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Absolute Heats of Formation of CHCl, CHF, and CClF. A Gas-Phase Experimental and G2 Theoretical Study

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The 298 K heats of formation of the singlet halocarbenes CHCl (**1**), CHF (**2**), and CClF (**3**) have been determined from measurements of the chloride dissociation energies of $CHCl_2^-$ (**1a**), $CHClF^-$ (**2a**), and CCl_2F^- (**3a**) and the gas-phase acidities of CH_2Cl_2 (**1b**), CH_2ClF (**2b**) and $CHCl_2F$ (**3b**), respectively. Analysis of the energy-resolved collision-induced dissociation cross sections for **1a**, **2a**, and **3a** obtained with a flowing afterglow−triple quadrupole instrument gives the 298 K chloride dissociation enthalpies: 37.0 ± 2.7, 22.7 ± 2.2, and 25.2 ± 1.5 kcal/mol, respectively. Proton transfer equilibrium and acid−base bracketing measurements carried out in the flow tube give gas-phase acidities, ΔH_{acid}, for **1b**, **2b**, and **3b** of 377.6 ± 0.7, 385.9 ± 0.3, and 361.3 ± 2.0 kcal/mol, respectively. The chloride dissociation enthalpies and gas-phase acidities are combined in simple thermochemical cycles to derive 298 K heats of formation for **1**, **2**, and **3** of 80.4 ± 2.8, 34.2 ± 3.0, and 7.4 ± 3.2 kcal/mol, respectively. Critical comparisons of these results with the results of prior experimental measurements and with the results of G2 molecular orbital calculations lead to the following *recommended* heats of formation (in kcal/mol): $\Delta H_{\mathrm{f,298}}(\mathrm{CHCl}) = 78.0 \pm 2.0$, $\Delta H_{\mathrm{f,298}}(\mathrm{CHF}) = 34.2 \pm 3.0$, $\Delta H_{\mathrm{f,298}}(\mathrm{CFCl}) = 7.4 \pm 3.2$, $\Delta H_{\mathrm{f,298}}(\mathrm{CCl_2}) = 55.0 \pm 2.0$, and $\Delta H_{\mathrm{f,298}}(\mathrm{CF_2}) = -44.0 \pm 2.0$. The recommended heats of formation are used to derive other thermochemical data, including halocarbene proton affinities, PA(CXY), halomethyl radical acidities, ΔH_{acid}(CHXY), and C−H bond strengths for halomethyl radicals, DH_{298}(H−CXY). An excellent linear correlation is found to exist between the divalent state stabilization energy (DSSE) of the halocarbenes and the measured or calculated singlet−triplet splittings.

Introduction

The structure, thermochemical properties, and reactivity of a carbene are sensitive functions of its ground state spin multiplicity and singlet−triplet energy gap.[1,2] Carbenes with electron-withdrawing, π-donor substituents such as R_2N-, RO−, and halogen are usually singlets, whereas carbenes with unsaturated, π-acceptor groups such as NC−, C_6H_5-, and $CH_2{=}CH-$ have triplet ground states.[3] Halocarbenes are archetypal singlet carbenes with a long history of experimental and theoretical investigation.[4] The relative ease of formation of halocarbenes in solution by base-catalyzed α-elimination reactions has led to the development of numerous organic synthetic strategies involving these species.[1a,5] The reduced unimolecular reactivity of monohalocarbenes, RCX, compared to unsubstituted carbenes, RCH, has been exploited in kinetic studies of 1,2-hydrogen and carbon rearrangements.[6,7] Because of their relative thermodynamic stabilities, dihalocarbenes are common fragments of photochemical and thermal decomposition reactions of freons and other haloalkanes,[8] and they are thought to play an important role in the chemistry of halon flame retardants.[9] Halocarbenes have been examined computationally by virtually every kind of *ab initio* and semiempirical quantum mechanical method.[10] The computed structures, vibrational frequencies, and singlet−triplet splittings of halocarbenes obtained from CI-, MP*n*-, and DFT-type calculations that employ at least double-ζ quality basis sets have been shown to be in good agreement with the limited experimental data that are available.[11−13] Theoretical predictions of unknown or uncertain S−T splittings for several halocarbenes and their isoelectronic analogs have been reported.[10]

TABLE 1: Experimental Heats of Formation of Chlorofluorocarbenes[a]

carbene	$\Delta H_{\mathrm{f,298}}$, kcal/mol	ref
CHCl	71 ± 5	*b*
	75.7 ± 4.8	*c*
	80.4 ± 2.8	this work
	78.0 ± 2.0	recommended
CHF	26 ± 3	*b*
	37.5 ± 4.3	*c*
	34.2 ± 3.0	this work; recommended
CClF	−2 ± 7	*b*
	7.4 ± 3.2	this work; recommended
CCl_2	39 ± 3	*b*
	57.2 ± 4.0	*d*
	51.0 ± 2.0	*e*
	52.1 ± 3.4	*f*
	55.0 ± 2.0	recommended
CF_2	−49 ± 3	*b*
	−40.9 ± 2.4	*c*
	<−39.4 ± 3.4	*f*
	−44.0 ± 2.0	recommended

[a] For a summary of previous measurements up through 1985, see ref 14. [b] Reference 14. [c] Reference 16. [d] Reference 20. [e] Reference 18. [f] Reference 17.

Despite the broad significance of halocarbenes, the thermodynamic properties of these species are not well-established. The heats of formation of the fluorine- and chlorine-containing carbenes, **1**−**5**, in particular, are still a matter of debate (Table 1). In 1985, Lias, Karpas, and Liebman (LKL)[14] summarized

CHCl	CHF	CClF	CCl_2	CF_2
1	**2**	**3**	**4**	**5**

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the available thermochemical data for **1**−**5** and noted the wide variation in the measured heats of formation for **4** (<30 to 55 kcal/mol) and for **5** (<−34.7 to −56 kcal/mol). LKL carried out proton affinity (PA) bracketing experiments with protonated halocarbenes in an ion cyclotron resonance (ICR) spectrometer (eq 1) and derived (298 K) heats of formation for **1**−**5** from thermochemical cycles involving the independently known[15] heats of formation of the corresponding fluorine- and chlorine-substituted carbocations (eq 2).

$$HCXY^{+} + B \rightarrow CXY + BH^{+} \qquad X, Y = F, Cl \quad (1)$$

$$\Delta H_f(CXY) = PA(CXY) + \Delta H_f(CHXY^{+}) - \Delta H_f(H^{+}) \quad (2)$$

Heats of formation of 71 ± 5, 26 ± 3, −2 ± 7, 39 ± 3, and −49 ± 3 kcal/mol for **1**−**5**, respectively, were reported by LKL. All of these values are at the lower end of the ranges of heats of formation measured by other techniques or estimated from literature data.[14]

Born, Ingemann, and Nibbering (BIN)[16] used a similar approach based on gas-phase negative ion cycles to determine heats of formation for **1** and **2** (as well as CHBr and CHI). The proton affinities of halocarbene anions, CHX^{-}, were bracketed in a Fourier transform ICR (eq 3), and the resulting estimates

$$HCX^{-} + HA \rightarrow CH_2X + A^{-} \qquad X = F, Cl \quad (3)$$

$$\Delta H_f(CHX) = \Delta H_{acid}(CH_2X) + EA(CHX) + \Delta H_f(CH_2X) - \Delta H_f(H^{+}) \quad (4)$$

for $\Delta H_{acid}(CH_2X)$ were combined with literature values for EA(CHX) and $\Delta H_f(CH_2X)$ according to eq 4 to yield $\Delta H_f(CHCl) = 75.7 \pm 4.8$ kcal/mol and $\Delta H_f(CHF) = 37.5 \pm 4.3$ kcal/mol. The value for CHCl is in fair agreement with the LKL result, while the heat of formation for CHF is more than 10 kcal/mol higher than the LKL estimate.

Heats of formation for **4** and **5** were determined in our laboratory by combining the measured threshold energies for collision-induced dissociation (CID) of halide ions from trihalomethyl anions (eq 5) with the gas-phase acidities and heats of formation of the corresponding trihalomethanes.[17]

$$CX_3^{-} \rightarrow CX_2 + X^{-} \qquad X = F, Cl \quad (5)$$

The 298 K heat of formation derived for **4** from these measurements, $\Delta H_f(CCl_2) = 52.1 \pm 3.4$ kcal/mol, is considerably higher than the value reported by LKL, but is in good agreement with high-level *ab initio* results and with the value 51.0 ± 2.0 kcal/mol reported by Kohn et al.,[18] which was derived from the measured ionization potential for CCl_2 and the known heat of formation of CCl_2^{+}.[19] A somewhat higher value for CCl_2, 57.2 ± 4.0 kcal/mol, was obtained by Grabowski[20] from the bracketed proton affinity of CCl_2^{-}. The CID measurements for **5** carried out in our laboratory were complicated by a competitive shift in the dissociation onset due to electron detachment, and the derived value for $\Delta H_f(CF_2)$, −39.4 ± 3.4 kcal/mol, is higher than the recommended heat of formation of −44 kcal/mol.[17,21]

In this work, we apply the CID threshold method to the remaining fluorine- and chlorine-containing methylenes, **1**−**3**. Chloride dissociation enthalpies, $DH[CXY{-}Cl^{-}]$, are determined for the series of chloromethyl and chlorofluoromethyl anions (eq 6)[22] and combined with the gas-phase acidities and heats of formation for the corresponding halomethanes, CHXYCl (**1b**−**3b**), and HCl according to eq 7 to derive heats of formation for the carbenes.

$$CXYCl^{-} \rightarrow CXY + Cl^{-} \quad (6)$$

1a: X = H, Y = Cl

2a: X = H, Y = F

3a: X = Cl, Y = F

$$\Delta H_f(CXY) = DH[CXY{-}Cl^{-}] + \Delta H_{acid}(CHXYCl) + \Delta H_f(CHXYCl) - \Delta H_{acid}(HCl) - \Delta H_f(HCl) \quad (7)$$

Comparisons with previous experimental results and with the results of *ab initio* calculations carried out at the G2 level of theory are made, and a set of “best values” for the absolute heats of formation for carbenes **1**−**5** is recommended. We use the recommended heats of formation to derive other thermochemical quantities of interest and to establish a quantitative correlation between the thermodynamic stabilities and singlet−triplet splittings of halocarbenes.

Experimental Section

The experiments described in this study were carried out at room temperature (298 ± 2 K) in a flowing afterglow−triple quadrupole instrument.[23] The pressure, flow rate, and flow velocity of the helium buffer gas in the 1 m × 7.3 cm (i.d.) flow tube were $P_{He} = 0.4$ Torr, $F_{He} = 190$ STP cm^3/s, and $\nu_{He} = 9000$ cm/s, respectively. Hydroxide ion was generated by electron impact ionization of a mixture of N_2O and CH_4 added near an electron emission source located at the upstream end of the flow tube. The halocarbanions **1a**−**3a** were produced in the flow reactor by proton transfer to OH^{-} from the corresponding halomethanes, **1b**−**3b**, added through downstream gas inlets. Other negative ions used for the acid−base bracketing measurements were also generated by proton abstraction from the corresponding conjugate acids by OH^{-}. The *t*-BuO^{-} ion used in the equilibrium experiments was generated by dissociative electron ionization of (*t*-BuO)$_2$. The negative ions were gently extracted from the flowing plasma through a small orifice in a nose cone into the detector chamber for either single-stage or tandem mass spectrometric analysis by the triple quadrupole analyzer. Collision-induced dissociation of mass-selected ions was carried out in the gas-tight, rf-only quadrupole collision cell (Q2) with either argon or neon target gases. The reactant ion axial kinetic energy (0−100 eV) was determined by the Q2 rod offset voltage, and the pressure of the CID target (0.02−0.06 mTorr) was measured with an absolute pressure transducer. Ions were detected with an electron multiplier operated in pulse-counting mode.

Kinetic measurements were performed by standard methods[24] using a pair of fixed-position ring inlets located at calibrated distances from the sampling orifice of 38 and 48 cm.[23] Gas flow rates were determined by measuring the pressure increase with time when the flow was diverted from the reactor to an external calibrated volume. Absolute rate coefficients are determined with typical precision better than ±10% and estimated accuracy of ±20%. Product branching ratios were determined either directly from the observed mass spectra when no secondary reactions occurred or from the slopes of plots of the product ion yields versus the extent of reactant ion conversion. For all quantitative measurements of reaction product distributions, the detector resolution was kept as low as possible so as to minimize ion mass discrimination. No corrections were made for differences in the diffusive loss rates for different ions. The estimated uncertainties in the product yields are ±10%.

Energy Threshold Measurements. Details of the procedures used for energy-resolved CID data collection and analysis are given elsewhere.[23,25,26] For the present experiments, the yield of the chloride ion CID product was monitored as a function of the axial kinetic energy of the halocarbanion reactant, E_{lab}, which was calibrated by retarding potential analysis.[23] An appearance curve was constructed by plotting the CID cross section, σ_{p}, versus the ion−target collision energy in the center-of-mass frame, $E_{\mathrm{CM}} = E_{\mathrm{lab}}\,[m/M + m]$, where m is the mass of the neutral target and M is the mass of the ion. The cross sections were calculated using the thin-target limited expression: $\sigma_{\mathrm{p}} = I_{\mathrm{p}}/INl$, where I_{p} and I are the intensities of the product and reactant ions, N is the number density of the target gas, and l is the effective collision path length.[23]

In order to derive the threshold dissociation energies, the appearance curves were fit with the model function given in eq 8, which takes into account the contribution to the total available energy from the reactant ion vibrational energy.[27,28] In this

$$\sigma = \sigma_0 \sum_{i=1}^{3n-6} g_i (E + E_i - E_0)^n / E \tag{8}$$

expression E_0 is the energy threshold, σ_0 is a scaling factor, n is an adjustable parameter, and i denotes vibrational states having energy E_i and population g_i ($\sum g_i = 1$). The vibrational energy distributions of the reactant ions were estimated from scaled harmonic vibrational frequencies obtained from semiempirical MO calculations.[29] The chloride ion appearance curves were fit by varying E_0, σ_0, and n in an iterative manner so as to minimize deviations between the data and the calculated cross sections in the steeply rising portion of the appearance curve.[30] During the fitting, the trial cross sections were convoluted with a Doppler broadening function,[31] which accounts for thermal motion of the target, and the kinetic energy distribution of the reactant ion, which was approximated by a Gaussian function with full-width at half-maximum of 1.5 eV, lab. The threshold energies obtained in this manner correspond to 0 K bond dissociation energies. The 298 K dissociation enthalpies were derived by adding the difference in the integrated heat capacities of the CID products and the reactants, plus a PV work term (RT = 0.6 kcal/mol at 298 K). Analysis of the data with a modified form[32] of eq 8 that accounts for possible shifts in the dissociation onset due to slow unimolecular dissociation on the experimental time scale[33] shows these effects to be negligibly small. This is expected because of the relatively small size and low dissociation energies of ions **1a**−**3a**. The "stationary electron" convention is used in this work.[15]

Gas purities were as follows: He (99.995%), Ar (99.955%), N_2O (99.99%), CH_4 (99%), Ne (99%), NF_3 (98%). All liquid reagents were obtained from commercial sources and used as supplied except for degassing prior to use.

Computational Details. *Ab initio* calculations for **1**−**5** were carried out using the G2 procedure,[34] which gives extrapolated total energies corresponding to a QCISD(T)/6-311+G(3df,2p) calculation for optimized geometries obtained at the MP2(full)/6-31G(d) level of theory. Calculations for selected species were also carried out using the G2(MP2) procedure,[35] which uses a different extrapolation scheme to estimate the large-basis QCISD(T) energies. Zero-point energies and 298 K enthalpy corrections were derived from scaled harmonic vibrational frequencies computed at the HF/6-31G(d) level (scale factor = 0.893[36]). The absolute heats of formation of the halocarbenes were calculated from the G2 atomization energies and the experimental heats of formation of the corresponding atoms.[37]

The 298 K heats of formation for **1**−**5** were also estimated from calculated G2 enthalpy changes for the isodesmic and isogyric dihydrogen transfer reaction shown in eq 9.

$$^1A_1\ CXY + CH_4 \rightarrow CH_2XY + {}^1A_1\ CH_2 \tag{9}$$

The enthalpy change for this reaction is referred to as the "carbene stabilization energy",[3b,38] and it has been used to quantify the stabilization or destabilization of a substituted carbene relative to methylene. The calculated values for ΔH_{298}(eq 9) were combined with the experimental 298 K heats of formation of CH_4,[39] CH_2XY[15] (*vide infra*), and $^1A_1$ CH_2[40] (Table 2) to compute the heat of formation for CXY.

All G2 calculations were performed using the Gaussian92/DFT[41] and Gaussian 94[42] suites of programs.

Results

Halocarbanions **1a**, **2a**, and **3a** were produced by proton abstraction from the corresponding halomethanes **1b**, **2b**, and **3b** by OH^-. High yields of Cl^- were also formed in each case, presumably by nucleophilic substitution. Collision-induced dissociation of each carbanion with either argon or neon target over the 1−10 eV (CM) energy range produces Cl^- as the only ionic fragment (eq 6). Representative cross sections for CID of **1a**, **2a**, and **3a** with neon target are shown in Figure 1.[43] The maximum cross sections for the dissociations with neon target are 2−4 Å^2 at collision energies near 5 eV (CM). The energy-resolved cross sections for CID of each carbanion were fit with the model function described by eq 8. The reactant ion internal energy convolution makes a small but non-negligible contribution to the calculated cross sections in the region of the dissociation onset. The average values for the CID thresholds, E_0, obtained from replicate measurements for each system are 1.57 ± 0.11, 0.96 ± 0.09, and 1.07 ± 0.06 eV for **1a**, **2a**, and **3a**, respectively. The assigned uncertainties reflect the precision of the data and the uncertainty in the energy scale (0.15 eV lab). The average values obtained for the adjustable shape parameter n in eq 8 are 1.56 ± 0.09, 1.53 ± 0.07, and 1.50 ± 0.06 for **1a**, **2a**, and **3a**, respectively. These are similar in magnitude to the values obtained from analysis of other carbene- and biradical-forming halide dissociations examined in our laboratory.[17,25,44] Combining the measured values of E_0 with the calculated difference in 0−298 K integrated heat capacities of the dissociation products and reactants gives Cl^- dissociation enthalpies, $DH_{298}[CXY{-}Cl^-]$, of 37.0 ± 2.7, 22.7 ± 2.2, and 25.2 ± 1.5 kcal/mol for **1a**, **2a**, and **3a**, respectively. A summary of the CID threshold results is given in Table 3.

In order to derive carbene heats of formation from the halocarbanion dissociation enthalpies, accurate gas-phase acidities for **1b**−**3b** are required (eq 7). The gas-phase acidity of dichloromethane (**1b**), $\Delta G_{\mathrm{acid}}(CH_2Cl_2)$, has been bracketed by Bohme et al. to be 366.8 ± 3.0 kcal/mol,[45] which is close to the accurately known acidity of *tert*-butyl alcohol, ΔG_{acid}(*t*-C_4H_9OH) = 369.3 ± 0.6 kcal/mol.[46] Also, a preliminary bracketing study in our lab[22] gave an apparent acidity for CH_2ClF (**2b**) that is similar to the well-established acidity of methanol, $\Delta G_{\mathrm{acid}}(CH_3OH)$ = 375.1 ± 0.2 kcal/mol.[47] Therefore, in order to further refine the gas-phase acidities of **1b** and **2b**, we carried out proton transfer equilibrium measurements with *tert*-butyl alcohol and methanol, respectively (eqs 10, 11).

$$CHCl_2^- + t\text{-BuOH} \rightleftharpoons CH_2Cl_2 + t\text{-BuO}^- \tag{10}$$

$$CHClF^- + MeOH \rightleftharpoons CH_2ClF + MeO^- \tag{11}$$

TABLE 2: Supplemental Thermochemical Data[a]

compound	$\Delta H_{f,298}$, kcal/mol	ref
CH_4	−17.83 ± 0.07	*b*
CH_3Cl	−19.6 ± 0.2	*c*
CH_3F	[−56.8 ± 2.0]	*d*
CH_2Cl_2	−22.9 ± 0.2	*c*
CH_2ClF	[−63.1 ± 2.0]	*d*
CH_2F_2	−108.1 ± 0.4	*e*
$CHCl_2F$	[−67.8 ± 2.0]	*d*
cis-ClHC=CHCl	1.0 ± 0.2	*c*
cis-FHC=CHF	(−71)	*c*
trans-ClFC=CClF	(−78)	*c*
HCl	−22.1	*c*
CH_2Cl	28.3 ± 2.0	*f*
CH_2F	−7.9 ± 2.2	*f*
$CHCl_2$	22.3 ± 1.0	*f*
CHClF	−15.8 ± 2.8	*f*
CHF_2	−57.0 ± 1.0	*f*
CH_2Cl^+	230.1 ± 2.0	*g*
CH_2F^+	200.6 ± 2.2	*g*
$CHClF^+$	187.4 ± 2.9	*g*
$CHCl_2+$	214.2 ± 1.0	*g*
CHF_2+	145.0 ± 1.3	*g*
$^1A_1$ CH_2	101.1 ± 0.5	*h*
H	52.1	*c*
Cl	29.0	*c*
F	19.0	*c*
Cl^-	−54.4	*c*
H^+	365.7	*c*

RH	$DH_{298}[R-H]$	ref
CH_4	104.9 ± 0.1	*i*
CH_3Cl	100 ± 2	*j*
CH_3F	101 ± 1	*k*
CH_2Cl_2	97.3 ± 1.0	*l*
CH_2ClF	99.4	*l*
CH_2F_2	103.2 ± 1.0	*c*
$CHCl_2F$	97.7	*l*

other		ref
$\Delta H_{acid}(HCl)$	333.4 ± 0.1	*c*
$IP(CH_2Cl)$	8.75 ± 0.01	*c*
$IP(CH_2F)$	9.04 ± 0.01	*c*
IP(CHClF)	8.81 ± 0.02	*c*
$IP(CHCl_2)$	8.32 ± 0.01	*c*
$IP(CHF_2)$	8.76 ± 0.03	*c*
IP(H)	13.6	*c*
EA(CHCl)	1.210 ± 0.005	*m*
EA(CHF)	0.542 ± 0.005	*m*
$EA(CCl_2)$	1.603 ± 0.008	*n*
$EA(CF_2)$	0.179 ± 0.005	*n*

[a] All data in kcal/mol except IPs and EAs, which are given in eV (1 eV = 23.061 kcal/mol). [b] Reference 39. [c] Reference 15. [d] Reference 55. [e] Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986. [f] Heats of formation for halomethyl radicals (R) were obtained by combining the heat of formation for the neutral halomethanes (RH) with the recommended C−H bond enthalpies. [g] Heats of formation for halomethyl cations (R^+) were obtained by combining the heats of formation for the halomethyl radicals (R) with the recommended ionization potentials. [h] Reference 40. [i] Berkowitz et al., ref 52. [j] Average of values from Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1988,** *110*, 7343, and McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. [k] Average of values obtained from G2(MP2) theory (this work) and McMillen et al. (see *j*). [l] Reference 60. [m] Reference 11b. [n] Reference 11a.

The equilibrium constants for the above reactions were determined from the ratios of the measured rate coefficients for the forward and reverse proton transfers, $K = k_f/k_r$. For the “forward” reactions, carbanions **1a** and **2a** were allowed to react with the neutral alcohol added to the flow reactor with a known, constant flow rate through either of two radial gas inlets located at fixed distances from the sampling orifice.[23] The intensity of the halocarbanion signal was then recorded for several different alcohol flow rates. The rate coefficients for the overall bimolecular ion−molecule reactions, k_{tot}, were obtained from semilog plots of the carbanion signal intensity versus alcohol flow rate. The average values of k_{tot} obtained from replicate measurements are summarized in Table 4, along with the corresponding collision rate coefficients, k_{coll}, estimated by parametrized trajectory theory.[48] The assigned uncertainties are one standard deviation and reflect the precision of the measurements. The reaction of **1a** with *tert*-BuOH and **2a** with MeOH both produce Cl^- as a primary product in addition to the alkoxides. Chloride ion is presumed to arise from a nucleophilic displacement reaction within the intermediate ion/molecule complex following proton transfer (eq 12, Y = F, Cl).

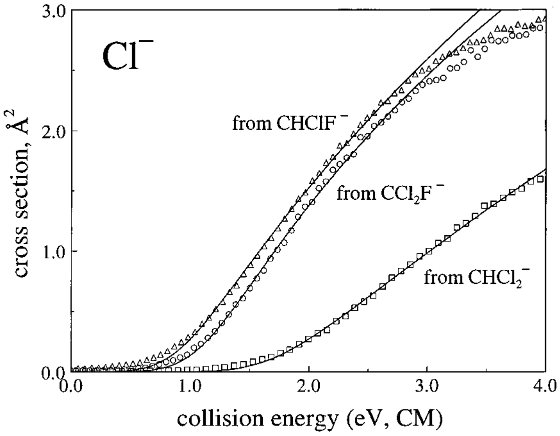

Figure 1. Cross sections for Cl^- dissociation from **1a**, **2a**, and **3a** resulting from collisional activation with Ne target at (3−5) × 10^{-5} Torr. The solid lines are the fully convoluted model appearance curve obtained by methods discussed in the text.

$$CHYCl^- + ROH \rightarrow [CH_2YCl\cdots RO^-] \rightarrow ROCH_2Y + Cl^- \quad (12)$$

The branching ratios for the proton transfer and Cl^- displacement channels for **1a** and **2a** were determined by monitoring the relative abundances of the alkoxide and chloride products with increasing extent of reactant ion depletion and then extrapolating to zero depletion. These data are given in Table 4. Multiplying the overall reaction rate coefficient by the branching fraction for proton transfer gives the total rate for proton transfer. Thus, the rate coefficients for proton transfer to **1a** and **2a** are determined to be 3.5 × 10^{-10} and 6.1 × 10^{-10} cm^3/(molecule s), corresponding to reaction efficiencies (k/k_{coll}) of 0.27 and 0.31, respectively.

Similar procedures were used to determine the rate coefficients for the “reverse” proton transfers between *t*-BuO$^-$ and **1b** and MeO$^-$ and **2b**. Direct displacement of Cl^- by the alkoxide ions competes with proton transfer in both cases and is the dominant process in the reaction of MeO$^-$ with **2b** (Table 4). Combining the overall reaction rate coefficients with the measured branching ratios for proton transfer gives rate coefficients for proton transfer of 5.9 × 10^{-10} for **1b** + *t*-BuO$^-$ and 4.0 × 10^{-11} cm^3/(molecule s) for **2b** + MeO$^-$, corresponding to efficiencies of 0.42 and 0.02, respectively.

The ratios of the rate coefficients for the forward and reverse reactions give the equilibrium constants $K_{10} = 0.6 \pm 0.3$ and $K_{11} = 15.3 \pm 0.3$. The uncertainty in *K*, σ_K, was computed from $(\sigma_K/K)^2 = (\sigma_{kf}/k_f)^2 + (\sigma_{kr}/k_r)^2$, where σ_{kf} and σ_{kr} are the standard deviations of the rate coefficients. These equilibrium constants correspond to $\Delta\Delta G_{acid}$ values at 298 K of 0.3 ± 0.3 and −1.6 ± 0.2 kcal/mol, respectively, where the uncertainties

TABLE 3: Experimental Thermochemical Data for Halocarbenes

CXY	$E_0(CXYCl^-)$[a] (eV)	n[b]	$DH_{298}[CXY-Cl^-]$ (kcal/mol)	$\Delta G_{acid}(CHXYCl)$ (kcal/mol)	ΔS_{acid} (eu)	ΔH_{acid} (kcal/mol)	$\Delta H_{f,298}(CXY)$[c] (kcal/mol)
CHCl	1.57 ± 0.11	1.56 ± 0.09	37.0 ± 2.7	369.0 ± 0.7	29.0	377.6 ± 0.7	80.4 ± 2.8
CHF	0.96 ± 0.09	1.53 ± 0.07	22.7 ± 2.2	376.7 ± 0.3	31.0	385.9 ± 0.3	34.2 ± 3.0
CClF	1.07 ± 0.06	1.50 ± 0.06	25.2 ± 1.5	352.5 ± 2.0	29.4	361.3 ± 2.0	7.4 ± 3.2

[a] CID threshold energy, eq 6. [b] Optimized shape parameter, eq 8. [c] Eq 7.

TABLE 4: Results of Kinetics Experiments[a]

reaction	k_{total}[b]	%, rxn	k_{rxn}[c]	k_{coll}[d]	efficiency[e]
$CHCl_2^- + t\text{-BuOH}$	$(3.9 \pm 0.5) \times 10^{-10}$	91, PT	3.5×10^{-10}	1.3×10^{-9}	0.27
		9, S_N2	3.5×10^{-11}		0.03
$CH_2Cl_2 + t\text{-BuO}^-$	$(6.4 \pm 1.8) \times 10^{-10}$	92, PT	5.9×10^{-10}	1.4×10^{-9}	0.42
		8, S_N2	5.1×10^{-11}		0.04
$CHFCl^- + MeOH$	$(1.3 \pm 0.1) \times 10^{-9}$	47, PT	6.1×10^{-10}	2.0×10^{-9}	0.31
		53, S_N2	6.9×10^{-10}		0.35
$CH_2FCl + MeO^-$	$(2.0 \pm 0.1) \times 10^{-9}$	2, PT	4.0×10^{-11}	2.2×10^{-9}	0.02
		98, S_N2	2.0×10^{-10}		0.91

[a] Rate coefficients in units of cm^3/(molecule s). [b] Rate coefficient for overall reaction. [c] Rate coefficient for indicated reaction channel. [d] Calculated ion/molecule collision rate coefficient obtained from parametrized trajectory theory, ref 48. [e] Efficiency = k/k_{coll}.

are computed from $(\sigma_{\Delta\Delta G})^2 = (RT/K)^2(\sigma_K)^2$. Combining these acidity differences with the gas-phase acidities of *tert*-BuOH and MeOH specified earlier gives ΔG_{acid}(**1b**) = 369.0 ± 0.7 kcal/mol and ΔG_{acid}(**2b**) = 376.7 ± 0.3 kcal/mol, where the uncertainties are the root-square-sum of the uncertainty of the alcohol acidities and the uncertainty in $\Delta\Delta G$.

In order to convert ΔG_{acid} to ΔH_{acid}, ΔS_{acid} must be measured or calculated. In the case at hand, statistical thermodynamics was used to estimate ΔS_{acid}.[49] For these estimates, the moments of inertia and harmonic vibrational frequencies for **1a** (C_s), **1b** (C_{2v}), **2a** (C_1), and **2b** (C_s) were obtained from semiempirical MO calculations.[29] Total entropies of 67.0, 64.0, 66.5, and 62.9 eu for **1a**, **1b**, **2a**, and **2b**, respectively, were computed using standard formulas.[49] Combining these values with the absolute entropy of the proton ($S^o(H^+)$ = 26.01 eu)[50] gives ΔS_{acid}(**1b**) = 29.0 eu and ΔS_{acid}(**2b**) = 31.0 eu.[51] The estimates for ΔS_{acid} combine with the measured values for ΔG_{acid} to yield the 298 K enthalpies: ΔH_{acid}(**1a**) = 377.6 ± 0.7 kcal/mol and ΔH_{acid}(**2b**) = 385.9 ± 0.3 kcal/mol (Table 3).

Simple bracketing experiments located the gas-phase acidity of $CHCl_2F$ (**3b**) near that of methanethiol ($\Delta G_{acid}(CH_3SH)$ = 351.6 ± 0.8 kcal/mol[52]). Therefore, an attempt was made to measure the equilibrium constant for proton transfer (eq 13).

$$CCl_2F^- + MeSH \rightleftharpoons CHCl_2F + MeS^- \qquad (13)$$

Proton transfer does proceed in both directions, but the measured yield of CCl_2F^- from the reaction between CH_3S^- and $CHCl_2F$ is less than 0.5%, the main process being nucleophilic displacement of Cl^-. This extremely low yield makes quantitation of the proton transfer channel and, therefore, the kinetic determination of K_{13} unreliable. Accordingly, a careful bracketing study with **3a** and **3b** was performed with an expanded series of reference acids and bases. A summary listing of the results in terms of the occurrence and nonoccurrence of proton transfer is given in Table 3 of the Supporting Information. The bracketing results are consistent with the apparent reversibility of reaction 13 and indicate an acidity for **3b** between that of $CF_3C(CH_3)_2OH$ (ΔG_{acid} = 353.5 ± 2.0 kcal/mol[15]) and $(CH_3CH_2)_3SiOH$ (ΔG_{acid} = 351.5 ± 2.0 kcal/mol[15]). On this basis, we assign ΔG_{acid}(**3b**) = 352.5 ± 2.0 kcal/mol. Absolute entropies for **3a** (C_s) and **3b** (C_s) of 62.2 and 58.8 eu, respectively, were estimated from the computed[29] geometries and frequencies using statistical mechanics,[49] which lead to ΔS_{acid}(**3b**) = 29.4 eu. The resulting value for ΔH_{acid}(**3b**) at 298 K is 361.3 ± 2.0 kcal/mol.

The remaining quantities needed to compute carbene heats of formation using eq 7 are the heats of formation of the corresponding halomethanes **1b**−**3b**, $\Delta H_{f,298}(CHXYCl)$. The 298 K heat of formation of **1b** has been measured calorimetrically to be −22.9 ± 0.2 kcal/mol.[15] The heats of formation of **2b** and **3b** have not been determined experimentally. Additivity methods with corrections for bond interactions lead to estimates of −62.3 and −67.2 kcal/mol for **2b** and **3b**, respectively.[53] An estimate for $\Delta H_{f,298}$(**2b**) of −62.6 ± 2.0 kcal/mol is given in the JANAF tables,[50] which was derived from a comparison of the experimental enthalpies of atomization of other chlorofluoromethanes. Estimates based on *ab initio* calculations are also available. Ignacio and Schlegel derived 298 K heats of formation for **1b**, **2b**, and **3b** of −22.5, −60.5, and −70.8, respectively, from isodesmic reaction energies obtained with a MP4/6-31G** procedure.[54] Berry et al.[55] calculated the heats of formation of all the chlorofluoromethanes using G2,[34] G2(MP2),[35] CBS-4,[56] and CBS-Q[CBS] methods and developed a bond additivity correction scheme to adjust for the systematic deviations between the experimental and theoretical values. The corrected G2 and G2(MP2) heats of formation displayed the lowest rms deviations from the available experimental data; values for **1b**, **2b**, and **3b** of −22.1, −63.1, and −67.8 kcal/mol, respectively, were reported. For the present work we will use the experimental heat of formation for **1b** and the corrected G2 estimates[55] for **2b** and **3b** and assign uncertainties of ±2.0 kcal/mol to the latter two values (Table 2).

Combining the measured chloride dissociation enthalpies, gas-phase acidities, and supplemental data according to eq 7 gives heats of formation for **1**, **2**, and **3** of 80.4 ± 2.8, 34.2 ± 3.0, and 7.4 ± 3.2 kcal/mol, respectively (Table 3). The indicated uncertainties are computed from the root-square-sum of the uncertainties in each term of eq 7.

Theoretical Results. *Ab initio* calculations were carried out at the G2 level of theory in order to obtain theoretical estimates for the carbene heats of formation and some of the other thermochemical quantities determined in this study. The G2 total energies, scaled zero-point energies, and temperature corrections and the resulting 298 K total enthalpies for carbenes **1**−**5**, halocarbanions **1a**−**3a**, halomethanes **1b**−**3b**, and various related molecules, ions, and atoms, as well as the MP2(full)/6-31G(d) optimized geometries and HF/6-31G* vibrational frequencies for selected species are available as Supporting Information.

TABLE 5: Thermochemical Quantities Derived from G2 Calculations[a]

CXY	$\Delta H_{f,298}(CXY)$[b] (kcal/mol)	$\Delta H_{acid}(CHXYCl)$[c] (kcal/mol)	$DH_{298}[CXY-Cl^-]$ (kcal/mol)
CHCl	75.7 (−2.3)	376.5 (−1.1)	32.2 (−4.8)
CHF	31.7 (−2.5)	385.0 (−0.9)	21.1 (−1.6)
CClF	5.9 (−2.5)	362.7 (1.4)	22.9 (−2.3)
CCl_2	53.6 (−1.4)		
CF_2	−48.2 (−4.2)		

[a] Deviation from recommended values or experimental values determined in this work shown in parentheses. [b] Average heat of formation predicted from atomization energy and isodesmic reaction enthalpy (eq 9). [c] Gas-phase acidity corrected for error in calculated acidity of methane.

The 298 K heats of formation for carbenes **1**−**5** were computed in the usual manner from the G2 atomization energies and the experimental heats of formation of the gaseous atoms. Values for $\Delta H_{f,298}(CXY)$ of 75.4, 31.1, 5.1, 53.5, and −49.3 kcal/mol for **1**−**5**, respectively, are obtained. The heat of formation of singlet methylene, $^1A_1$ CH_2, predicted from the G2 atomization energy is 101.4 kcal/mol, compared to the experimental value of 101.9 ± 0.5 kcal/mol (Table 2). As an independent check, we also derived the halocarbene heats of formation from the calculated 298 K enthalpy changes for the isodesmic and isogyric reaction shown in eq 9 in conjunction with the known[15,39,40] heats of formation for $^1A_1$ CH_2, CH_4, and CH_2XY. The resulting values, 76.0, 32.3, 6.7, 53.7, and −47.0 kcal/mol, are in good agreement with those determined from the atomization energies. The averages of the values obtained from the two different approaches are listed in Table 5, along with the differences between the recommended experimental (*vide infra*) and calculated heats of formation.

The gas-phase acidities for the halomethanes **1b**−**3b**, ΔH_{acid}(CHXYCl), were computed from the differences in 298 K G2 enthalpies of CHXYCl and $CXYCl^-$ plus the 298 K enthalpy of a proton, 1.48 kcal/mol. This gives ΔH_{acid} values of 378.2, 386.7, and 364.4 kcal/mol for **1b**, **2b**, and **3b**, respectively. The G2 acidity for methane is 418.4 kcal/mol[57] compared to the experimental value of 416.7 ± 0.7 kcal/mol.[15] Assuming the same 1.7 kcal/mol deviation for the halomethanes[58] gives final G2 acidity estimates for **1b**−**3b** of 376.5, 385.0, and 362.7 kcal/mol, respectively (Table 5).

Finally, chloride dissociation enthalpies for **1a**−**3a**, $DH_{298}[CXY-Cl^-]$, were computed directly from the differences in G2 total enthalpies of the products and reactants of eq 6. These are also listed in Table 5.

Discussion

General Considerations. The accuracy of the present approach to carbene thermochemistry depends critically upon the determination of the correct thermochemical dissociation energy for the halocarbanions from the energy-resolved CID cross sections. Potential complications include reverse activation barriers for the dissociations, kinetic shifts in the dissociation onsets due to slow unimolecular decomposition, and competitive shifts in the onsets due to collision-induced electron detachment from the halocarbanions. We argue below that these factors are inconsequential in the present measurements.

First of all, dissociation of a halide ion from an activated halocarbanion to produce a singlet carbene is spin- and state-symmetry allowed. Therefore, no electronic barriers (curve-crossings) exist that may give rise to a dissociation barrier in excess of the reaction endothermicity. The reverse reaction, nucleophilic addition to a singlet carbene, has been examined experimentally and computationally for simple cases and has been shown to occur without a barrier.[59]

Second, the relatively small size and low dissociation energies of the halocarbanions **1a**−**3a** mean that kinetic shifts in the CID threshold due to slow unimolecular decomposition[33] are unlikely. Fits of the data with a modified form of eq 8 that explicitly accounts for dissociation lifetime effects[32] show these factors to be negligible. The dissociations all appear to proceed with “normal” efficiencies compared to other negative ion dissociations examined in our lab,[17,25,26,44] exhibiting maximum cross sections for CID with Ne target in the 2−4 Å^2 range (slightly higher with Ar target) and steeply rising cross sections in the post-threshold regions.

Finally, in a negative ion CID experiment the dissociation onset could become shifted to higher energy if the electron detachment rate of the activated ion significantly exceeds the dissociation rate. Such “competitive shifts” would lead to erroneously high heats of formation for the carbenes. However, this is unlikely in the present experiments because the halide dissociation energies of **1a**−**3a** are less than, or comparable to, the electron detachment energies. The electron affinities of the corresponding halomethyl radicals, EA(CXYCl), can be derived from the acidities for **1b**−**3b** determined in this work and literature values or theoretical estimates for the C−H bond energies[60] according to eq 14. The resulting electron binding

$$\mathrm{EA(CXYCl)} = D[\mathrm{H-CXYCl}] - \Delta H_{acid}(\mathrm{CHXYCl}) + \mathrm{IP(H)} \quad (14)$$

energies are 1.4, 1.2, and 2.2 eV for **1a**, **2a**, and **3a**, respectively, compared to Cl^- dissociation thresholds of 1.57, 0.96, and 1.07 eV (Table 3). Thus, only for $CHCl_2^-$ (**1a**) does the dissociation energy exceed the detachment energy, but only by 0.17 eV. Our experience has been that collision-induced electron detachment of polyatomic anions is an inefficient process that becomes competitive with direct-cleavage type dissociations only at energies in excess of 1 eV or so above the thermochemical threshold.[17,25,26,44] As indicated in the preceding paragraph, the CID cross sections for **1a**−**3a** are all in the normal range for processes of this type and are inconsistent with electron loss as the primary decomposition pathway.

Comparison of Experimental and Theoretical Results. A summary listing of the experimentally determined heats of formation for **1**−**5** reported since the 1985 work by LKL[14] (including the present study) is given in Table 1. Also shown are the recommended heats of formation, which are defined and defended below. As indicated earlier, the LKL values are all significantly lower than those obtained in subsequent measurements using other techniques. The heats of formation for **1** and **2** obtained in the present study are higher and lower, respectively, than the values obtained by BIN[16] but are within the assigned uncertainties.

Considering its well-documented record of success, one might normally look to the G2 results for adjudication. However, the recent work by Berry et al.[55] clearly indicates that the absolute heats of formation of chlorofluoromethanes predicted by G2 theory are systematically too low (too negative) compared to experimental values by 2−3 kcal/mol. It is likely that the G2 heats of formation for the halocarbenes **1**−**5** listed in Table 5 are similarly afflicted. However, the magnitudes of the errors are unknown, and the bond additivity correction terms derived by Berry et al. for the halomethanes[55] are inapplicable. If we take the G2 heats of formation listed in Table 5 as lower limits, then the following conclusions can be drawn. The LKL values for the heats of formation of carbenes **1**−**5** determined by ICR studies of reaction 1 are all too low. For **1**, the true heat of

TABLE 6: Derived Thermochemical Quantities and Carbene Singlet−Triplet Splittings[a]

	$PA(CXY)$[b]		$\Delta H_{acid}(CHXY)$[c]		$DH_{298}[H-CXY]$[d]	DSSE[e]	$DH_{298}[YXC{=}CXY]$[f]	
CXY	this work	LKL[g]	this work	lit	this work	this work	this work	$\Delta E_{ST}(CXY)$
CHCl	213.6	207	387.5	384.8[h]	101.8	−1.8	155.0	4.2[j]
CHF	199.3	193	395.3	398.7[h]	94.2	6.8	139.4	14.9[j]
CClF	185.7	186			75.3	24.1	92.8	(38.4)[k]
CCl_2	206.5	193	361.4	362.4[i]	84.8	12.5	112.1	(22)[l]
CF_2	176.7	173	374.6	377.4[h]	65.1	38.1	69.9	56.7[m]

[a] All data in kcal/mol; theoretical values in parentheses. [b] Derived with use of eq 2. [c] Derived with use of eq 4. [d] Eq 15. [e] "Divalent state stabilization energy", eq 17. [f] Eq 16. [g] Reference 14. [h] Reference 16. [i] Reference 20. [j] Reference 11b. [k] G2 calculations, this work. [l] Selected value based on calculations reported in ref 10. [m] Reference 12.

formation most likely lies between the BIN value and the value determined in the present work; $\Delta H_f(\mathbf{1}) = 78$ kcal/mol is assigned with an uncertainty of no more than 2 kcal/mol. For carbenes **2** and **3**, the heats of formation determined in the present study are probably the most accurate. The heats of formation for **4** reported by Kohn et al.[18] and by us[17] are both too low, while the value reported by Grabowski[20] is slightly high. The true value is probably about 55 (±2) kcal/mol. Finally, the value for $\Delta H_f(\mathbf{5})$ of −44 kcal/mol measured by Berman et al.[21] and recommended in our earlier study[17] is most likely the correct one.

Unlike the absolute heats of formation, the gas-phase acidities of **1b**−**3b** predicted by G2 theory (Table 5) are in excellent accord with the experimentally measured acidities (Table 3), with nonsystematic deviations in ΔH_{acid} that are less than ±1.5 kcal/mol. The G2 acidities were corrected for the error in the computed acidity of methane. The directly calculated ΔH_{acid} values for **1b**−**3b** are systematically too high, with an rms deviation of 2.3 kcal/mol.

The chloride dissociation enthalpies for **1a**−**3a** predicted by the G2 calculations are systematically lower than the measured values. The fact that they are all too low suggests that the G2 energies of the carbenes are the primary source of error, since the computed heats of formation of the carbenes were also too low.

Derived Thermochemistry. The recommended values for the absolute heats of formation of the carbenes given in Table 1 can be used in conjunction with the supplemental data listed in Table 2 to derive other thermochemical quantities, some of which relate to the measurements of BIN and LKL. A listing of these quantities is given in Table 6, along with the experimental or "best" theoretical value for the singlet−triplet splittings of each carbene. The proton affinities (PAs) of the carbenes were calculated with use of eq 2 and the updated values for $\Delta H_f(CHXY^+)$ listed in Table 2. For **1**, **2**, and **4**, the derived PAs are higher than the values reported by LKL by 6−13 kcal/mol. For carbene **3** there is a good match, and for **5** the difference is within the uncertainties in both values. In deriving $\Delta H_f(CXY)$ from their measured PAs, LKL used values of 229, 199, 178, 212, and 143 kcal/mol for the heats of formation of $ClCH_2^+$, FCH_2^+, $ClFCH^+$, Cl_2CH^+, and F_2CH^+, respectively. These are close to the updated values listed in Table 2 for all but $ClFCH^+$, where the difference is more than 9 kcal/mol. Thus, we can trace the origins of the discrepancies between the recommended heats of formation for carbenes **1**−**5** and the values reported by LKL to problems with the PA bracketing procedure for **1**, **2**, and **4**, use of an incorrect value for $\Delta H_f(ClFCH^+)$ for **3**, and small deviations in both $PA(CF_2)$ and $\Delta H_f(F_2CH^+)$ for **5**.

The gas-phase acidities of halomethyl radicals, $\Delta H_{acid}(CHXY)$, were computed with eq 4. The uncertainty in these values is no more than ±3 kcal/mol. The derived values for CH_2F, CH_2Cl, and CF_2 differ in a non-systematic way from the acidities given by BIN,[16] but the uncertainty intervals are well-overlapped. The heats of formation for the halomethyl radicals, $\Delta H_f(CHXY)$, used in the present work (Table 2) are the same as those used by BIN. The acidity derived for $CHCl_2$ is in good agreement with the bracketed value,[20] which means that the relatively high value for $\Delta H_f(\mathbf{4})$ reported by Grabowski is due, in part, to the ancillary data that were used.

The carbene heats of formation can also be used to compute the C−H bond dissociation enthalpies of halomethyl radicals, $DH_{298}[H-CXY]$, according to eq 15, and the C=C bond strengths in haloalkenes, $DH_{298}[YXC{=}CXY]$, according to eq 16.

$$DH_{298}[H-CXY] = \Delta H_f(CXY) + \Delta H_f(H) - \Delta H_f(CHXY) \tag{15}$$

$$DH_{298}[YXC{=}CXY] = 2\Delta H_f(CXY) - \Delta H_f(YXC{=}CXY) \tag{16}$$

The derived values listed in Table 6 have uncertainties of no more than ±3 kcal/mol. These bond energies have been used in quantitative models of carbene stability. For instance, the difference between the first and second C−H bond enthalpies of a halomethane defines the "divalent state stabilization energy" (DSSE)[61] of the corresponding carbene (eq 17):

$$DSSE(CXY) = DH_{298}[H-CHXY] - DH_{298}[H-CXY] \tag{17}$$

The larger the DSSE, the more stable the singlet carbene. The quantitative connections between DSSE values and singlet−triplet splittings of carbenes and silylenes have been examined by several groups.[61−64] From the data in Tables 1 and 6 we compute DSSE values of −1.8, 6.8, 24.1, 12.5, and 38.1 for **1**−**5**, respectively, compared to a value of −14.0 for $^1A_1$ CH_2. The DSSEs for **4** and **5** differ from the values derived in our earlier study[17] due to the changes in the carbene heats of formation. The small, negative value for **1** is not considered significant; it is more likely that the second C−H bond energy of CH_3Cl is the same as, or slightly smaller than, the first. An excellent linear correlation between DSSE(CXY) and $\Delta E_{ST}(CXY)$ is found (eq 18), which is illustrated in Figure 2a.

$$\Delta E_{ST} = 1.33(DSSE) + 6.11\ \text{kcal/mol}\ (r^2 = 0.9995) \tag{18}$$

The existence of such a correlation was anticipated in many of the previous accounts of carbene thermochemistry.[61−64] The present study provides the critically evaluated data needed to formulate it. The linear relationship derived from the chlorofluorocarbene data[65] has some predictive value for other singlet carbenes. For example, it makes good predictions for vinylidene,[66] $CH_2{=}C$: (DSSE = 29 kcal/mol; ΔE_{ST}(eq 18) = 45 kcal/mol; ΔE_{ST}(exp) = 47.6 kcal/mol[67]) and hydroxycarbene, HCOH (DSSE = 12 kcal/mol; [68] ΔE_{ST}(eq 18) = 22 kcal/mol; ΔE_{ST}(theor) = 21 kcal/mol[69]), but it slightly overestimates the

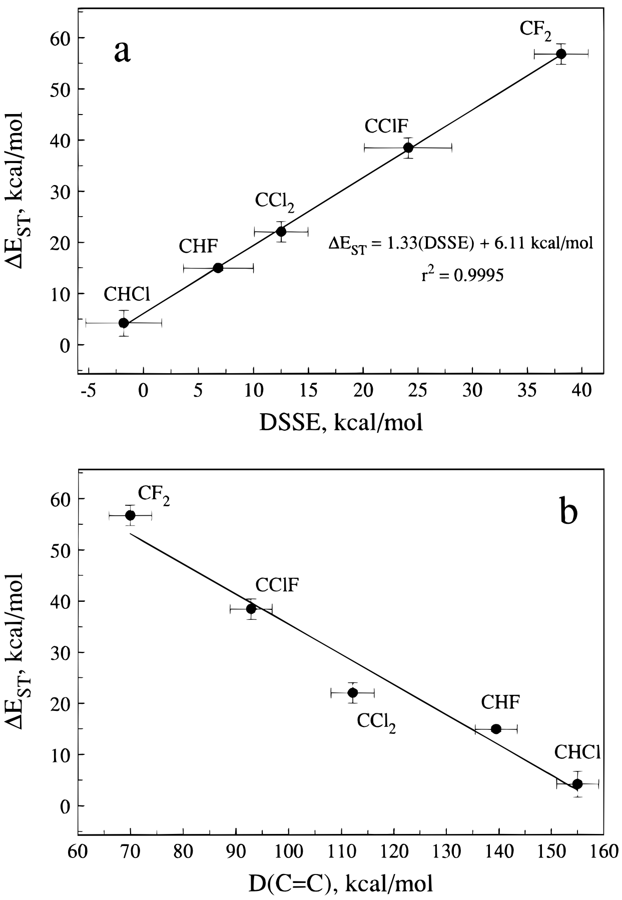

Figure 2. Correlation of the singlet−triplet splittings for carbenes **1**−**5**, ΔE_{ST}(CXY), with two different thermochemical quantities: (**a**) divalent state stabilization energy, DSSE(CXY); the difference between the first and second C−H bond strengths of the corresponding halomethanes; (**b**) adiabatic C═C bond dissociation enthalpy of the symmetrically substituted haloalkenes, DH_{298}(YXC═CXY).

S−T gap for HCBr (DSSE = 1.5 kcal/mol;[16] ΔE_{ST}(eq 18) = 8 kcal/mol; ΔE_{ST}(exp) = 2.6 kcal/mol),[11] and fails spectacularly for propadienylidene, CH_2═C═C: (DSSE = −11.3 kcal/mol; ΔE_{ST}(eq 18) = −9 kcal/mol; ΔE_{ST}(exp) = 29.7 kcal/mol).[70] A further examination of the scope, utility, and limitations of this correlation will be published elsewhere.

Carter and Goddard proposed[62] that the difference between the adiabatic bond dissociation enthalpies of ethylene, DH_{298}(CH_2═CH_2) = 173.3 kcal/mol, and a substituted ethylene, DH_{298}(XYC═CXY), can be used to estimate ΔE_{ST}(CXY) when CXY has a singlet ground state, eq 19.

$$\Delta E_{ST}(\mathrm{CXY}) = {}^{1}/_{2}[DH_{298}(\mathrm{CH_2{=}CH_2}) - DH_{298}(\mathrm{XYC{=}CXY})] \quad (19)$$

Although there does appear to be a fair correlation between DH_{298}(XYC═CXY) and ΔE_{ST}(CXY), as illustrated in Figure 2b, the slope (−0.6) and intercept (94.3 kcal/mol) of the linear fit differ significantly from the values (−0.5, 86.7 kcal/mol) required by eq 19, and the ΔE_{ST}(CXY) values estimated with this equation are in error by as much as 8 kcal/mol. However, the poor performance of eq 19 is more likely to be due to inaccuracies in the haloalkene thermochemical data rather than deficiencies of the model.

Conclusions

We have presented new measurements of the absolute heats of formation for CHCl, CHF, and CClF and the gas-phase acidities for CH_2Cl_2, CH_2ClF, and $CHCl_2F$. From a careful consideration of the results of past and the present measurements, along with the results of G2 calculations, we recommend the following heats of formation for the chlorofluorocarbenes (in kcal/mol): $\Delta H_{f,298}$(CHCl) = 78.0 ± 2.0, $\Delta H_{f,298}$(CHF) = 34.2 ± 3.0, $\Delta H_{f,298}$(CClF) = 7.4 ± 3.2, $\Delta H_{f,298}$(CCl_2) = 55 ± 2.0, and $\Delta H_{f,298}$(CF_2) = −44.0 ± 2.0. In keeping with the recent theoretical analysis of halon thermochemistry by Berry and co-workers,[55] we find that the G2 method gives absolute heats of formation for chlorofluorocarbenes that are systematically low. The G2 acidities for chlorofluoromethanes obtained from an isodesmic reaction approach are in excellent agreement with experiment. The recommended heats of formation for the halocarbenes have been used to derive new values for several related thermochemical quantities, including carbene proton affinities and homolytic and heterolytic C−H bond strengths for halomethyl radicals. We have examined the quantitative relationships between the singlet−triplet splittings of the chlorofluorocarbenes and their thermodynamic stabilities, as defined by the difference in first and second C−H bond strengths in chlorofluoromethanes (DSSE) and by the strengths of C═C bonds in chlorofluoroalkenes. An excellent linear correlation exists between DSSE and ΔE_{ST} that has some predictive value for other types of singlet carbenes.

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Supporting Information Available: G2 total energies, scaled zero-point energies and temperature corrections, resulting 298 K total enthalpies for carbenes **1**−**5**, halocarbanions **1a**−**3a**, halomethanes **1b**−**3b**, and various related molecules, ions, and atoms, and MP2(full)/6-31G(d) optimized geometries and HF/6-31G* vibrational frequencies for selected species (5 pages). Ordering information is given on any current masthead page.

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