Relation between singlet–triplet gaps and bond energies. J Phys Chem

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shortened (strengthened). The parenthetical equivalents are justified because of the well-established correlation between bond length and bond strength. Indeed, the lower interaction energy for the H_2O proton acceptor case (II) can be rationalized by the shortened SiO bond.

Figure 2 shows deformation electron density maps for the optimized silanol–H_2O structures displayed in Figure 1. The peak in the electron density of the SiO bond in silanol is shifted toward the oxygen and toward the inside of the SiOH angle, joining the charge density of the OH bond to form a continuum of density around the inside of the SiOH angle. This feature is also present in silanol with adsorbed H_2O molecules. Although the bond length changes induced upon adsorption are significant, the corresponding changes in electron density are not as marked. The second positive contour in the electron density region within the SiOH angle of the deformation density maps best shows the change in electron density. The contour joins between OH and SiO when the SiO bond shortens and separates when the SiO bond lengthens.

To examine the structure and energetics of two water molecules simultaneously adsorbed on an isolated silanol group, we have optimized the geometry (within C_s symmetry) of a $H_3Si(OH)\cdot 2H_2O$ complex with the waters in the proton donor and acceptor positions, using the 6-31G* basis. Figure 1D summarizes the final optimized geometry for $H_3Si(OH)\cdot 2H_2O$. Whereas for $H_3Si(O-H)\cdot OH_2$ (II) the plane of the water molecule is perpendicular to the mirror plane of the whole complex, for $H_3Si(OH)\cdot 2H_2O$ the proton acceptor H_2O is rotated into the mirror plane. Relative to the single water complexes, the water molecules are closer together, and the O⋯H distance between the water molecules is

consistent with a long hydrogen bond. This water–water interaction enhances the total energy of the whole complex, which explains the larger interaction energies for the second water molecule addition compared with the single adsorption.

In exploring the bond length variations upon adsorption of a second water molecule, comparisons can be made with the single water complexes and with silanol without water. For both comparisons (see Figure 1), the bond length variations follow the empirical rules stated previously. The net bond length changes for the double water adsorption are approximately the combined changes for the two single water complexes considered individually. The SiO bond is slightly shortened by 0.012 Å and the OH bond is slightly lengthened by 0.037 Å.

Our calculations corroborate empirical bond length variation rules,[14] which can be used to predict structural rearrangements upon adsorption for both the substrate and the adsorbed molecule. When more than one molecule is adsorbed, the effect on the substrate appears to be additive. Because our models of the adsorbent are so limited in extent, we expect that the induced bond length changes in the real substrates will diminish within closer range to the interaction site. For the geometry optimization calculations, the bond length variation rules also provide guidelines for efficiently constructing initial molecular geometries for the adsorbed complexes.

Relation between Singlet–Triplet Gaps and Bond Energies

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We propose that the dominant effect in bond energy trends of $CXYH_2$, $SiXYH_2$, and substituted olefins is the singlet–triplet energy splitting in CXY or SiXY. New predictions of singlet–triplet gaps in AXY (A = C, Si) molecules, heats of formation of substituted olefins, and Si–H bond strengths in substituted silanes are obtained.

The effects of substituents on bond energies can be quite dramatic. Thus, the C–C bond energy of ethylene (**1**) is 172 ±
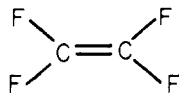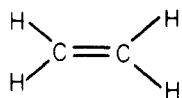

2 kcal/mol[1] whereas the C–C bond energy of tetrafluoroethylene (**2**) is only 76.3 ± 3 kcal/mol.[2] The point of this paper will be to show that these dramatic changes can be understood in terms of changes in the energetics of the fragments (CH_2 vs. CF_2) within the assumption that the actual character of the C–C double bonds is rather similar. The GVB orbitals of the C–C double bond have the form in (**3**) involving singly occupied σ and π orbitals on each
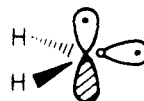

C spin-paired with a corresponding orbital on the other C.[3]

Unpairing the orbitals and separating the fragments leads then to
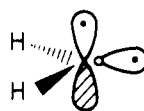
with each CXY fragment in the *triplet* state. However, depending upon the fragment, the ground state of CXY may be either the triplet ($\sigma\pi$) or the singlet state (σ^2).
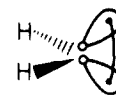
$$\sigma\pi \qquad\qquad \sigma^2$$

(1) Chupka, W. A.; Lifshitz, C. *J. Chem. Phys.* **1968**, *48*, 1109.
(2) Zmbov, K. F.; Uy, O. M.; Margrave, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 5090.
(3) Plots of GVB orbitals for ethylene may be found in Hay, P. J.; Hunt, W. J.; Goddard III, W. A. *J. Am. Chem. Soc.* **1972**, *94*, 8293.

[†] National Science Foundation Predoctoral Fellow, 1982–1985.
[‡] Contribution no. 7333.

Figure 1.

Figure 2.

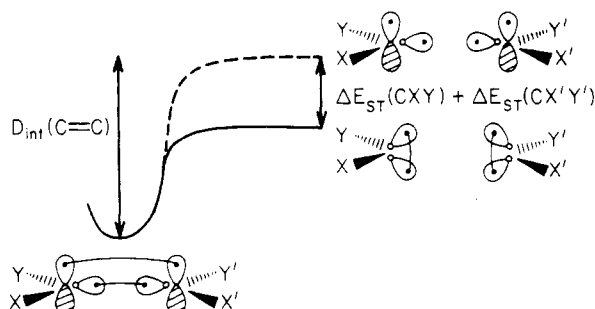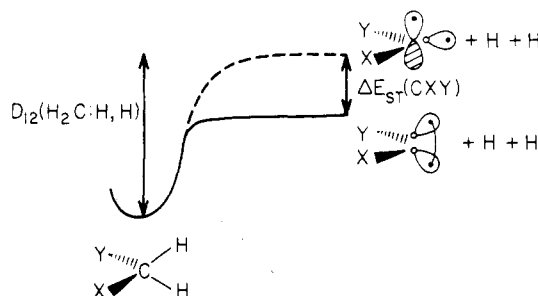Consider the simplest carbene, CH_2. It has a triplet $\sigma\pi$ ground state ($^3B_1$) with the σ^2 excited state ($^1A_1$) lying 9 kcal/mol higher.[4] Notice that while the $\sigma\pi$ ground state of CH_2 is set up to form covalent bonds, the σ^2 excited state cannot, since it has no open shell electrons. If we assume that the character of all C–C double bonds is similar at the equilibrium bond distance, a case in which the ground state of CXY is σ^2 would result in a bond energy decreased by just the sum of the σ^2 to $\sigma\pi$ excitation energies [$\Delta E_{ST}(CXY)$] as illustrated in Figure 1. Considering the intrinsic C–C bond energy to be $D_{int}(C=C) = 172 \pm 2$ kcal/mol (since ethylene dissociates to ground-state fragments), we obtain

$$D(XYC=CX'Y') =$$
$$D_{int}(C=C) - [\Delta E_{ST}(CXY) + \Delta E_{ST}(CX'Y')] \quad (1)$$

for the bond energy in any substituted olefin in which the CXY fragments have a σ^2 ground state. Hence for CXY = CX'Y' = CF_2, since $\Delta E_{ST} \sim 46.5$ kcal/mol,[5] we obtain

$$D(F_2C=CF_2) = 172 \pm 2 - 2(46.5) = 79 \pm 2 \text{ kcal/mol}^6$$

for the C–C bond energy in tetrafluoroethylene, in good agreement with the measured bond energy of 76.3 ± 3 kcal/mol. There are of course other factors (e.g. electronegativities, steric bulk, etc.) that can change with substitution; however, we will show that this $\sigma\pi-\sigma^2$ excitation energy of the CXY products dominates the changes in the C=C bond energy.[7]

An analogous effect occurs in the bond energies of saturated hydrocarbons. Thus for CH_4 the sum of the first two C–H bond energies is

$$D_{12}(H_2C:H,H) = D_1(H_3C-H) + D_2(H_2C-H)$$

(4) (a) Leopold, D. G.; Murray, K. K.; Lineberger, W. C. *J. Chem. Phys.* **1984**, *81*, 1048. (b) Harding, L. B.; Goddard III, W. A. *Chem. Phys. Lett.* **1978**, *55*, 217.

(5) Bauschlicher, C. W., Jr.; Schaefer III, H. F.; Bagus, P. S. *J. Am. Chem. Soc.* **1977**, *99*, 7106.

(6) The uncertainty in this number is larger than the quoted value since we have not included any estimate for the uncertainty in the theoretical singlet–triplet splitting.

(7) In CXY systems with σ^2 ground states it is possible that the ground state of the doubly bonded olefin will have banana bonds rather than σ and π bonds. Thus for $H_2Si=SiH_2$, Horowitz and Goddard (*J. Am. Chem. Soc.*, to be submitted) showed that the banana bond description is 3.5 kcal/mol lower than the σ and π bond description for the simple GVB-PP wave function. However, with a full GVB-CI in the double bond, they find a difference of only 0.1 kcal/mol, indicating that our assumption of the $\sigma\pi$ description is valid. [R. P. Messmer (private communication) has also shown that C_2F_4 leads to a banana bond description at the GVB-PP level.]

as indicated schematically in Figure 2. We will argue that the sum of these two bond energies should be independent of substituent unless CXY has a σ^2 ground state. Indeed

$$D_{12}(H_2C:H,H) = 214.2 \pm 1.0 \text{ kcal/mol}^8$$

whereas

$$D_{12}(F_2C:H,H) = 168.0 \pm 1^9 = 214 - 46 \text{ kcal/mol}$$

is weaker by just the $\sigma^2-\sigma\pi$ excitation energy for CF_2! Thus for CXY systems with a σ^2 ground state we expect

$$D_{12}(XYC:H,H) = D_1(XYHC-H) + D_2(XYC-H) \approx$$
$$D_{12}(H_2C:H,H) - \Delta E_{ST}(CXY) \quad (2)$$

for the sum of the first two C–H bond strengths in substituted methanes.

What are the physical effects which result in carbenes (or silylenes) with singlet σ^2 ground states? Two electronic factors contribute to the formation of σ^2 CXY:[10]

(a) If X and/or Y are electronegative, they will prefer to form ionic bonds. Then the C–X and C–Y bonds will utilize C p orbitals since they have the lowest valence ionization potential, leaving more s character for nonbonding C σ orbital.

(b) If X and/or Y have pπ lone pairs (which can donate electron density into the C pπ orbital), this disfavors pπ occupation by one of the C valence electrons.

Both contributions lead to relative stabilization of the σ nonbonding orbital, resulting in a singlet ground state. Thus CXY systems where X and/or Y = F, Cl, OR, NRR', etc. are expected to have singlet ground states.

For silylenes, SiXY, the much larger s–p energy difference for second row atoms greatly favors the s^2p^2 state of Si and hence the σ^2 state of SiXY. Thus these systems are expected to have singlet ground states for the above substituents (and for X and/or Y = H, alkyl). [For carbon, the small s–p energy splitting renders sp^2 hybridization more accessible, resulting in a triplet ground state for CR_2 (R = H, alkyl).] Triplet ground states are also favored by aryl and bulky alkyl substituents (since the $\sigma\pi$ state favors a large bond angle whereas the σ^2 state prefers a small bond angle), as well as by electropositive moieties (more favorable electron donation into sp^2).

In general, then, for CXY (SiXY) with electronegative substituents such as F and Cl, the σ^2 ground state should manifest itself in weaker bonds of CXY to anything. Indeed, we can obtain a quantitative estimate for this bond weakening by assuming that two single σ bonds or one double bond should be weaker compared to the CH_2 case by just the energy cost to promote the ground-state singlet to the triplet necessary for bond formation.

Before examining trends in bond energies and their implications, we will test the basic assumption that the C=C and C–H intrinsic bond energies remain approximately constant even though the actual bond energies vary over a range of ~ 100 kcal/mol (see Table III). From the two dissociation processes in eq 1 and 2, we obtain the following relation

$$[\Delta H_f^\circ_{298}(XYC=CX'Y') - \Delta H_f^\circ_{298}(CXYH_2) -$$
$$\Delta H_f^\circ_{298}(CX'Y'H_2)] = [2D_{12}(H_2C:H,H) -$$
$$D^\circ_{298}(H_2C=CH_2) - 4\Delta H_f^\circ_{298}(H)] =$$
$$[\Delta H_f^\circ_{298}(C_2H_4) - 2[\Delta H_f^\circ_{298}(CH_4)]] \quad (3)$$

where $D_{12}(H_2C:H,H)$ and $D^\circ_{298}(H_2C=CH_2)$ are taken to be intrinsic C–H and C–C bond energies. Notice that the right-hand side is independent of X and Y, suggesting that the difference in heats of formation on the left-hand side of (3) [$\Delta(\Delta H_f^\circ_{298})$] should be a constant equal to $428.4 - 172.0 - 208.4^{8c} = 48.0$

(8) Data for (a) $\Delta H_f^\circ_{298}(CH_2)$ is from ref 1; (b) $\Delta H_f^\circ_{298}(CH_4)$ is from Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695; (c) $D^\circ_{298}(H-H)$ is from McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(9) Data for (a) $\Delta H_f^\circ_{298}(CF_2)$ is from Berman, D. W.; Bomse, D. S.; Beauchamp, J. L. *Int. J. Mass. Spectrom. Ion Phys.* **1981**, *39*, 263; (b) $\Delta H_f^\circ_{298}(CF_2H_2)$ is from ref 6b.

(10) Goddard III, W. A.; Harding, L. B. *Annu. Rev. Phys. Chem.* **1978**, *29*, 363.

TABLE I: Test of the Validity of Eq 3, $\Delta(\Delta H_f°_{298}) = \Delta H_f°_{298}(CXY=CX'Y') - \Delta H_f°_{298}(CXYH_2) - \Delta H_f°_{298}(CX'Y'H_2) = 48.0$ kcal/mol, for the Ideal Limit[a]

CXY	CX'Y'	$\Delta H_f°_{298}(CXY=CX'Y')$	$\Delta H_f°_{298}(CXYH_2)$	$\Delta H_f°_{298}(CX'Y'H_2)$	$\Delta(\Delta H_f°_{298})$
CH_2	CH_2	$+12^b$	-18.0^b	-18.0	$+48.0$
CF_2	CF_2	-164.7 ± 5^c	-108.0^b	-108.0	$+51.3 \pm 5$
		(-168.0)			
CCl_2	CCl_2	-2.7 ± 2.0^d	-22.8 ± 0.2^e	-22.8 ± 0.2	$+42.9 \pm 2.4$
		$(+2.4)$			
CH_2	CF_2	-82.0^b	-18.0	-108.0	$+44.0$
		(-78.0)			
$\cdot CH_2$	CCl_2	$+0.61 \pm 0.36^d$	-18.0	-22.8 ± 0.2	$+41.4 \pm 0.56$
		$(+7.2)$			
CH_2	CHF	-33.2^b	-18.0	-56	$+40.8$
		(-26.0)			
CH_2	$CHCl$	$+8.6 \pm 0.3^d$	-18.0	-19.5	$+46.1 \pm 0.3$
		$(+10.5)$			
E-CHF	CHF	-70.0^b	-56^b	-56	$+42.0$
		(-64.0)			
E-CHCl	CHCl	$+1.2 \pm 2.1^d$	-19.5^b	-19.5	$+40.2 \pm 2.1$
		$(+9.0)$			
CF_2	CHF	-117^b	-108.0	-56	$+47.0$
		(-116.0)			
CF_2	CFCl	-125 ± 4^d	-108.0	-62.6 ± 3^f	$+45.6 \pm 7$
		(-122.6)			

^{a} All values in kcal/mol. ^{b} Reference 8b. ^{c} Derived from $D°_{298}(F_2C=CF_2)$ and $\Delta H_f°_{298}(CF_2)$ from ref 2 and 9a, respectively. ^{d} Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970. ^{e} Rodgers, A. S.; Chao, J.; Wilhoit, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1974**, *3*, 117. ^{f} JANAF Thermochemical Tables, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1971**, *No. 37.*

TABLE II: Predicted CXY Singlet–Triplet Gaps from Relative A–H Bond Strengths of $AXYH_2$ Molecules (kcal/mol)

			ΔE_{ST}^b	
$AXYH_2$	$D_{12}(XYA: H, H)^a$	AXY	this work	calcd
CH_4	214.2 ± 1	CH_2		-9.0^c
CF_2H_2	168.0 ± 1	CF_2	46.2 ± 2	46.5^d
CCl_2H_2	181.9 ± 2	CCl_2	32.3 ± 3	$13.5,^d 25.9^e$
$CFClH_2$	174.8 ± 3	CFCl	39.4 ± 4	
CFH_3	186.2 ± 3	CHF	28.0 ± 4	9.2^d
$CClH_3$	194.7 ± 5	CHCl	19.5 ± 6	1.6^d
SiH_4	180.8 ± 3.5^f	$^3SiH_2$		16.8^g
SiF_2H_2	107.3 ± 3.5^h	SiF_2		73.5^g
$SiCl_2H_2$	138.1 ± 3.6^i	$SiCl_2$	42.7 ± 7.1	51.5 ± 6^j
$SiFH_3$	143.1 ± 3.5^h	SiHF		37.7^g
$SiClH_3$	153.4 ± 6^k	SiHCl	27.4 ± 9.5	

$^a D_{12}(XYA: H, H)$ = the sum of the first two A–H bond energies in $AXYH_2$ at 298 K. $^b \Delta E_{ST} = E_{triplet} - E_{singlet}$ for AXY listed in the adjacent column. ^{c} Reference 4 (experimental work). ^{d} Reference 5. ^{e} Reference 12. ^{f} Derived from ref 11a and 11b. ^{g} Reference 13. ^{h} In these cases the theoretical ΔE_{ST} was combined with eq 2 for Si and used to predict $D_{12}(XYSi: H, H)$. ^{i} Derived from ref 11a [$\Delta H_f°_{298}$-($SiCl_2H_2$)] and from Farber, M.; Srivastava, R. D. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1672 [$\Delta H_f°_{298}(SiCl_2)$]. ^{j} Reference 11a. ^{k} Derived from ref 11a.

TABLE III: Predicted CXY Singlet–Triplet Gaps from Relative C=C Bond Strengths of Substituted Olefins (kcal/mol)

			ΔE_{ST}^a	
olefin	$D_f°_{298}(C=C)$	CXY	this work	calcd
$CH_2=CH_2$	172 ± 2	CH_2		-9.0^b
$CF_2=CF_2$	76.3 ± 3	CF_2	47.9 ± 2.5	46.5^c
$CCl_2=CCl_2$	112.5 ± 4	CCl_2	29.8 ± 3	$13.5,^c 25.9^d$
$CH_2=CF_2$	129.8 ± 2	CF_2	42.2 ± 4	46.5
$CH_2=CCl_2$	146.3 ± 3.4	CCl_2	25.7 ± 5.4	$13.5, 25.9$
$CH_2=CHF$	151.2 ± 4	CHF	20.8 ± 6	9.2^c
$CH_2=CHCl$	154.4 ± 6.3	CHCl	17.6 ± 8.3	1.6^c
E-CHF=CHF	122.0 ± 6	CHF	25.0 ± 4	9.2
E-CHCl=CHCl	140.8 ± 12.1	CHCl	15.6 ± 7	1.6
$CF_2=CHF$	98.8 ± 4	CHF	26.7 ± 6^e	9.2
$CF_2=CFCl$	88.8 ± 5	CFCl	36.7 ± 7^e	

$^a \Delta E_{ST} = E_{triplet} - E_{singlet}$ for CXY listed in the adjacent column. ^{b} Reference 4 (experimental work). ^{c} Reference 5. ^{d} Reference 12. ^{e} Derived by assuming $\Delta E_{ST}(CF_2) = 46.5$ kcal/mol.

TABLE IV: Additional Heats of Formation Used in This Study (kcal/mol)

CXY	$\Delta H_f°_{298}(CXY)$	$SiXY/SiXYH_2$	$\Delta H_f°_{298}$-($SiXY/SiX-YH_2$)
CH_2	92 ± 1^a	$^3SiH_2$	$+84.8 \pm 3^f$
CF_2	-44.2 ± 1^b	$SiCl_2$	-40.6 ± 0.6^g
CCl_2	$+54.9 \pm 2^c$	SiHCl	$+17.0 \pm 3^f$
CFCl	$+8.0^d$	SiH_4	$+8.2 \pm 0.5^h$
CHF	$+26 \pm 3^e$	$SiCl_2H_2$	-74.5 ± 3^f
CHCl	$+71 \pm 5^e$	$SiClH_3$	-32.2 ± 3^f

^{a} Reference 1. ^{b} Reference 9a. ^{c} Rademann, K.; Jochims, H.-W.; Baumgärtel, H. *J. Phys. Chem.* **1985**, *89*, 3459. ^{d} *GMELIN Handbuch der Anorganischen Chemie*, Kohlenstoff, Teil D2, System No. 14; Springer-Verlag: Berlin, 1974. ^{e} Lias, S. G.; Karpas, Z.; Liebman, J. F. *J. Am. Chem. Soc.*, in press. ^{f} Reference 11a. ^{g} Farber, M.; Srivastava, R. D. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1672. ^{h} Reference 11b.

kcal/mol. This equation eliminates heats of formation and excitation energies of CXY, cancelling out substituent effects. Examination of Table I reveals that $\Delta(\Delta H_f°_{298})$ is very nearly constant, lending credence to the assumption that C=C and C–H bonds have the same character and thus the same intrinsic bond energies independent of substitution. The values deviating most from 48.0 kcal/mol all have significant uncertainties in the olefin heats of formation. Thus by assuming (3) and using $\Delta(\Delta H_f°_{298})$ = 48.0 kcal/mol, we have estimated new values for $\Delta H_f°_{298}$-(XYC=CX'Y') listed in parentheses under the experimental values in Table I.

Given that the C=C and C–H intrinsic bond energies are essentially constant, we can utilize (1) and (2) to predict singlet–triplet energies for two very different bonding scenarios (two σ bonds to hydrogens vs. one σ and one π bond to carbon).

In Table II we display experimental values for $D_{12}(XYA:H, H)$ for a variety of substituted methanes and silanes. As the electronegativity of the substituent increases, the A–H bond energy decreases (going from Cl to F), and as two hydrogens are replaced by F or Cl, the bond energy decreases further. Equation 2 suggests

that $\Delta E_{ST}(CXY) = D_{12}(H_2C:H,H) - D_{12}(XYC:H,H)$ for the methane series and $\Delta E_{ST}(SiXY) = D_{12}(H_2Si:H,H) - D_{12}$-(XYSi:H,H) for the silane series, where

$D_{12}(H_2Si:H,H) =$

$\Delta H_f°_{298}(^3SiH_2) - \Delta H_f°_{298}(SiH_4) + D°_{298}(H-H) =$

$84.8\ (\pm 3) - 8.2\ (\pm\ 0.5) + 104.2 = 180.8\ (\pm 3.5)$ kcal/mol[11]

This leads to the predicted singlet–triplet gaps in the next to last column of Table II. As expected, increasingly electronegative X and Y lead to larger singlet–triplet gaps.

Analogous predictions are given in Table III where we show the effects of electronegative substituents on C=C (experimental) bond energies. Equation 1 allows another set of singlet–triplet gaps to be predicted. A wide variety of systems now reveals internally consistent predictions for these splittings. For instance, using (1) and (2) lead to

$$\Delta E_{ST}(CF_2) = 46.2 \pm 2, \ 47.9 \pm 2.5, \ 42.2 \pm 4 \ \text{kcal/mol}$$

all in good agreement with the theoretical value of 46.5 kcal/mol.[5] On the other hand, (1) and (2) result in

$$\Delta E_{ST}(CCl_2) = 32.3 \pm 3, \ 29.8 \pm 3, \ 25.7 \pm 5.4 \ \text{kcal/mol}$$

whereas the theoretical value is $\Delta E_{ST}(CCl_2) = 13.5$ kcal/mol.[5] Other predictions are

$$\Delta E_{ST}(CHF) =$$
$$28.0 \pm 4, \ 20.8 \pm 6, \ 25.0 \pm 4, \ 26.7 \pm 6 \ \text{kcal/mol}$$

compared to an ab initio value of $\Delta E_{ST}(CHF) = 9.2$ kcal/mol.[5] Also predicted is

$$\Delta E_{ST}(CHCl) = 19.5 \pm 6, \ 17.6 \pm 8.3, \ 15.6 \pm 7 \ \text{kcal/mol}$$

compared to a theoretical value of $\Delta E_{ST}(CHCl) = 1.8$ kcal/mol.[5] We also predict

$$\Delta E_{ST}(CFCl) = 39.4 \pm 4 \quad \text{and} \quad 36.7 \pm 7 \ \text{kcal/mol}$$

which has not been previously estimated.

We are concerned that there is a difference between our predicted values for the ΔE_{ST} and some of the previously calculated values. However, these calculations were performed at a very simple level (Hartree–Fock for the $\sigma\pi$ state and GVB(1/2)PP for the σ^2 state) and we suspect that correlation effects may play an important role in obtaining ΔE_{ST}. In order to test this suspicion, we carried out ab initio GVB-CI calculations for CCl_2, the case for which values for $\Delta E_{ST}(CCl_2)$ show the greatest discrepancy ($\sim$15–20 kcal/mol) between the previous theoretical calculations and our present estimates. These new GVB-CI calculations lead to a $\Delta E_{ST}(CCl_2) = 25.9$ kcal/mol, in excellent agreement with our empirical estimates (29 $\pm$ 3 kcal/mol). The dominant correlations, which were not included in the previous theoretical work [$\Delta E_{ST}(CCl_2) = 13.5$ kcal/mol],[5] but which were found to be important in our CI calculations, were π donation from Cl $p\pi$ orbitals to the empty C $p\pi$ orbital with simultaneous σ electron

transfer to the chlorines from the carbon (with excitations to virtual orbitals to allow the orbital shape readjustments needed to properly describe simultaneous electron transfer in the σ and π frameworks). These correlations stabilize the singlet state more than the triplet state of halocarbenes and hence inclusion of these charge-transfer configurations (requiring up to selected sextuple excitations) is essential for an accurate description of the ΔE_{ST} for halocarbenes.[12]

The silane thermochemical data offer further new predictions of ΔE_{ST} and Si–H bond energies. $\Delta E_{ST}(SiCl_2) = 42.7 \pm 7.1$ kcal/mol is in reasonable agreement with a previous theoretical value of 51.5 ± 6 kcal/mol.[11a] Experimental data allow the prediction of the previously unknown $\Delta E_{ST}(SiHCl) = 27.4 \pm 9.5$ kcal/mol, while reliable theoretical calculations[13] of $\Delta E_{ST}(SiXY)$ allow the predictions of two previously unreported $D_{12}(XYSi{:}H, H) = 143.1 \pm 3.5$ and 107.3 ± 3.5 kcal/mol for X = H, Y = F, and X = Y = F, respectively.

In conclusion, we suggest that the dominant factor in determining bond energy trends in molecules involving CXY fragments is the singlet–triplet energy splitting. In many cases the thermochemical data[14] are incomplete or controversial so that relations such as (1)–(3) can provide useful estimates of unknown data. The inverse relation of bond strength to singlet–triplet splitting has been shown to be quantitatively accurate and internally consistent for a variety of systems. The fact that many of these values for ΔE_{ST} are significantly different from those obtained from previous ab initio calculations suggests that more extensive basis sets and CI calculations are called for in these systems.[15]

(11) Values for (a) $\Delta H_f^\circ{}_{298}({}^3SiH_2)$ (shorthand for SiH_2, ${}^3B_1$) is from Ho, P.; Coltrin, M. E.; Binkley, J. S.; Melius, C. F. *J. Phys. Chem.* **1985**, *89*, 4647; (b) $\Delta H_f^\circ{}_{298}(SiH_4)$ is from JANAF Thermochemical Tables *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1978** update in *J. Phys. Chem. Ref. Data* **1978**, *7*, 793–940.

(12) Carter, E. A.; Goddard III, W. A., to be submitted for publication.

(13) Colvin, M. E.; Grev. R. S.; Schaefer III, H. F.; Bicerano, J. *Chem. Phys. Lett.* **1983**, *99*, 399.

(14) Additional thermochemical data used in this work are displayed in Table IV.

(15) Subsequent to the submission of this Letter, it has been brought to our attention that recent HF*S*D-CI and GVB(1/2)PP*S*D-CI calculations by Scuseria et al.[16] on CHF and CHCl yielded revised values for ΔE_{ST} of 13.2 and 5.4 kcal/mol, respectively. These results are still in substantial disagreement with our estimates, presumably due to the lack of inclusion of important charge transfer configurations.

(16) Scuseria, G. E.; Durán, M.; Maclagan, R. G. A. R.; Schaefer III, H. F., to be submitted for publication.