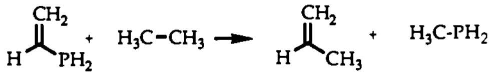
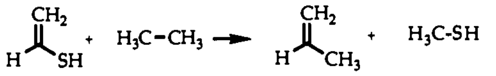
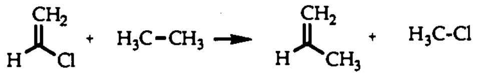
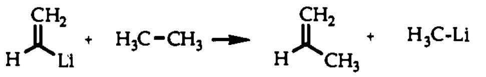
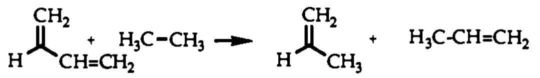
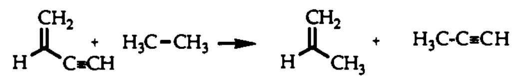
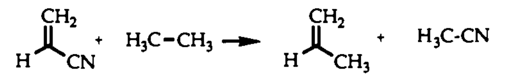
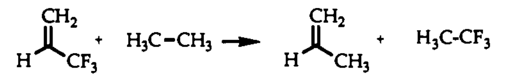
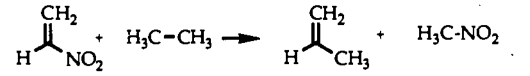
[14] Schade, C.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1399.

[15] Wheland, G. W. *Resonance in Organic Chemistry*; John Wiley & Sons: New York, 1955; p 109.

[16] Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1978; pp 5–32. Fukui, K. *Theory of Orientation and Stereoselection*; Springer-Verlag, New York, 1975; pp 40–51.

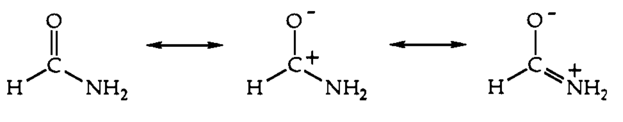
[17] Wiberg, K. B.; Breneman, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 831. Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.*, accepted for publication.

Table III. Isodesmic Reactions

Reaction	ΔH obs[a]	ΔH(calc)[b] MP2/6-31G*	MP3/6-311++G**	G2
 $H_2C{=}CH{-}H + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}H$	-5.6	-6.0	-5.1	-5.7
 $H_2C{=}CH{-}NH_2 + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}NH_2$	na	+7.2	+6.2	+6.4
 $H_2C{=}CH{-}OH + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}OH$	na	+8.0	+5.7	+6.3
 $H_2C{=}CH{-}F + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}F$	+2.1±2.1	+4.7	+2.6	+2.4
 $H_2C{=}CH{-}SiH_3 + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}SiH_3$	na	-2.3	-3.0	-3.3
 $H_2C{=}CH{-}PH_2 + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}PH_2$	na	-0.6	-0.9	-1.2
 $H_2C{=}CH{-}SH + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}SH$	na	+1.5	+0.6	-0.5
 $H_2C{=}CH{-}Cl + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}Cl$	-3.7±0.4	+1.0	+0.3	+0.2
 $H_2C{=}CH{-}Li + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}Li$	na	+0.6	-1.6	-0.7
 $H_2C{=}CH{-}CH{=}CH_2 + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}CH{=}CH_2$	+3.3±0.4	+3.8	+2.8	+3.2
 $H_2C{=}CH{-}C{\equiv}CH + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}C{\equiv}CH$	na	+1.7	+0.1	-1.7
 $H_2C{=}CH{-}CN + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}CN$	-3.0±1.7	-0.8	-2.3	-2.0
 $H_2C{=}CH{-}CF_3 + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}CF_3$	na	-4.0	-5.1	
 $H_2C{=}CH{-}NO_2 + H_3C{-}CH_3 \rightarrow H_2C{=}CH{-}CH_3 + H_3C{-}NO_2$	na	+0.2	-1.7	

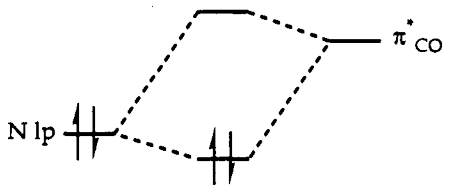
[a] The experimental data were taken from ref 13. [b] Calculated ΔE corrected for the zero-point energy change.

three resonance structures rather than two, as shown below.



Donation of π-charge density from nitrogen to the electron deficient carbon is clearly involved in the stabilization of the planar form of the amides. However, as we have pointed out previously, the π interaction is only part of the total interaction involving the amide group.[17] During the rotation about the C–N bond, there is an opposite flow of electrons in the σ-system as a result of the increased electronegativity of the sp^2-hybridized nitrogen in the planar form as compared to the rotated form that makes its bond to carbon using orbitals with high p character. Both the σ and π terms contribute to the rotational barrier.

In the FMO approach, the energetic stabilization in the π-system arises from a favorable HOMO–LUMO type of orbital interaction. The lone pair orbital on nitrogen is relatively high in energy, and its overlap with the low-lying π^*_{CO}-orbital that resides largely at carbon results in mixing between the two that lowers the energy of the lone pair and raises the energy of the (empty) π^*_{CO}-orbital. Since only two electrons must be placed in the two orbitals, the mixing leads to net stabilization:



This approach also ignores the significant changes that occur in the σ-system.

In the case of vinylamine and other vinyl derivatives, however, neither of these arguments gives a satisfying explanation for the

Table IV. Calculated and Experimental C–X Bond Dissociation Energies, 0 K, kcal/mol[a]

X	CH_2═CHX G2	CH_2═CHX obs	CH_3COX G2	CH_3COX obs	HC≡CX G2	HC≡CX obs	MeX G2	MeX obs
CH_3	100.4	100.0 ± 0.8	83.5	82.8 ± 0.4	126.3	124.1 ± 0.8	88.3	88.0 ± 0.3
NH_2 (gs)	101.8		97.8	98.4 ± 1.6	121.1		83.8	83.9 ± 0.3
NH_2 (ts)	96.8		83.9					
OH (gs)	109.9	109.1 ± 2.2	109.5	108.6 ± 0.6	123.3		91.5	90.6 ± 0.4
OH (ts)	105.9		97.9					
F	125.1	123.0 ± 0.9	122.5	120.7 ± 0.9	131.2		110.6	
SiH_3	96.0		69.8		127.7		87.3	86.8 ± 2.5
PH_2	81.0		61.5		108.3		70.2	
SH (gs)	84.6		74.3	72.1 ± 2.1	108.6		73.0	73.0 ± 0.8
SH (ts)	83.9		66.2					
Cl	95.2	91.0 ± 0.9[b]	84.9	84.0 ± 0.4	111.6		82.9	82.4 ± 0.3
CH_2═CH	115.7	115.8 ± 1.2		97.0 ± 1.6	136.7		100.4	100.0 ± 0.8
HC≡C	136.7						126.3	124.1 ± 0.8
CN	132.6	132.0 ± 1.0			153.0		122.5	122.7 ± 1.8

[a] The G2 energy of the acetyl radical was –152.935 42, and the energies of the other radicals are given in ref 11. The experimental ΔH_f of the acetyl radical was –2.4 ± 0.3 kcal/mol at 298 K (–0.9 at 0 K): Niiranen, J. T.; Gutman, D.; Krasnoperov, L. N.; *J. Phys. Chem.* **1992**, *96*, 5881. [b] It is likely that the experimental heat of formation of vinyl chloride is incorrect (see text) and that the bond dissociation energy derived from it is too low.

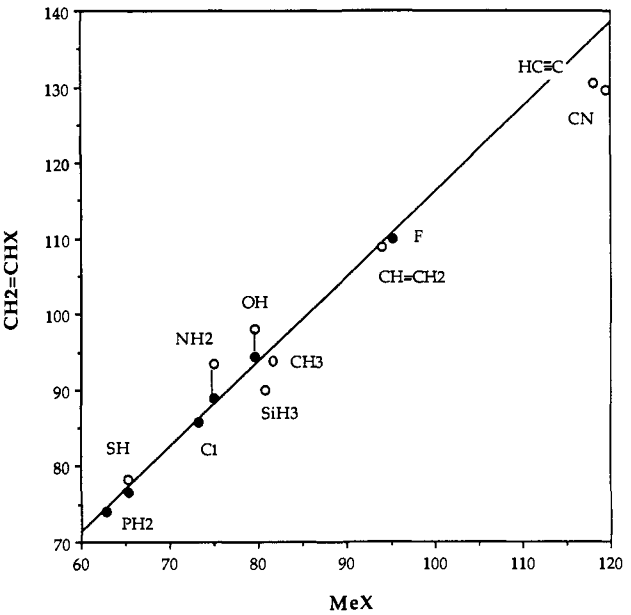


Figure 1. Relationship between vinyl–X and methyl–X bond dissociation energies. With X = NH_2, OH, and SH the solid circles give the BDE for the 90°-rotated (unconjugated) forms. The line is based on the solid circles.

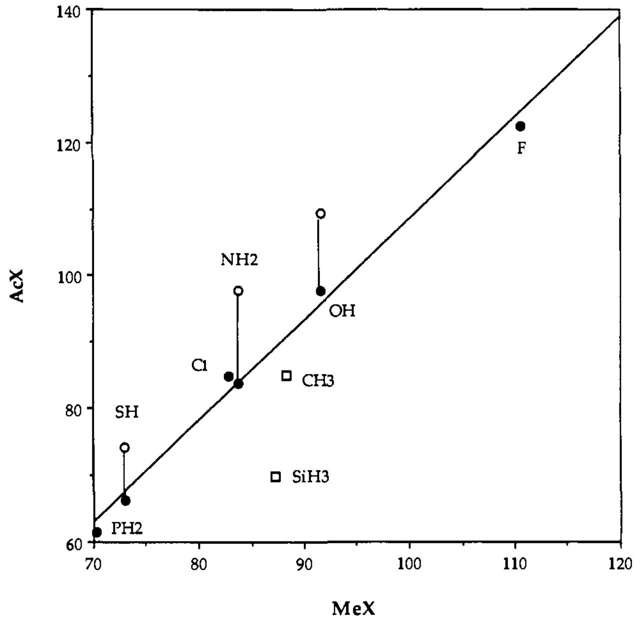
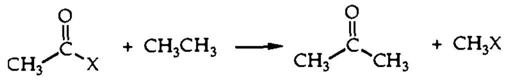


Figure 2. Relationship between acetyl–X and methyl–X bond dissociation energies. With X = NH_2, OH, and SH the solid circles give the BDE for the 90°-rotated (unconjugated) forms. The line is based on the solid circles.

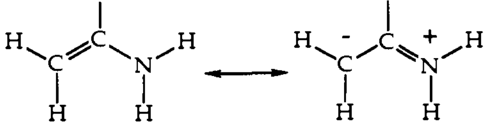
Table V. G2 Energies and Energies of Group Separation Reactions for Acetyl Derivatives



$$CH_3C(=O)X + CH_3CH_3 \longrightarrow CH_3C(=O)CH_3 + CH_3X$$

compound	E_0 G2	ΔE (isodesmic, kcal/mol) MP3	G2	obs
acetone	–192.813 54			
acetamide (gs)	–208.880 31	+18.9	+19.3	+19.6 ± 0.3
acetamide (ts)	–208.858 08	6.4	5.4	
acetic acid (gs)	–228.753 78	22.8	22.7	23.4 ± 0.4
acetic acid (ts)	–228.735 42	11.4	11.2	
acetyl fluoride	–252.763 41	17.0	16.7	17.9 ± 1.3
acetylsilane	–443.820 13	–12.1	12.7	
acetylphosphine	–495.082 49	–3.4	–3.9	
thioacetic acid (gs)	–551.340 79	6.0	6.1	4.5 ± 2.0
thioacetic acid (ts)	–551.327 95	–1.3	–2.0	
acetyl chloride	–612.747 38	7.2	6.8	6.6 ± 0.3

favorable interaction of the lone pair with the C═C π-bond. Resonance theory would require the participation of a structure such as that shown below. However, this type of structure, which invokes a transfer of charge from a more electronegative element (nitrogen) to a less electronegative element (carbon), should be strongly disfavored.



The FMO approach fares no better. The interaction between the lone pair on nitrogen and the π_{CC}-bond will be *unfavorable*, since it involves two filled orbitals. The π^*_{CC}-orbital, on the other hand, ought to lie too high in energy to allow a strongly favorable interaction. Nonetheless, the net interaction does appear to be favorable and closely resembles in both concept and magnitude the π-interactions known to stabilize the planar conformers of butadiene and its heteroanalogues.[18] It might also be noted that

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[18] Wiberg, K. B.; Rablen, P. R.; Marquez, M. *J. Am. Chem. Soc.* **1992**, *114*, 8654.

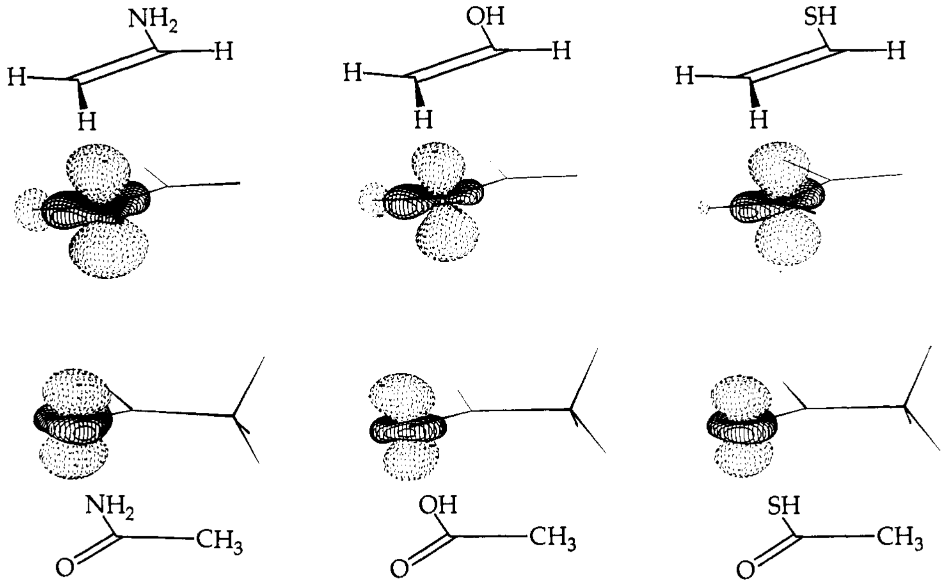

Figure 3. Charge density difference maps for the terminal methylene group of rotated minus conjugated forms of vinyl derivatives (upper row) and for the carbonyl group of the corresponding acetyl derivatives (lower row). Dashed lines indicate charge depletion in the rotated form, and solid lines indicate increased charge in the rotated forms. From left to right X = NH_2, OH, and SH. In each case, the charge density changes for the other atoms have been eliminated so that the changes of interest may more easily be seen. The contour level is 3.0×10^{-3} e/au^3.

enamines have pyramidal amino groups in contrast to the nearly planar amino groups of amides, indicating a much smaller π-system interaction.

The interaction may conveniently be studied via charge density difference maps. Here, the geometry of the vinyl group was fixed at that of the higher energy form[19] so that a direct comparison could be made. The differences between the conjugated and 90°-rotated forms are shown in Figure 3, where solid lines indicate regions in which the rotated form has the greater charge density and dashed lines indicate regions in which the charge density is greater for the conjugated rotamer. The charge density associated with the substituent and the proximal CH has been removed in each case in order to more clearly show the changes at the terminal methylene group. The upper plots are for the vinyl derivatives. Both σ- and π-regions are easily seen, and the shifts are in opposite directions. Thus, there is π-donation from the lone pair to the terminal methylene in the conjugated form as well as simultaneous σ-withdrawal.

As far as the π-electrons are concerned, the simple resonance picture is correct. The shift of π-electron density from nitrogen to the double bond, despite the unfavorable difference in electronegativity between carbon and nitrogen, probably results from the high concentration of charge density in a lone pair. Moving some of this charge density to the methylene group will reduce electron repulsion and would lead to net stabilization. But, as is often the case, there is an important change in the σ-system. As is frequently found, it is in the opposite direction to the π shifts. This phenomenon is observed in the σ- and π-systems of amides during rotation of the amino group, as described earlier. As the amino group rotates into the molecular plane and the nitrogen approaches planarity, the lone pair becomes more electron donating, while the σ-orbitals on the nitrogen simultaneously become more electron withdrawing, and the two effects tend to counteract one another. This may be seen in the charge density plots in the bottom row of Figure 3, which are for the acetyl compounds corresponding to the vinyl derivatives.

Table VI. Integration of σ- and π-Regions for Vinyl and Acetyl Compounds[a]

compound	π	σ	total
vinylamine	−0.072	0.025	−0.048
vinyl alcohol	−0.046	0.017	−0.029
ethylenethiol	−0.053	0.019	−0.034
acetamide	−0.049	0.025	−0.023
acetic acid	−0.042	0.015	−0.027
thioacetic acid	−0.036	0.014	−0.022

[a] The integration is for the terminal methylene group of the vinyl compounds and the carbonyl oxygen of the acetyl compounds.

The σ- and π-charges may be made more quantitative by integrating the charge in each of the regions shown in Figure 3. The results are given in Table VI. The calculations were performed in the following manner. The difference density was summed for all points in a three-dimensional grid which could be reached from a particular starting point without crossing any contours representing a difference density less than a given cutoff value. This procedure was carried out for the σ- and π-regions of each compound using a standard series of cutoff values.[20] The results were then plotted against the cutoff value, and a quadratic equation was fit to the set of points corresponding to each region (σ or π) of each compound. The numbers in Table VI are the y-intercepts of the fitted polynomials; i.e., they represent an extrapolation of the calculated values to a contour cutoff of 0. As might be expected, the amino groups give the largest π-shifts. It is interesting that SH is about as effective as OH in shifting π-density. This probably results from the smaller electronegativity of S as compared to O. The shifts to the carbonyl oxygen of the acetyl compounds are less than that for the vinyl derivatives, despite the much larger rotational barriers for the acetyl compounds. This is in accord with our observation that with the acetyl compounds most of the charge shift is to and from the carbonyl carbon rather than the oxygen. The most important observation is that none of the shifts shown in Figure 3 are large.

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(19) The geometry for the rotated conformer was obtained by optimization at the RMP2(fc)/6-31G* level of theory but with the substituent constrained to be at 90° to the vinyl group and the vinyl group itself constrained to be planar. The geometry for the conjugated rotamer was obtained by allowing the substituent complete freedom in a subsequent RMP2(fc)/6-31G* optimization while restricting the vinyl group to the geometry for the rotated conformer. Wave functions for use in the difference density analysis were obtained from RHF/6-311++G**(6d) single-point calculations at these geometries.

(20) The standard contour cutoff values were 0.005 00, 0.004 50, 0.004 00, 0.003 50, 0.003 00, 0.002 50, 0.002 00, 0.001 75, 0.001 50, 0.001 25, 0.001 00, 0.000 80, 0.000 60, and 0.000 40 electrons per cubic bohr. However, not all of these values could be used with all of the compounds. As the cutoff value gets smaller, there comes a point when the regions of interest are no longer isolated, i.e., they become contiguous with other, unrelated regions of the difference density grid. This is the reason why one must extrapolate to an effectively zero contour rather than perform a direct calculation with an exact zero contour. For each compound, all the cutoff values in the list given above which maintained the integrity of the region of interest were used.

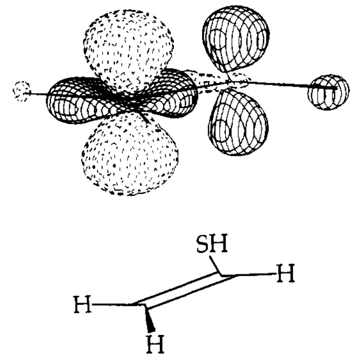

Figure 4. Charge density difference map for the vinyl group of the rotated minus planar form of ethylenethiol. The contour level is 2.2×10^{-3} e/au^3. The changes in charge density at sulfur have been eliminated.

In the case of ethylenethiol, the relatively long C–S bond made it possible to examine the change in population at the substituted carbon (Figure 4). It can be seen that the π-polarization is opposite to that found at the terminal methylene group. This shows that the effect of the sulfur lone pair is to shift π–charge density from the CH group to the methylene group. The lack of σ-polarization at the CH group shows that the σ/π shift at the terminal methylene results from an effort to reduce electron repulsion between the two types of electrons.

4. Interaction of Substituents with Ethynyl Groups

Acetylene is quite different from ethylene in its properties, and this results largely from the considerably increased percent s character in the orbitals used by carbon in forming σ bonds. It is reflected in the relatively high acidity of the C–H bonds[21] and the reversal in sign of the C–H bond dipole on going from ethylene to acetylene.[22] Therefore, the interaction of acetylene with substituents might prove to be quite different from that with ethylene or saturated hydrocarbon groups. The energies for group separation reactions involving ethynyl derivatives have been examined by Schleyer,[7] who found an inverse correlation with electronegativity as compared to the vinyl derivatives. We have examined a series of ethynyl derivatives at the G2 level, and the energies are summarized in Table I. The group separation reactions with ethane are given in Table VII.

In agreement with Schleyer's observations, the energy changes become progressively more negative on going from X = NH_2 to X = F, in contrast to the positive energies found with the vinyl derivatives. Again, we have examined the bond dissociation energies in order to find the origin of the difference between the two series. The calculated BDEs are given in Table IV. The energies of the group separation reactions for vinyl fluoride and ethynyl fluoride may be expressed in terms of the BDEs as follows:

vinyl fluoride	
$CH_2{=}CHF \rightarrow CH_2{=}CH^\bullet + F^\bullet$	+125.1
$CH_3CH_3 \rightarrow 2CH_3^\bullet$	+88.3
$CH_3^\bullet + CH_2{=}CH^\bullet \rightarrow CH_3CH{=}CH_2$	−100.4
$CH_3^\bullet + F^\bullet \rightarrow CH_3F$	−110.6
$CH_2{=}CHF + CH_3CH_3 \rightarrow CH_3CH{=}CH_2 + CH_3F$	+2.4
ethynyl fluoride	
$HC{\equiv}CF \rightarrow HC{\equiv}C^\bullet + F^\bullet$	+131.2
$CH_3CH_3 \rightarrow 2CH_3^\bullet$	+88.3
$CH_3^\bullet + HC{\equiv}C^\bullet \rightarrow CH_3C{\equiv}CH$	−126.3
$CH_3^\bullet + F^\bullet \rightarrow CH_3F$	−110.6
$HC{\equiv}CF + CH_3CH_3 \rightarrow CH_3C{\equiv}CH + CH_3F$	−17.4

An examination of the components of the reactions makes it clear that the major factor that determines the difference in sign for the two reactions is the much greater C–C bond dissociation energy in propyne as compared to propene. The high bond dissociation energy is well established experimentally[23] and probably results from the high s character in the bond from the ethynyl group coupled with the difference in electronegativity which leads to an unusually polar C–C bond. The difference in electronegativity is easily seen in the location of the bond critical point for the C–C bond, which is located 0.19 Å closer to the methyl carbon than to the acetylenic carbon.[24]

It is useful to compare the ethynyl–X bond dissociation energies with those for the corresponding MeX compounds, as was done for the vinyl derivatives. With the ethynyl compounds, it is not possible to "turn off" the π-interaction by rotating about a bond. However, the π-electron interaction might be estimated to be about the same as for the vinyl derivatives. A plot showing the relationship to the methyl BDEs is shown in Figure 5. A comparison with Figures 1 and 2 shows essentially the same pattern for the effect of substituents. The slope of the plot is only 0.6, as might be expected for the much lower polarizability and higher electronegativity of the acetylenic sp orbitals as compared to the methyl sp^3 orbitals.

The charge distributions may be compared by making use of deformation density plots in which the charge density corresponding to a set of spherically symmetrical proatoms at the same atomic coordinates is subtracted from the charge density for the molecule in question.[25] These plots allow comparisons of compounds even when the coordinates of the atoms are somewhat different. Plots for the molecular planes of propyne and ethynyl fluoride are shown in Figure 6 where the substituent is at the left. Solid lines indicate an increase in charge density with respect to the proatoms, and dashed lines indicate a decrease in charge density. It can be seen that the deformation densities for the π-region and for the terminal CH of these compounds are remarkably similar despite the large change in electronegativity of the substituent. In fact, these regions are essentially superimposable. The plots for the other compounds are quite similar.

In each case, the charge densities for the right-hand negative region (region A), for the small positive region between the terminal carbon and hydrogen (region B), and for the positive region corresponding to the π-bond (region C) were integrated numerically, giving the values shown in Table VIII. It can be seen that the total charge density in region B is essentially invariant to changes in substituents. In region A, the first-row substituents CH_3 to F give essentially the same value, and this also is true for the second-row substituents SiH_3 to Cl. Thus, the values appear to depend more on the type of substituent (i.e. first vs second row) than on its electronegativity. The same is true for region C. The

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(21) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data*, **1988**, *17*, Suppl. 1, 669.

(22) Wiberg, K. B.; Wendoloski, J. J. *J. Phys. Chem.* **1984**, *88*, 586.

(23) The bond dissociation energy of propyne is known from its heat of formation (ref 13), the heat of formation of the HC≡C radical (Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750), and the heat of formation of the methyl radical (Chase, M. W., Jr.; Davies, C. A.; Downery, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, Suppl. 1).

(24) For the relationship between the location of the bond critical point and the relative electronegativity of the atoms forming the bond, see: Boyd, R. J.; Boyd, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652.

(25) We have used the same definitions for proatoms as in the past (e.g., Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.*, accepted for publication). For those atoms with a half-filled outer shell, an ROHF calculation was performed for the appropriate state. This category includes hydrogen (doublet state; half-filled 1s orbital), nitrogen (quartet state; filled 2s orbital and half-filled 2p shell), and phosphorus (quartet state; filled 3s orbital and half-filled 3p shell). For most of the remaining atoms, GVB (generalized valence bond) calculations were performed in which the partially filled outer p shell orbitals all had equal partial occupancies so as to guarantee spherical symmetry. For instance, oxygen was forced to have a filled 2s orbital and three 2p orbitals each with an occupancy of 1.333 333, while fluorine had partial occupancies of 1.666 667 in its 2p shell. The authors thank Michael J. Frisch of Lorentzian, Inc., for this suggestion. These ROHF and GVB calculations necessarily yielded spherically symmetric wave functions. In all cases the same basis set was used for the proatoms and for the molecular electron density from which the proatoms were subtracted to yield the deformation density. The same approach has recently been used by Lin and Wang: Lin, K.; Wang, Y. *J. Phys. Chem.* **1993**, *97*, 3176.

Table VII. Isodesmic Reactions of Ethynyl Derivatives, 0 K, kcal/mol

reaction	ΔH (calc) MP2/6-31G*	MP3/6-311++G**	G2
$HC{\equiv}CH + H_3CCH_3 \rightarrow HC{\equiv}CCH_3 + CH_4$	−9.0	−7.3	−8.6
$HC{\equiv}CNH_2 + H_3CCH_3 \rightarrow HC{\equiv}CCH_3 + H_3CNH_2$	0.7	−0.1	−0.2
$HC{\equiv}COH + H_3CCH_3 \rightarrow HC{\equiv}CCH_3 + H_3COH$	−4.4	−5.8	−6.2
$HC{\equiv}CF + H_3CCH_3 \rightarrow HC{\equiv}CCH_3 + H_3CF$	−13.7	−15.9	−17.4
$HC{\equiv}CSiH_3 + H_3CCH_3 \rightarrow HC{\equiv}CCH_3 + H_3CSiH_3$	4.1	2.7	2.5
$HC{\equiv}CPH_2 + H_3CCH_3 \rightarrow HC{\equiv}CCH_3 + H_3CPH_2$	0.7	−0.1	0.1
$HC{\equiv}CSH + H_3CCH_3 \rightarrow HC{\equiv}CCH_3 + H_3CSH$	−2.5	−2.9	−2.4
$HC{\equiv}CCl + H_3CCH_3 \rightarrow HC{\equiv}CCH_3 + H_3CCl$	−9.3	−9.9	−9.3
$HC{\equiv}CLi + H_3CCH_3 \rightarrow HC{\equiv}CCH_3 + H_3CLi$	23.1	23.0	21.8
$HC{\equiv}CCN + H_3CCH_3 \rightarrow HC{\equiv}CCH_3 + H_3CCH_3$	−4.1	−4.4	−7.5
$HC{\equiv}CCH{=}CH_2 + H_3CCH_3 \rightarrow HC{\equiv}CCH_3 + H_3CCH{=}CH_2$	1.7	1.7	−1.7
$HC{\equiv}CCF_3 + H_3CCH_3 \rightarrow HC{\equiv}CCH_3 + H_3CCF_3$	−12.8	−14.2	
$HC{\equiv}CNO_2 + H_3CCH_3 \rightarrow HC{\equiv}CCH_3 + H_3CNO_2$	−19.2	−23.0	

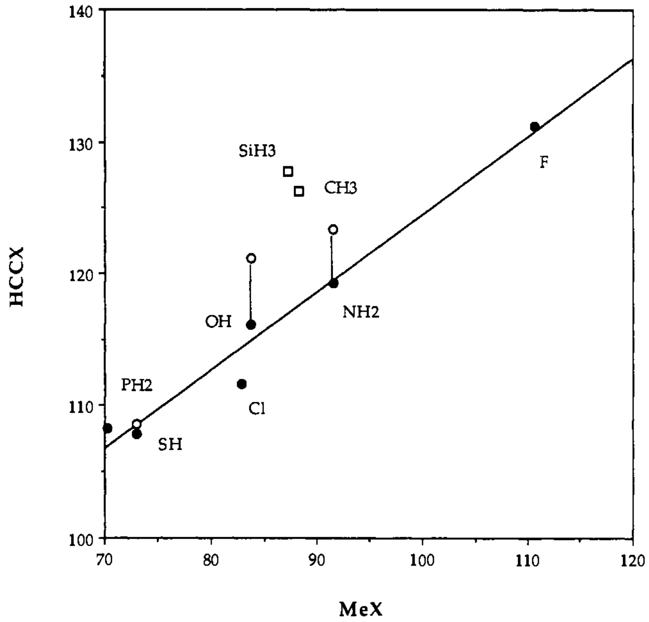

Figure 5. Relationship between ethynyl–X and methyl–X bond dissociation energies. The π interaction energies were assumed to be the same as for the vinyl compounds. The line is based on the solid circles.

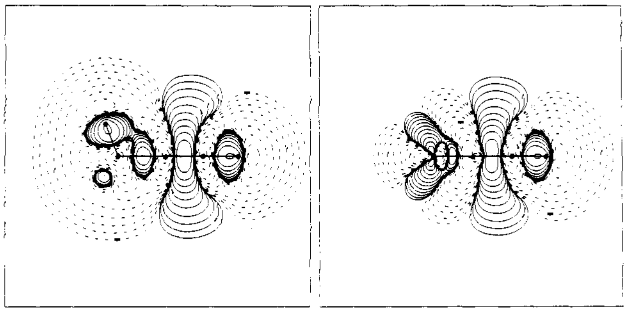

Figure 6. Deformation density plots for propyne (left) and ethynyl fluoride (right). The positions of the atoms are shown by the solid circles.

Table VIII. Integration of Charge Densities for Deformation Density Plots

substituent	region A	B	C	total
Li	−0.402	0.182	0.587	0.367
CH_3	−0.431	0.179	0.598	0.346
NH_2	−0.410	0.179	0.611	0.380
OH	−0.414	0.177	0.611	0.374
F	−0.437	0.175	0.597	0.335
SiH_3	−0.488	0.179	0.573	0.264
PH_2	−0.469	0.179	0.563	0.273
SH	−0.456	0.178	0.562	0.284
Cl	−0.456	0.176	0.570	0.290
CN	−0.530	0.177	0.505	0.152
NO_2	−0.537	0.175	0.517	0.155
CF_3	−0.514	0.177	0.539	0.202

Table IX. G2 Calculated Heats of Formation, 0 K, kcal/mol

compound	ΔH_f(obs)	ΔH_f(G2)	ΔH_f(correl)
CH_4	−15.9 ± 0.1	−16.7	−16.4
C_2H_6	−16.6 ± 0.1	−16.8	−16.6
CH_3NH_2	−2.0 ± 0.1	−1.9	−2.1
CH_3OH	−45.6 ± 0.1	−46.8	−45.7
CH_3SiH_3	−3.2 ± 2.0	−3.6	−3.7
CH_3SH	−3.2 ± 0.2	−2.9	−3.0
CH_3Cl	−17.7 ± 0.1	−18.6	−18.3
$CH_3CH{=}CH_2$	8.4 ± 0.2	9.0	8.5
$CH_3C{\equiv}CH$	45.9 ± 0.2	47.3	45.7
CH_3CN	17.1 ± 1.7	19.8	19.0
$CH_2{=}CH_2$	14.6 ± 0.1	14.8	14.2
$CH_2{=}CHOH$	−27.1 ± 2.0	−27.3	−26.7
$CH_2{=}CHF$	−31.3 ± 0.4	−33.0	−32.3
$CH_2{=}CHCH{=}CH_2$	29.8 ± 0.3	31.5	30.4
$CH_2{=}CHCN$	44.8 ± 0.4	47.6	46.0
$HC{\equiv}CH$	54.7 ± 0.2	56.0	54.2
$H_2C{=}O$	−25.1 ± 0.1	−27.0	−26.5
CH_3CHO	−37.2 ± 0.1	−38.4	−37.6
CH_3COCH_3	−48.0 ± 0.2	−49.1	−47.9
CH_3CO_2H	−100.2 ± 0.4	−101.8	−99.1
CH_3CONH_2	−53.1 ± 0.2	−53.4	−52.2
CH_3COF	−103.4 ± 0.8	−105.3	−102.6
CH_3COSH	−38.9 ± 2.0	−41.2	−40.3
CH_3COCl	−55.9 ± 0.2	−57.7	−56.3
rms dev		1.4	0.8

total charge density for these regions is given in the last column of the table. The common first-row substituents give 0.36 ± 0.02 e, the second-row substituents give 0.28 ± 0.01 e, and the last three substituents give 0.17 ± 0.02 e. The latter substituents are unique in that they are electron withdrawing, but have a positive charge at the atom joined to the ethynyl group.

5. Calculation of Heats of Formation Using the G2 Model

It has been well established that the G2 model reproduces the heats of atomization (and, hence, the heats of formation) of a wide variety of molecules with one or two non-hydrogen atoms with an average error of only 1–2 kcal/mol.[11] This investigation, along with another from this laboratory,[26] has obtained G2 energies for a number of additional organic compounds. It was then of interest to see if there were any systematic differences between the heats of formation predicted by G2 and the experimental values for the organic compounds (Table IX). The two quantities are compared in Figure 7, and with $r^2 = 0.999$, the best line has the form

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(26) Wiberg, K. B.; Nakaji, D. Y. To be published

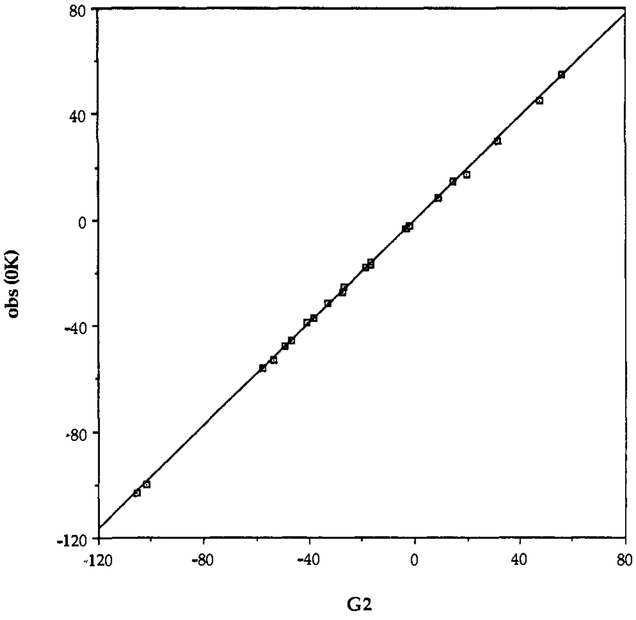

Figure 7. Relationship between G2 calculated heats of formation and the observed energies.

$$\Delta H(\text{obs,0 K}) = -0.221 + 0.972\Delta H(\text{G2})$$

The energies derived from this correlation are given in the last column of the table as ΔH_f(correl). The root mean square (rms) error was 0.8 kcal/mol, whereas the rms deviation between ΔH(obs,0 K) and ΔH(G2) for this data set was 1.4 kcal/mol. Although the rms error is reduced using this correlation, it is not clear that the difference is statistically significant in view of the small sample size and the uncertainties associated with the experimental heats of formation. It is worth noting that the larger deviations were found with acetonitrile and acrylonitrile, suggesting that the G2 method may underestimate the energies of nitriles.

6. Conclusions

The bond dissociation energies in the vinyl–X series are linearly related to those in the methyl–X series with a slope close to unity. Changes in electronegativity and changes in hybridization fall on the same straight line, showing that there is no fundamental difference in the interactions between the hydrocarbon group and the substituents in these two series. The only difference was found with X = NH_2 or OH, where there was a small (~5 kcal/mol) π-electron interaction in the vinyl series.

These results are in sharp contrast to acetyl–X series, where the change in BDE was considerably greater than for the methyl–X compounds and where the correlation line for changes in electronegativity was different from that for changes in hybridization. Here, the π-electron effects with NH_2 and OH were considerably larger, ~15 kcal/mol. Thus, there is a fundamental difference between the way in which a carbonyl group and a vinyl group interact with substituents. This appears to be due to the polarization of the carbonyl group in the sense $C^+–O^-$, leading to strong Coulombic interactions.

Charge density difference plots show that substituents such as NH_2 will transfer some π-charge density from its lone pair to the terminal CH_2 of a vinyl group or the carbonyl oxygen of an acetyl group. However, the charge transfer is quite small and is accompanied with a σ-charge shift in the opposite direction. Despite the considerably larger rotational barriers with the acetyl derivatives as compared to vinyl, the π-charge transfer was smaller for the former than the latter. This again indicates that the principal interaction in amides involves the N and C rather than the O.

In the case of the ethynyl derivatives, the group separation reactions involving substituents such as NH_2, OH, and F showed that they preferred a methyl group to ethynyl, whereas with vinyl and acetyl derivatives, they did not prefer a methyl group. The difference between these series of compounds was found to result from two main factors: (a) the remarkably large C–C bond dissociation energy for propyne and (b) a smaller effect of electronegativity on BDEs than found with methyl derivatives.

Calculations

The ab initio calculations were carried out using GAUSSIAN-91[27] and GAUSSIAN-92[28] and standard basis sets.[29]

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Supplementary Material Available: Calculated structural data (MP2/6-31G*) in Z matrix format (6 pages). Ordering information is given on any current masthead page.

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