

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 $172 \pm$



2 kcal/mol^1 whereas the C-C bond energy of tetrafluoroethylene (**2**) is only $76.3 \pm 3 \text{ kcal/mol}^2$. 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

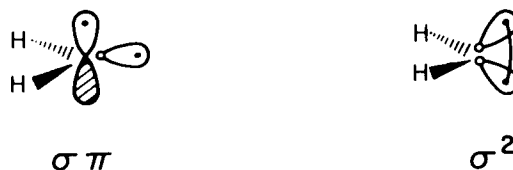


C spin-paired with a corresponding orbital on the other C.³

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).



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(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.

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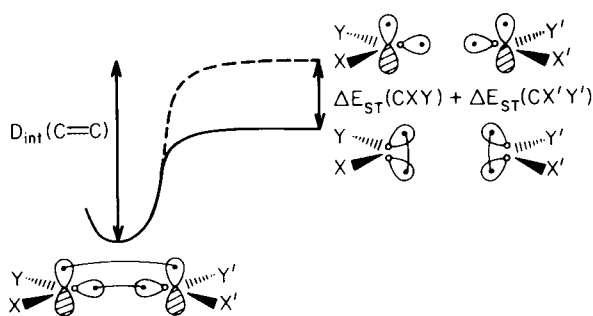


Figure 1.

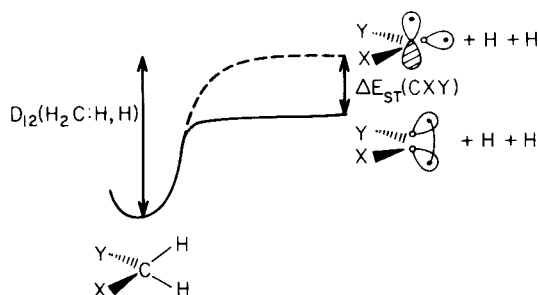


Figure 2.

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 [$\Delta E_{\text{ST}}(\text{CXY})$] as illustrated in Figure 1. Considering the intrinsic C-C bond energy to be $D_{\text{int}}(\text{C}=\text{C}) = 172 \pm 2$ kcal/mol (since ethylene dissociates to ground-state fragments), we obtain

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

for the bond energy in any substituted olefin in which the CXY fragments have a σ^2 ground state. Hence for $\text{CXY} = \text{CX}'\text{Y}' = \text{CF}_2$, since $\Delta E_{\text{ST}} \sim 46.5$ kcal/mol,⁵ we obtain

$$D(\text{F}_2\text{C}=\text{CF}_2) = 172 \pm 2 - 2(46.5) = 79 \pm 2 \text{ kcal/mol}^6$$

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 $\sigma\pi$ - σ^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

$$D_{12}(\text{H}_2\text{C}:\text{H},\text{H}) = D_1(\text{H}_3\text{C}-\text{H}) + D_2(\text{H}_2\text{C}-\text{H})$$

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

$$D_{12}(\text{H}_2\text{C}:\text{H},\text{H}) = 214.2 \pm 1.0 \text{ kcal/mol}^8$$

whereas

$$D_{12}(\text{F}_2\text{C}:\text{H},\text{H}) = 168.0 \pm 1^9 = 214 - 46 \text{ kcal/mol}$$

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

$$D_{12}(\text{XYC}:\text{H},\text{H}) = D_1(\text{XYHC}-\text{H}) + D_2(\text{XYC}-\text{H}) \approx D_{12}(\text{H}_2\text{C}:\text{H},\text{H}) - \Delta E_{\text{ST}}(\text{CXY}) \quad (2)$$

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 $p\pi$ lone pairs (which can donate electron density into the C $p\pi$ orbital), this disfavors $p\pi$ 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

$$[\Delta H_f^\circ{}_{298}(\text{XYC}=\text{CX}'\text{Y}') - \Delta H_f^\circ{}_{298}(\text{CXYH}_2) - \Delta H_f^\circ{}_{298}(\text{CX}'\text{Y}'\text{H}_2)] = [2D_{12}(\text{H}_2\text{C}:\text{H},\text{H}) - D^\circ{}_{298}(\text{H}_2\text{C}=\text{CH}_2) - 4\Delta H_f^\circ{}_{298}(\text{H})] = [\Delta H_f^\circ{}_{298}(\text{C}_2\text{H}_4) - 2[\Delta H_f^\circ{}_{298}(\text{CH}_4)]] \quad (3)$$

where $D_{12}(\text{H}_2\text{C}:\text{H},\text{H})$ and $D^\circ{}_{298}(\text{H}_2\text{C}=\text{CH}_2)$ 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 $428.4 - 172.0 - 208.4^{\text{sc}} = 48.0$

(8) Data for (a) $\Delta H_f^\circ{}_{298}(\text{CH}_2)$ is from ref 1; (b) $\Delta H_f^\circ{}_{298}(\text{CH}_4)$ is from Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695; (c) $D^\circ{}_{298}(\text{H}-\text{H})$ is from McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(9) Data for (a) $\Delta H_f^\circ{}_{298}(\text{CF}_2)$ is from Berman, D. W.; Bomse, D. S.; Beauchamp, J. L. *Int. J. Mass. Spectrom. Ion Phys.* **1981**, *39*, 263; (b) $\Delta H_f^\circ{}_{298}(\text{CF}_2\text{H}_2)$ is from ref 6b.

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(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 $\text{H}_2\text{Si}=\text{SiH}_2$, 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.]

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

CXY	CX'Y'	$\Delta H_f^\circ(CXY=CX'Y')$	$\Delta H_f^\circ(CXYH_2)$	$\Delta H_f^\circ(CX'Y'H_2)$	$\Delta(\Delta H_f^\circ)_{298}$
CH ₂	CH ₂	+12 ^b	-18.0 ^b	-18.0	+48.0
CF ₂	CF ₂	-164.7 ± 5 ^c (-168.0)	-108.0 ^b	-108.0	+51.3 ± 5
CCl ₂	CCl ₂	-2.7 ± 2.0 ^d (+2.4)	-22.8 ± 0.2 ^e	-22.8 ± 0.2	+42.9 ± 2.4
CH ₂	CF ₂	-82.0 ^b (-78.0)	-18.0	-108.0	+44.0
CH ₂	CCl ₂	+0.61 ± 0.36 ^d (+7.2)	-18.0	-22.8 ± 0.2	+41.4 ± 0.56
CH ₂	CHF	-33.2 ^b (-26.0)	-18.0	-56	+40.8
CH ₂	CHCl	+8.6 ± 0.3 ^d (+10.5)	-18.0	-19.5	+46.1 ± 0.3
E-CHF	CHF	-70.0 ^b (-64.0)	-56 ^b	-56	+42.0
E-CHCl	CHCl	+1.2 ± 2.1 ^d (+9.0)	-19.5 ^b	-19.5	+40.2 ± 2.1
CF ₂	CHF	-117 ^b (-116.0)	-108.0	-56	+47.0
CF ₂	CFCl	-125 ± 4 ^d (-122.6)	-108.0	-62.6 ± 3 ^f	+45.6 ± 7

^aAll values in kcal/mol. ^bReference 8b. ^cDerived from $D^\circ_{298}(F_2C=CF_2)$ and $\Delta H_f^\circ(CF_2)$ from ref 2 and 9a, respectively. ^dCox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970. ^eRodgers, A. S.; Chao, J.; Wilhoit, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1974**, *3*, 117. ^fJANAF 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 AX₂H₂ Molecules (kcal/mol)

AX ₂ H ₂	$D_{12}(XYA: H, H)^a$	AXY	ΔE_{ST}^b	
			this work	calcd
CH ₄	214.2 ± 1	CH ₂		-9.0 ^c
CF ₂ H ₂	168.0 ± 1	CF ₂	46.2 ± 2	46.5 ^d
CCl ₂ H 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	³ SiH ₂		16.8 ^g
SiF ₂ H ₂	107.3 ± 3.5 ^h	SiF ₂		73.5 ^g
SiCl ₂ H 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 AX₂H₂ at 298 K. ^b $\Delta E_{ST} = E_{\text{triplet}} - E_{\text{singlet}}$ for AXY listed in the adjacent column. ^cReference 4 (experimental work). ^dReference 5. ^eReference 12. ^fDerived from ref 11a and 11b. ^gReference 13. ^hIn these cases the theoretical ΔE_{ST} was combined with eq 2 for Si and used to predict $D_{12}(XYSi: H, H)$. ⁱDerived from ref 11a [$\Delta H_f^\circ(CSiCl_2H_2)$] and from Farber, M.; Srivastava, R. D. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1672 [$\Delta H_f^\circ(SiCl_2)$]. ^jReference 11a. ^kDerived from ref 11a.

kcal/mol. This equation eliminates heats of formation and excitation energies of CXY, cancelling out substituent effects. Examination of Table I reveals that $\Delta(\Delta H_f^\circ)_{298}$ 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 $\Delta(\Delta H_f^\circ)_{298} = 48.0$ kcal/mol, we have estimated new values for $\Delta H_f^\circ(CXY=CX'Y')$ 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

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

olefin	$D_f^\circ(C=C)$	CXY	ΔE_{ST}^a	
			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 $\Delta E_{ST} = E_{\text{triplet}} - E_{\text{singlet}}$ for CXY listed in the adjacent column. ^bReference 4 (experimental work). ^cReference 5. ^dReference 12. ^eDerived by assuming $\Delta E_{ST}(CF_2) = 46.5$ kcal/mol.

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

CXY	$\Delta H_f^\circ(CXY)$	SiXY/SiXYH ₂	ΔH_f° (SiXY/SiXYH ₂)
CH ₂	92 ± 1 ^a	³ SiH ₂	+84.8 ± 3 ^f
CF ₂	-44.2 ± 1 ^b	SiCl ₂	-40.6 ± 0.6 ^e
CCl ₂	+54.9 ± 2 ^c	SiHCl	+17.0 ± 3 ^f
CFCl	+8.0 ^d	SiH ₄	+8.2 ± 0.5 ^h
CHF	+26 ± 3 ^e	SiCl ₂ H ₂	-74.5 ± 3 ^f
CHCl	+71 ± 5 ^e	SiClH ₃	-32.2 ± 3 ^f

^aReference 1. ^bReference 9a. ^cRademann, K.; Jochims, H.-W.; Baumgärtel, H. *J. Phys. Chem.* **1985**, *89*, 3459. ^d*GMEILIN Handbuch der Anorganischen Chemie*, Kohlenstoff, Teil D2, System No. 14; Springer-Verlag: Berlin, 1974. ^eLias, S. G.; Karpas, Z.; Liebman, J. F. *J. Am. Chem. Soc.*, in press. ^fReference 11a. ^gFarber, M.; Srivastava, R. D. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1672. ^hReference 11b.

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

$$D_{12}(H_2Si:H,H) = \Delta H_f^\circ(^3SiH_2) - \Delta H_f^\circ(SiH_4) + D^\circ_{298}(H-H) = 84.8 (\pm 3) - 8.2 (\pm 0.5) + 104.2 = 180.8 (\pm 3.5) \text{ kcal/mol}^{11}$$

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

$$\Delta E_{ST}(\text{CF}_2) = 46.2 \pm 2, 47.9 \pm 2.5, 42.2 \pm 4 \text{ kcal/mol}$$

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

$$\Delta E_{ST}(\text{CCl}_2) = 32.3 \pm 3, 29.8 \pm 3, 25.7 \pm 5.4 \text{ kcal/mol}$$

whereas the theoretical value is $\Delta E_{ST}(\text{CCl}_2) = 13.5 \text{ kcal/mol}$.⁵ Other predictions are

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

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

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

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

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

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 $\Delta E_{ST}(\text{CCl}_2)$ show the greatest discrepancy (~ 15 – 20 kcal/mol) between the previous theoretical calculations and our present estimates. These new GVB-CI calculations lead to a $\Delta E_{ST}(\text{CCl}_2) = 25.9 \text{ kcal/mol}$, in excellent agreement with our empirical estimates ($29 \pm 3 \text{ kcal/mol}$). The dominant correlations, which were not included in the previous theoretical work [$\Delta E_{ST}(\text{CCl}_2) = 13.5 \text{ kcal/mol}$],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. $\Delta E_{ST}(\text{SiCl}_2) = 42.7 \pm 7.1 \text{ kcal/mol}$ is in reasonable agreement with a previous theoretical value of $51.5 \pm 6 \text{ kcal/mol}$.^{11a} Experimental data allow the prediction of the previously unknown $\Delta E_{ST}(\text{SiHCl}) = 27.4 \pm 9.5 \text{ kcal/mol}$, while reliable theoretical calculations¹³ of $\Delta E_{ST}(\text{SiXY})$ allow the predictions of two previously unreported $D_{12}(\text{XYSi:H, H}) = 143.1 \pm 3.5$ and $107.3 \pm 3.5 \text{ kcal/mol}$ 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 data¹⁴ 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

Acknowledgment. This work was supported by the Shell Development Company, Houston, TX and the National Science Foundation (Grant No. CHE83-18041).

(11) Values for (a) $\Delta H_f^\circ_{298}(\text{}^3\text{SiH}_2)$ (shorthand for SiH_2 , ${}^3\text{B}_1$) is from Ho, P.; Coltrin, M. E.; Binkley, J. S.; Melius, C. F. *J. Phys. Chem.* **1985**, *89*, 4647; (b) $\Delta H_f^\circ_{298}(\text{SiH}_4)$ 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.

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(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.