Enthalpies of Hydrogenation of Heteroatom-Substituted Alkenes

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Abstract: The heats of hydrogenation of a series of heteroatom-substituted ethenes were calculated at the MP2 and MP3/6-311++G** and G2 theoretical levels. Although there are small differences between the sets of values, the corresponding hydrogen transfer energies were essentially the same. The bond dissociation energies of the products were calculated at the G2 level so that the hydrogenation energies could be converted to π-bond energies. With correction for σ-compression in forming the double bonds, the strengths of the σ and π bonds for the first row were about equal. The effect of methyl substitution was studied at the MP2 and MP3/6-311++G** theoretical levels. It was found that increased electronegativity of the heteroatom substituent (X) led to increased stabilization by methyl when substituted at carbon and destabilization when substituted at X.

1. Introduction

A knowledge of the enthalpies of hydrogenation of heteroatom-substituted alkenes is essential if one is to interpret the stabilization of heteroatom-substituted aromatic systems.[1] They also are useful in estimating the energies of π-bonds in the alkenes. A direct experimental study of the hydrogenation enthalpies is hampered by the kinetic instability of the parent compounds. Formaldehyde exists as a trimer in the pure state[2] and only has a limited lifetime in aqueous solution where it is protected as the hydrate. Both 1-azacyclohexene[3] and 1-azacyclopentene[4] undergo rapid trimerization and can be observed only as the trimer. Silaethylene[5] can only be observed in a matrix at low temperature. Many of the other compounds of interest have never been observed.

As a result, the only available way in which to study most of the compounds is via theoretical calculations. Extensive studies of some of these compounds have been reported by Schmidt, Truong, and Gordon[6] by Sun, Hrovat, and Borden,[7] by Kutzelnigg,[8] and by Schleyer and Kost.[9] Despite this work, it appeared worthwhile to extend these studies making use of a higher theoretical level, and to include additional substituents. Therefore, in the present study, we have examined the hydrogenation enthalpies of systems with two heavy atoms using the G2 formalism[10] that has been found to be remarkably able to reproduce experimental data. Then, for use with larger systems, we will examine what level of theory is needed to reproduce the G2 results. It is known that methyl substitution leads to a significant change in energy for ethene. Therefore, we will present data for some methyl-substituted derivatives.

In addition to the energies, we are interested in seeing how heteroatom substitution affects the atom and bond properties of the compounds. As a result, we have also calculated the atomic charges making use of Bader's theory of atoms in molecules[11] and have calculated the bond orders using the method developed by Cioslowski and Mixon.[12]

2. Calculations

The structures of a series of compounds of the type $X = CH_2$ where $X = BH, CH_2, NH, O, AlH, SiH_2, PH,$ and S have been obtained by geometry optimization at the MP2/6-31G* level which usually gives results that are in good agreement with experimental data. The energies are given in Table I and the structures are summarized in Table II along with the available experimental data. G2 energies, which are effectively QCISD(T)/6-311+G(3df,2p)//MP2/6-31G* including the zero-point energies and a higher order correction, are known to reproduce experimental data remarkably well.[10] These energies have been reported for some of these compounds,[10] and in the other cases they were calculated and are recorded in Table I. We also wished to see how well a lower theoretical level that would be more practical for larger molecules might serve to reproduce the data. A theoretical level that has proven useful in other cases we have examined is MP3/6-311++G**,[13] and these energies also are recorded in the table. Recently, Curtiss, Raghavachari, and Pople[14] have suggested that the MP2 relative energies may be more satisfactory than MP3. The present data allow these energies to be compared with the G2 relative energies.

The energies of the compounds were calculated from the G2 energies and the values thus derived are compared with the experimental energies in Table I. In most cases there was good agreement. In the case of formaldehyde, there are two experimental values. A measurement of the heat of sublimation of polyoxymethylene combined with the well-established heat of formation of the latter gave $\Delta H_f(298\ K) = -28.7 \pm 0.1$ kcal/mol (−27.8 at 0 K), and a measurement of the heat of combustion of gaseous formaldehyde gave −26.0 ± 0.1 kcal/mol at 298 K (−25.1 at 0 K).[15] The former value is in good agreement with the G2 energy. In view of the difficulty in handling gaseous formaldehyde, the value derived by heat of combustion might be in error. Therefore we prefer the energy

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Table I. Calculated Energies Using Mp2/6-31G* Geometries[a]

compd	MP2/6-311++G**	MP3/6-311++G**	ZPE[b]	G2	ΔH_f(0 K)	
					calc[d]	obs[e]
CH₂=BH	-64.467 83	-64.489 41	20.2	-64.533 25	52	
CH₃—BH₂	-65.711 14	-65.740 75	33.2	-65.768 29	8	
CH₂=CH₂	-78.349 38	-78.371 88	30.7	-78.415 93[c]	14.8	14.6 ± 0.1
CH₃—CH₃	-79.574 18	-79.604 04	44.7	-79.630 90[c]	-16.7	-16.6 ± 0.1
CH₂=NH	-94.384 73	-94.398 14	24.3	-94.463 28[c]	22.6	
CH₃—NH₂	-95.597 23	-95.619 25	38.6	-95.666 91[c]	-1.9	-2.0 ± 0.1
CH₂=O	-114.247 08	-114.249 39	16.3	-114.338 88[c]	-27.0	-27.8 ± 0.1; -25.1 ± 0.1[f]
CH₃—OH	-115.450 10	-115.464 23	31.0	-115.534 89[c]	-46.8	-45.6 ± 0.1
CH₂=AlH	-281.660 01	-281.677 71	16.8	-281.730 31	80	
CH₃—AlH₂	-282.929 25	-282.957 37	28.5	-282.994 70	17	
CH₂=SiH₂	-329.329 96	-329.355 05	24.3	-329.412 40	47	
CH₃—SiH₃	-330.585 27	-330.616 54	36.5	-330.657 67	-4	
CH₂=PH	-380.593 66	-380.617 77	20.3	-380.692 11[c]	30.3	
CH₃—PH₂	-381.813 48	-381.846 25	32.9	-381.906 04[c]	-0.6	
CH₂=S	-436.818 32	-436.837 59	15.0	-436.933 69[c]	28.7	24 ± 7; 33.1 ± 1.5[g]
CH₃—SH	-438.039 44	-438.068 68	27.8	-438.148 47[c]	-2.8	-3.2 ± 0.2
H₂	-1.160 30	-1.166 27	5.9	-1.166 36[c]		

[a] The MP2 and MP3 energies do not include the zero-point energies. However, the G2 energies include this term. Six Cartesian d functions were used in the MP3 calculations. The total energies are given in hartree, and the ZPE and ΔH terms are given in kcal/mol. [b] HF/6-31G* values scaled by 0.8934. [c] Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221. [d] Calculated values given as integers are based on heats of atomization of the elements that have a 1–3-kcal/mol uncertainty. The others are based on heats of atomization with an uncertainty of 0.1–0.2 kcal/mol. [e] Reference 14 with a correction from 298 to 0 K. [f] See text. The more negative value (-27.8 kcal/mol) will be used with an increased uncertainty (±1.0 kcal/mol) in the following tables. [g] Reference 16.

derived from the heat of sublimation. In the case of thioformaldehyde, there are two estimates derived from mass spectrometric data, 33.1 ± 1.5 and 24 ± 7.[16] The G2 estimate is approximately the average of these values.

As part of the study, the energies of the reduced derivatives were needed, and they were studied in the same fashion. The interpretation of the calculated data requires correction for zero-point energies. They were estimated by carrying out HF/6-31G* vibrational frequency calculations and scaling the calculated frequencies by 0.893. The ab initio calculations were carried out with GAUSSIAN-91.[17]

We also were interested in the atomic electron populations and bond orders in the compounds. The former were obtained by using Bader's theory of atoms in molecules.[11] Here, one first locates the point of minimum charge density along the bond between a pair of atoms. Starting at this critical point, rays are developed normal to the bond for which the charge density decreases most rapidly. A set of such rays will define a surface that separates the two atoms, and a set of surfaces will divide a molecule into unique atomic domains. The electron population is derived by numerical integration of the charge density within each of the atomic volumes. The calculations were carried out using PROAIM.[18] Bond orders were derived from the atomic overlap matrices using BONDER.[12]

Information on methyl-substituted derivatives of the heteroethenes was obtained in a similar fashion. The MP2/6-311++G** and MP3/6-311++G** energies were obtained using the RHF/6-31G* structures.

3. Hydrogenation Energies and Hydrogen Transfer Energies

The hydrogenation energies may be estimated from the data in Table I and are summarized in Table III. The G2 energy changes are in good agreement with the few available experimental data. This is expected since they reproduce atomization energies with an average error of only ∼1 kcal/mol.[10] For the cases in which experimental data are not available, these calculated energies should be quite reliable. The MP2/6-311++G** energy changes are only 1–2 kcal/mol more negative than the G2 values and are more satisfactory than the MP3 values. One might expect that the change in correlation energy between H₂ and two C–H

bonds might be difficult to reproduce at a lower level of correction for this energy. The problem should be minimized if one uses a hydrogen transfer reaction such as

$$CH_3—CH_3 + CH_2=NH \rightarrow CH_2=CH_2 + CH_3—NH_2$$
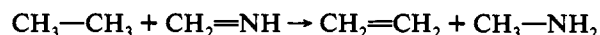
Here, the bonds to hydrogen are similar on both sides of the equation, and differences in correcting for electron correlation should be minimized.

The energies for these reactions are also summarized in Table III. Both the MP2/6-311++G** and the MP3 energy changes are close to the G2 values. Positive values indicate that the double bond to the heteroatom is preferred, and negative values indicate that the heteroethene is destabilized. It can be seen that CH₂=NH and CH₂=O are stabilized with respect to ethene, that CH₂=PH and CH₂=S are comparable to ethene, and that CH₂=BH, CH₂=AlH, and CH₂=SiH₂ are all strongly destabilized compared to ethene.

These results are reasonable and agree with the results of other studies. However, as Schmidt et al. have pointed out, they do not represent just the differences in π energy with respect to ethene for the number of bonds between hydrogen and the heteroatom also changes.[7] If there is a difference in bond energy between a C–H and a X–H bond, it will be reflected in the calculated hydrogen transfer energies.

4. Bond Dissociation Energies

If the bond dissociation energies were known, it would be possible to correct the hydrogenation energies to obtain the π-bond strengths. This has been done by Schmidt et al.,[7] but some of the dissociation energies had to be estimated. The G2 procedure is rather satisfactory for calculating dissociation energies, and for a series of simple hydrides, there is a remarkably good agreement with the experimental data (Table IV).[19] Thus, the energies of the radicals were calculated (Table V). The BDE's derived from these data are compared with the available experimental data in Table V. There are fewer experimental data with which they may be compared, but there is good agreement with these limited data.

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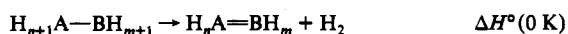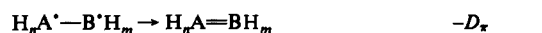
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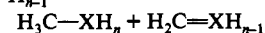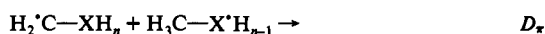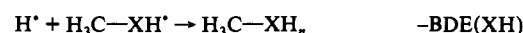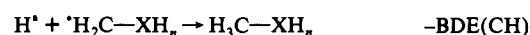
Table II. Calculated Structures, MP2/6-31G* [a]

compd	param	calc	obs	compd	param	calc	obs
HB=CH$_2$	r_{BC}	1.3846		H$_2$N—CH$_3$	r_{NC}	1.4635	1.471(2)
	r_{CH}	1.0861			r_{NH}	1.0174	1.010(5)
	r_{BH}	1.1755			r_{CH_a}	1.1000	1.099(5)[b]
	∠HCH	115.49			r_{CH_g}	1.0921	
	∠HBC	180.00			∠HNC	109.63	
H$_2$C=CH$_2$	r_{CC}	1.3349	1.337[20]		∠H$_a$CN	115.43	113.2
	r_{CH}	1.0848	1.086		∠H$_g$CN	108.88	108.8
	∠HCH	116.59	117.37		τ(H$_g$CNH$_a$)	121.56	
HN=CH$_2$	r_{NC}	1.2806			τ(HNCH$_a$)	57.97	
	r_{NH}	1.0261		HO—CH$_3$	r_{OC}	1.4224	1.425(2)
	r_{CH_c}	1.0946			r_{CH_a}	1.0896	1.094(3)[b]
	r_{CH_t}	1.0890			r_{CH_g}	1.0969	
	∠HNC	109.81			r_{OH}	0.9699	0.945
	∠H$_c$CN	125.43			∠H$_a$CO	106.34	107.1
	∠H$_t$CN	118.39			∠H$_g$CO	112.37	112.1
	∠HCH	116.19			∠HOC	107.48	108.5
O=CH$_2$	r_{OC}	1.2200	1.206[26]		τ(H$_g$COH$_a$)	118.50	
	r_{CH}	1.1039	1.108	H$_2$Al—CH$_3$	r_{AlC}	1.9612	
	∠HCH	115.62	116.8		r_{HAl}	1.5941	
HAl=CH$_2$	r_{AlC}	1.7950			r_{CH_a}	1.0968	
	r_{HAl}	1.5744			r_{CH_g}	1.0935	
	r_{CH}	1.0872			∠HAlC	120.71	
	∠HAlC	180.00			∠H$_a$CAl	110.22	
	∠HCH	114.91			∠H$_g$CAl	112.38	
	∠HCAl	122.55			τ(H$_g$CAlH$_a$)	118.79	
H$_2$Si=CH$_2$	r_{SiC}	1.7131			τ(HAlCH$_a$)	89.45	
	r_{SiH}	1.4770		H$_3$Si—CH$_3$	r_{SiC}	1.8803	
	r_{CH}	1.0854			r_{SiH}	1.4866	
	∠HSiH	115.03			r_{CH}	1.0927	
	∠HCH	115.96			∠HSiC	110.59	
HP=CH$_2$	r_{PC}	1.6749	1.673(2)[27]		∠HCSi	111.00	
	r_{PH}	1.4213	1.420(6)	H$_2$P—CH$_3$	r_{PC}	1.8581	
	r_{CH_c}	1.0856	1.090(15)		r_{PH}	1.4166	
	r_{CH_t}	1.0863	1.090(15)		r_{CH_a}	1.0904	
	∠HPC	97.28	97.4(4)		r_{CH_g}	1.0918	
	∠H$_c$CP	124.87	124.4(8)		∠HPC	97.99	
	∠H$_t$CP	119.23	118.4(12)		∠H$_a$CP	113.69	
S=CH$_2$	r_{SC}	1.6156	1.6138(4)[28]		∠H$_g$CP	109.00	
	r_{CH}	1.0900	1.0962(6)		τ(H$_g$CPH$_a$)	121.45	
	∠HCH	115.92	116.16(6)		τ(HPCH$_a$)	47.98	
H$_2$B—CH$_3$	r_{BC}	1.5605		HS—CH$_3$	r_{SC}	1.8143	
	r_{CH_a}	1.1022			r_{CH_a}	1.0902	
	r_{CH_g}	1.0917			r_{CH_g}	1.0900	
	r_{BH}	1.1963			r_{SH}	1.3404	
	∠H$_a$CB	104.97			∠H$_a$CP	106.62	
	∠H$_g$CB	114.29			∠H$_g$CP	111.63	
	∠HBC	121.01			∠HSC	96.79	
	τ(H$_g$CBH$_g$)	116.03			τ(H$_g$CPH$_a$)	118.29	
	τ(HBCH$_a$)	88.19					
H$_3$C—CH$_3$	r_{CC}	1.5249	1.532(2)				
	r_{CH}	1.0929	1.111(2)				
	∠HCC	111.18					

[a] Bond angles are given in Å and bond angles in deg. [b] Average values.

The hydrogenation energies may now be corrected as follows:

$$H_{n+1}A—BH_{m+1} \rightarrow H_nA^{\bullet}—BH_{m+1} + H^{\bullet} \qquad D(A\text{-}H)$$

$$H_nA—BH_{m+1} \rightarrow H_nA^{\bullet}—B^{\bullet}H_m + H^{\bullet} \qquad D(B\text{-}H)$$

$$H_nA^{\bullet}—B^{\bullet}H_m \rightarrow H_nA=BH_m \qquad -D_\pi$$

$$2H^{\bullet} \rightarrow H_2 \qquad -D(H\text{-}H)$$

$$H_{n+1}A—BH_{m+1} \rightarrow H_nA=BH_m + H_2 \qquad \Delta H°(0\ K)$$

$$D_\pi = D(A\text{-}H) + D(B\text{-}H) - \Delta H°(0\ K) - D(H\text{-}H) \qquad (1)$$
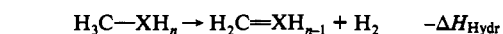
It is assumed that $D(H_nA^{\bullet}\text{-}BH_m—H) \approx D(H_{n+1}A\text{-}BH_m—H)$. Using the calculated hydrogenation and bond dissociation energies, we obtain the values given in Table VI under "this work".

5. Disproportionation Reactions and π-Bond Energies

Another way in which to examine the π energies of the heteroethenes is via an examination of disproportionation reactions

such as:[8]

$$H_3C—XH_n \rightarrow H_2C=XH_{n-1} + H_2 \qquad -\Delta H_{Hydr}$$

$$H^{\bullet} + {}^{\bullet}H_2C—XH_n \rightarrow H_3C—XH_n \qquad -BDE(CH)$$

$$H^{\bullet} + H_3C—XH^{\bullet} \rightarrow H_3C—XH_n \qquad -BDE(XH)$$

$$H_2 \rightarrow 2H^{\bullet} \qquad BDE(H_2)$$

$$H_2{}^{\bullet}C—XH_n + H_3C—X^{\bullet}H_{n-1} \rightarrow \qquad D_\pi$$
$$H_3C—XH_n + H_2C=XH_{n-1}$$

When a consistent set of data are employed, the π-bond energies obtained in this fashion must be identical to those derived with eq 1. This is the case with the G2 calculated energies.

An alternate way of obtaining the π-bond energies has been proposed by Schleyer and Kost[9] which first involves a comparison of a C=X bond with two C—X single bonds via the following isodesmic reaction:

Table III. Energy Changes (kcal/mol) for Reactions

compd	MP2/6-311++G**	MP3/6-311++G**	G2	obs(0 K)	obs(298 K)
		(a) Hydrogenation			
CH_2=BH	−45.0	−46.3	−43.1		
CH_2=CH_2	−32.3	−33.3	−30.5	−31.2 ± 0.3	−32.7 ± 0.3
CH_2=NH	−24.5	−26.1	−23.4		
CH_2=O	−18.0	−21.7	−18.6	−17.8 ± 1.0	−19.5 ± 1.0
CH_2=AlH	−62.6	−65.4	−61.5		
CH_2=SiH_2	−51.5	−53.4	−49.4		
CH_2=PH	−30.5	−32.4	−29.9		
CH_2=S	−31.3	−33.8	−30.4		
		(b) Hydrogen Transfer Energies from Ethane			
CH_2=BH	−12.6	−13.0	−12.6		
CH_2=NH	8.0	7.2	7.1		
CH_2=O	14.4	11.6	11.9	13.4 ± 1.0	
CH_2=AlH	−30.2	−32.1	−31.0		
CH_2=SiH_2	−19.2	−20.1	−18.9		
CH_2=PH	1.7	0.9	0.7		
CH_2=S	1.1	−0.5	0.1		

Table IV. Calculated Bond Dissociation Energies (kcal/mol) of Simple Hydrides at 0 K[a]

compd	G1	G2	obs(0 K)	obs(298 K)	Δ(G1)	Δ(G2)
BH_3	105.1	105.2				
CH_4	103.7	104.0	103.2 ± 0.1	104.8 ± 0.1	0.5 ± 0.1	0.8 ± 0.1
NH_3	105.8	106.4	107.1 ± 1.5	108.6 ± 1.5	1.3 ± 1.5	0.7 ± 1.5
H_2O	116.8	118.1	117.9 ± 0.3	119.2 ± 0.3	1.1 ± 0.3	0.2 ± 0.3
AlH_3	84.9	84.7				
SiH_4	91.4	91.3	90.3 ± 0.5	91.8 ± 0.5[b]	1.1 ± 0.5	1.0 ± 0.5
PH_3	81.1	81.5				
H_2S	89.3	90.2	88.5 ± 1.2	90.3 ± 1.2	0.8 ± 1.2	1.7 ± 1.2

[a] Data from ref 20 unless otherwise noted. [b] Seetula, J. A.; Feng, Y.; Gutman, D.; Sealans, P. W.; Pilling, M. J. *J. Phys. Chem.* **1991**, *95*, 1658.

$$H_2C=XN_n + CH_4 + XH_{n+2} \rightarrow 2H_3C-XH_{n+1}$$

The energy of this reaction, when subtracted from two times the C—X bond dissociation energy, gives the total double bond energy ($\sigma + \pi$). If the σ part is taken as the C—X dissociation energy, the π part may then be obtained. This procedure has, however, the disadvantage that it assumes constant C–H and X–H bond dissociation energies, which is not correct.[20,21]

The π energies derived by the several available methods are summarized in Table VII. The first column gives the energies derived by Schleyer and Kost. The second gives the energies calculated by Schmidt et al. for a 90° rotation of the π-bond. The third column gives the energies they derived from the energies of hydrogenation corrected for the difference in bond dissociation energies. The fourth column gives our calculated values based on the G2 energies. It can be seen that there is generally good agreement between the values in columns 2–4. The π energies decrease in the order =O > =NH > =CH_2 > =S > =BH > =P > =SiH_2 > =AlH. The latter is found to have a remarkably weak π-bond, and CH_2=SiH_2 gives a π-energy about half of the strongest π-bonds.[22]

The π energies thus obtained do, however, contain a contribution from the destabilization of the σ system resulting from the decrease in bond length on going to the unsaturated system. The change in bond length is remarkably constant (Table VII). The σ compressive energies were estimated by calculating the energies of the saturated systems at the unsaturated central bond lengths. These energies are given in Table VII. The column in Table VI

(20) The BDE (0 K) for the successive removals of hydrogen atoms from methane are 103.2, 108.3, 100.6, and 80.4 kcal/mol, respectively (ref 21).

(21) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Fruip, D. J.; McDonald, R. A.; Syverd, A. N. *J. Phys. Chem. Ref. Data* **1985**, *14*, 661.

(22) The very weak Al–C π bond suggests that a single determinant may not be appropriate for calculations on HAl=CH_2. A CASSCF(6,6)/6-31G* calculation, which included the three highest occupied orbitals with B_2, A_1, and B_1 symmetry and the three lowest virtual orbitals having the same symmetries, found the HF reference configuration to be by far the most important (coefficient = 0.964).

marked σ corr gives the π dissociation energies corrected for the σ compression energies. They are compared to the σ bond energies in the last column of the table. With this correction, the σ- and π-bond energies for the first-row substituents are similar in value, although of course with different equilibrium bond lengths. However, for the second-row substituents, the σ-bond energies are considerably greater than the π energies. It is generally agreed that π-bonding is less effective with the second-row elements than with the first row.[8]

It was noted by Schleyer and Kost that there was a trend toward higher π energies with increasing electronegativity of X.[9] This continues to be the case with the present data ($r^2 = 0.82$). This is, however, not the case with the σ-dissociation energies (Table VI). Here, there is a trend toward increasing bond strength with increasing difference in electronegativity. The smaller BDE for methylamine as compared to ethane is probably a result of the change in hybridization, but then it increases from methylamine (83.9 kcal/mol) to methanol (90.6 kcal/mol) and methyl fluoride (108.7 kcal/mol). Similarly, the BDE for methylborane (104 kcal/mol) is greater than that for ethane (88.0 kcal/mol). With the second-row elements, methylsilane (86.8 kcal/mol) and methyl chloride (82.4 kcal/mol) have higher BDE's than either methyl phosphine (70 kcal/mol) or methanethiol (73.0 kcal/mol). These changes are presumably a result of the increased polarity of the bonds with increased electronegativity difference, leading to internal Coulombic stabilization. The reason for the different behavior of the π BDE's is not clear.

6. Atom and Bond Properties

The atom and group charges derived from the wave functions making use of Bader's theory of atoms in molecules are summarized in Table VIII.[23] It may be noted that some of the charges are rather large. They are the first term of a series that includes atomic dipole and higher moments. When both the charges and the atomic dipoles are used, the data reproduce the molecular dipole moments. Thus, they are not charges for spherically symmetrical atoms, but they also take into account the shift in charge density on bond formation.[24] In the present context, the relative values are of more importance than the absolute values.

It is readily possible to separate the charges into σ and π components for these planar systems, and both charges are given. With the first-row substituents, the carbon σ and π charges are approximately equal, whereas for the second-row substituents they start about equal, but the π charge increases rapidly whereas

(23) A more complete table is available as supplementary material.

(24) For a detailed discussion of atomic charges and a comparison of charges derived using different methods, see: Wiberg, K. B.; Rablen, P. R. *J. Comput. Chem.* To be published.

Table V. Calculated Energies of Radicals and G2 Bond Dissociation Energies for Their Formation[a]

radical	MP2/6-31G*	MP3/6-311++G**	ZPE	G2	BDE	obs(0 K)	obs(298 K)
·CH$_2$BH$_2$	-65.010 96	-65.087 07	25.9	-65.117 85	94.4		
CH$_3$BH·	-64.996 73	-65.071 84	26.3	-65.102 43	104.1		
CH$_3$CH$_2$·	-78.844 66	-78.936 71	35.5	-78.946 66	100.8	99.1 ± 0.4	100.5 ± 0.5[b]
·CH$_2$NH$_2$	-94.868 59	-94.964 24	30.2	-95.018 53	93.1	93 ± 2	94 ± 2[c]
CH$_3$NH·	-94.860 87	-94.956 04	29.7	-95.008 83	99.2	102 ± 2	103 ± 2[d]
·CH$_2$OH	-114.703 40	-114.804 34	22.5	-114.881 61	96.2	95 ± 2	96 ± 2[c]
CH$_3$O·	-114.693 09	-114.784 15	22.6	-114.867 47	105.1	103 ± 1	104.3 ± 0.9[e]
·CH$_2$AlH$_2$	-282.211 67	-282.298 76	21.1	-282.339 10	97.6		
CH$_3$AlH·	-282.241 08	-282.322 69	24.0	-282.358 71	85.3		
·CH$_2$SiH$_3$	-329.842 70	-329.950 61	28.1	-329.996 60	101.1		
CH$_3$SiH$_2$·	-329.866 38	-329.967 83	30.8	-330.010 59	92.3		
·CH$_2$PH$_2$	-381.081 31	-381.182 59	24.0	-381.249 80	98.0		
CH$_3$PH·	-381.122 37	-381.216 45	26.6	-381.277 72	80.5		
·CH$_2$SH	-437.315 98	-437.408 51	19.0	-437.496 56	95.1	95 ± 2	98 ± 2[f]
CH$_3$S·	-437.345 98	-437.429 67	21.6	-437.511 23	86.1	88 ± 1	89 ± 1[f]
H·	-0.498 23	-0.499 82	0.0	-0.500 00			

[a] The MP2, MP3, and G2 energies are given in hartrees, and the ZPE, BDE, and obs energies are given in kcal/mol. The BDE's are for the formation of the radicals and hydrogen atom from their precursors. [b] Davies, J. W.; Hanning-Lee, M. A.; Pilling, M. J. *Spectrochim. Acta* **1990**, 46A, 581.[c] Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1981**, 103, 1586. [d] Golden, D. M.; Solly, R. K.; Gac, N. A.; Benson, S. W. *J. Am. Chem. Soc.* **1972**, 94, 363. [e] Meot-Ner (Mautner), M.; Sieck, L. W. *J. Phys. Chem.*, **90**, 6687. Engelking, P. C.; Ellison, G. B.; Lineberger, W. C. *J. Chem. Phys.* **1987**, 69, 1826. [f] Shum, L. G. S.; Benson, S. W. *Int. J. Chem. Kinet.* **1983**, 15, 433.

Table VI. π-Bond Energies (kcal/mol)

			D_π			
compd	Schleyer[9]	bond rot.[6]	hydrog corr[6]	this work	σ corr	D_σ,[a]
CH$_2$=BH	53.7			51.0	64	104[b]
CH$_2$=CH$_2$	69.6	65.4	62	66.8	86	88
CH$_2$=NH	80.8	63.3	65	64.5	84	84
CH$_2$=O	93.4		77	78.2	102	91
CH$_2$=AlH	9.4			17.1	19	82[b]
CH$_2$=SiH$_2$	36.1	35.6	37	39.5	47	87
CH$_2$=PH	49.4	43.1	45	44.3	55	70[b]
CH$_2$=S	55.7			53	46.4	61	73

[a] CH$_3$-X bond dissociation energies of corresponding saturated compounds. [b] Estimate based on G2 energies.

Table VII. σ-Bond Compression Energies[a]

compd	Δr(C-X)	MP3/6-311++G**	ΔE
CH$_3$BH$_2$	0.1759	-65.720 29	12.8
CH$_3$CH$_3$	0.1900	-79.574 59	18.5
CH$_3$NH$_2$	0.1829	-95.588 59	19.2
CH$_3$OH	0.2024	-115.425 99	24.0
CH$_3$AlH$_2$	0.1662	-282.147 82	2.0
CH$_3$SiH$_3$	0.1672	-330.604 23	7.7
CH$_3$PH$_2$	0.1832	-381.829 96	10.2
CH$_3$SH	0.1987	-438.046 04	14.2

[a] Δr are given in Å, MP3 in hartrees, and ΔE in kcal/mol.

the σ charge remains relatively constant. This is another indication of the difference between the two rows, as has been discussed by Kutzelnigg.[8]

The covalent bond orders also may be derived from the results of this analysis,[12] are given in Table IX, and again are separated into the σ and π components. The C—X covalent bond orders have a maximum value when the electronegativity difference is smallest, i.e. with X=C in the first row and with X=S in the second. In all cases, the total bond order is composed of approximately equal σ and π terms. With a carbonyl group, for which a dipolar resonance structure is commonly written: the
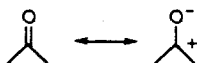
latter is commonly associated with the π system. However, the data show that the σ-bond is polarized about the same as the π-bond. This is true for all of the compounds that have a significant difference in electronegativity.

Table VIII. Atom and Group Charges

	C			X		
compd	charge	π charge	σ charge	charge	π charge	σ charge
HB=CH$_2$	-1.337	-0.494	-0.843	1.969	0.657	1.312
H$_2$C=CH$_2$	0.017	0.065	-0.048	0.017	0.065	-0.048
HN=CH$_2$	0.964	0.409	0.555	-1.307	-0.346	-0.961
O=CH$_2$	1.248	0.579	0.669	-1.240	-0.549	-0.691
HAl=CH$_2$	-1.422	-0.610	-0.812	2.207	0.768	1.439
H$_2$Si=CH$_2$	-1.263	-0.411	-0.852	2.731	0.631	2.100
HP=CH$_2$	-0.993	-0.137	-0.856	1.588	0.274	1.314
S=CH$_2$	-0.621	0.125	-0.746	0.521	-0.078	0.599

	CH$_2$			XH$_n$		
compd	charge	π charge	σ charge	charge	π charge	σ charge
HB=CH$_2$	-1.281	-0.576	-0.705	1.283	0.577	0.706
H$_2$C=CH$_2$	0.000	0.000	0.000	0.000	0.000	0.000
HN=CH$_2$	0.951	0.363	0.588	-0.951	-0.363	-0.588
O=CH$_2$	1.240	0.549	0.691	-1.240	-0.549	-0.691
HAl=CH$_2$	-1.430	-0.718	-0.712	1.430	0.718	0.712
H$_2$Si=CH$_2$	-1.227	-0.498	-0.729	1.227	0.498	0.729
HP=CH$_2$	-0.932	-0.202	-0.720	0.933	0.202	0.720
S=CH$_2$	-0.522	0.078	-0.600	0.521	-0.078	0.599

Table IX. Covalent Bond Orders, 6-311++G**

		SCF			MP2		
compd	bond	bond order	σ	π	bond order	σ	π
HB=CH$_2$	B—C	1.034	0.520	0.513	1.114	0.572	0.543
H$_2$C=CH$_2$	C—C	1.919	1.043	0.875	1.886	1.052	0.833
HN=CH$_2$	N—C	1.625	0.830	0.796	1.672	0.880	0.792
O=CH$_2$	O—C	1.407	0.754	0.652	1.488	0.795	0.693
HCl=CH$_2$	Al—C	0.887	0.514	0.373	0.985	0.560	0.425
H$_2$Si=CH$_2$	Si—C	1.036	0.516	0.520	1.100	0.551	0.550
HP=CH$_2$	P—C	1.548	0.720	0.827	1.545	0.760	0.785
S=CH$_2$	S—C	2.061	1.117	0.943	2.012	1.124	0.888
H$_2$B—CH$_3$	B—C	0.488			0.524		
H$_3$C—CH$_3$	C—C	1.021			1.000		
H$_2$N—CH$_3$	N—C	0.954			0.980		
HO—CH$_3$	O—C	0.837			0.873		
H$_2$Al—CH$_3$	Al—C	0.383			0.399		
H$_3$Si—CH$_3$	Si—C	0.454			0.484		
H$_2$P—CH$_3$	P—C	0.790			0.816		
HS—CH$_3$	S—C	1.098			1.092		

7. Methyl Substitution

A series of methyl-substituted derivatives of the heteroethenes was studied via HF/6-31G* geometry optimizations, followed by MP2/6-311++G** and MP3/6-311++G** energy calcu-

Table X. Energies of Methyl-Substituted Alkenes Calculated at HF/6-31G* Geometries[a]

compd	MP2/6-311++G**	MP3/6-311++G**	ZPE	ΔH_f(298 K)[b]	ΔH_f(0 K)
$CH_2=CH-CH_3$	−117.549 83	−117.582 49	47.8	4.8 ± 0.2	8.4 ± 0.2
$CH_3-CH_2-CH_3$	−118.770 86	−118.811 12	61.9	−25.0 ± 0.1	−19.7 ± 0.1
$CH_2=CH-NH_2$	−133.583 29	−133.607 17	41.6		
E-$CH_3CH=NH$	−133.589 92	−133.613 89	41.4		
Z-$CH_3CH=NH$	−133.588 33	−133.612 49	41.4		
$CH_3CH_2NH_2$	−134.796 38	−134.828 88	55.8	−11.3 ± 0.2	
$CH_3-N=CH_2$	−133.574 32	−133.598 29	41.2		
CH_3NHCH_3	−134.782 84	−134.815 51	55.7	−4.4 ± 0.2	
$CH_3CH=O$	−153.454 96	−153.469 13	33.6	−39.7 ± 0.1	−37.2 ± 0.1
$H_2C=CHOH$	−153.435 99	−153.452 48	34.2	−29.8 ± 2.0[c]	−27.1 ± 2.0
CH_3CH_2OH	−154.650 87	−154.675 90	48.2	−56.2 ± 0.1	−52.0 ± 0.1
$CH_2=CH-SiH_3$	−368.554 15	−368.591 11	40.3		
$CH_3-CH=SiH_2$	−368.526 27	−368.561 02	41.5		
$CH_3-CH_2-SiH_3$	−369.775 25	−369.819 66	53.9		
$CH_3-SiH=CH_2$	−368.540 88	−368.576 35	41.7		
$CH_3-SiH_2-CH_3$	−369.793 19	−369.837 64	53.9		
C_1-$CH_2=CH-PH_2$	−419.787 03	−419.822 47	36.2		
C_s-$CH_2=CH-PH_2$	−419.788 31	−419.823 62	36.3		
E-$CH_3-CH=PH$	−419.794 91	−419.828 29	37.6		
Z-$CH_3-CH=PH$	−419.795 08	−419.828 51	37.6		
$CH_3-CH_2-PH_2$	−421.010 46	−421.053 34	50.2		
$CH_3-P=CH_2$	−419.797 69	−419.831 35	37.9		
$CH_3-PH-CH_3$	−421.015 81	−421.058 39	50.4		
$CH_3CH=S$	−476.025 05	−476.053 49	32.3		
$H_2C=CHSH$	−476.018 04	−476.048 84	31.0		
CH_3CH_2SH	−477.210 16	−477.276 92	45.1	−11.1 ± 0.2	
CH_3-CH_3	−79.572 76	−79.603 80	44.6	−20.0 ± 0.1	
$CH_2=CH_2$	−78.339 98	−78.371 27	30.7	12.5 ± 0.1	
$CH_2=NH$	−94.355 99	−94.397 36	24.3		
$CH_2=O$	−114.188 78	−114.249 52	16.3		
$CH_2=SiH_2$	−329.306 84	−329.354 91	24.2		
$CH_2=PH$	−380.570 16	−380.617 37	20.3		
$CH_2=S$	−436.790 66	−436.837 37	15.0		

[a] Frozen core calculations. [b] Reference 14. [c] Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1982**, *104*, 2648.

Table XI. Energies (kcal/mol) of Transferring Hydrogens from Ethane to a Double Bond, 0 K

compd	MP2/6-311++G**	MP3/6-311++G**	obs
$CH_3-CH=CH_2$	2.9	2.6	3.1 ± 0.3
$CH_3CH=NH$	12.3	11.5	
$CH_3-CH=O$	19.2	16.9	16.4 ± 0.3
$CH_3-CH=SiH_2$	−16.3	−17.9	
$CH_3-CH=PH$	4.9	3.5	
$CH_3-CH=S$	6.8	4.6	
$CH_3-N=CH_2$	11.1	10.2	
$CH_3-SiH=CH_2$	−18.6	−19.7	
$CH_3-P=CH_2$	3.1	2.0	
$CH_2=CH-NH_2$	8.0	7.1	
$CH_2=CH-OH$	6.6	5.9	6.3 ± 2.0
$CH_2=CH-SiH_3$	2.3	2.2	
$CH_2=CH-PH_2$	1.9	1.7	
$CH_2=CH-SH$	3.7	3.0	

Table XII. Energies (kcal/mol) of Methyl Transfer Reactions from Propane, 0 K

X	MP2/6-311++G**	MP3/6-311++G**	obs
(a) $H_2C=X + CH_3CH_2CH_3 \rightarrow CH_3HC=X + CH_3CH_3$			
CH_2	−2.9	−2.6	−3.1 ± 0.3
NH_2	−6.4	−6.0	
O	−7.8	−7.7	−6.3 ± 1.0
SiH_2	0.2	0.8	
PH	−3.1	−2.3	
S	−6.4	−5.5	
(b) $H_2C=XH + CH_3CH_2CH_3 \rightarrow H_2C=XCH_3 + CH_3CH_3$			
CH	−2.9	−2.6	−3.1 ± 0.3
N	+3.2	+3.6	
SiH	−8.8	−8.7	
P	−4.6	−3.9	

lations. These levels of theory were shown to give hydrogen transfer energies in good agreement with the much more computationally demanding G2 energies. The energies are summarized in Table X and the hydrogen transfer reaction energies are given in Table XI. It can be seen that the MP2 and MP3 hydrogen transfer energies are close to each other and are in good accord with the few experimental data that are available. In the case of acetaldehyde, the MP3 value is the more satisfactory, but in view of the limited experimental data, it is difficult to know which is generally the more satisfactory. The general trends with substitution are similar to those for the unsubstituted compounds.

Our main interest in examining these compounds was to see the effect of methyl substitution. Therefore, we have calculated the energies involved in transferring a methyl group from propane to the parent compounds. The data are shown in Table XII. When the methyl is attached to the methylene group, the stabilization increases with increasing electronegativity of X both for the first- and second-row substituents. The increased methyl-

stabilization effect with increasing electronegativity of X is well established experimentally in comparisons of alkenes and carbonyl compounds.[25]

The opposite effect was seen when the methyl group was attached to X. Here, increasing electronegativity led to less stabilization, and when X = N, it led to destabilization. This effect is interesting since the bond length of Me–X compounds increases with increasing electronegativity difference. Here, the trend is in the opposite direction. This may be associated with the remarkable ability of hydrogen to donate charge density to electronegative atoms (and accept charge density from electropositive atoms). A methyl group is less able to transfer charge than is a hydrogen, and thus an electronegative atom may be

(25) Wiberg, K. B.; Crocker, L. S.; Morgan, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 3447.

(26) Harmony, M. D.; Laurie, V. N.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619.

(27) Kroto, H. W.; Nixon, J. F.; Ohno, K. *J. Mol. Spectrosc.* **1981**, *90*, 367.

(28) Cox, A. P.; Hubbard, S. D.; Kato, H. *J. Mol. Spectrosc.* **1982**, *93*, 196.

better stabilized by a hydrogen substituent than a methyl substituent. These energy changes are important for interpreting energy changes for the hydrogenation of compounds such as pyridine.

8. Conclusions

The energies of C—X and C=X compounds are well described by G2 theoretical calculations. The C-X bond dissociation energies also are well reproduced. Using these data, the π-bond energies have been estimated and were found to decrease in the order =O > =NH > =CH$_2$ > =SH > =BH > =SiH$_2$ > =AlH. The C=Al π-bond is calculated to be remarkably weak. Hydrogenation energies are well reproduced by the G2 calculations, and hydrogen transfer reactions were reproduced by both G2 and the less computationally intensive MP2 and MP3/6-311++G**//MP2/6-31G* theoretical level. Hydrogen transfer energies for methyl substituted derivatives were calculated at the same levels, and gave reaction energies that agreed well with the available experimental data. In general, the MP2 relative energies were somewhat more satisfactory than MP3 for a given basis set. It was found that when the methyl was attached to the methylene carbon, the stabilization of the double bond increases with increasing electronegativity of X. The opposite trend was found when the methyl was substituted at the X atom.

An analysis of the charge density distribution found that both the σ and π bond orders were largest with X=CH$_2$ in the first row, and with X=S in the second row, corresponding to the minimum difference in electronegativity. With a C=O group, both the σ and π bond orders were reduced as a result of the difference in electronegativity.

Supplementary Material Available: Tables of MP2/6-31G* energies and of atom and bond properties (7 pages). Ordering information is given on any current masthead page.