7° and H7C1C2C3 = 2.4°). As a result the charge tends to localize at C3, which is consistent with the Mulliken population analysis and the fact that C2–C3 is longer than C1–C2 by 0.013 Å. The structure is also in accord with the electronegativity of fluorine, its preference for bonding at sp^3 centers, and its relatively poor π-donating abilities. The geometry of 1-hydroxyallyl anion (**7a**), on the other hand, reflects the fact that oxygen is not as electronegative as fluorine and is a better π-electron donor. The negative charge is shifted away from the substituent leading to a flattening out at C3 (O4C3C2C1 = 2.9° and H5C3C2C1 = 9.7°), increased pyramidalization at C1 (H7C1C2C3 = 17.5° and H6C1C2C3 = 4.2°), and a large difference in bond lengths (0.052 Å) between C1–C2 (long) and C2–C3 (short). 1-Aminoallyl anion (**1a**), in stark contrast to **4a** and **7a**, is calculated to be planar, and the geometry is quite similar to that of the parent ion.[39] Nitrogen only has one lone-pair of electrons and it is orthogonal to the π-system. This eliminates the driving force for distorting the carbon framework and means that the strong π-donating ability of an amino group is not destabilizing in this instance. The greater delocalization in **1a**, relative to **4a** and **7a**, offsets the smaller amount of inductive stabilization. A subtle balance exists in each of the three anions and leads to the different geometries and the failure of linear free energy relationships.

The interaction between a charged site and a substituent directly bound to it depends to some degree on the particular system. First-row substituents ($N(CH_3)_2$, OCH_3, and F) do not affect the acidity of propene, but this observation cannot be generalized to every substrate; different compounds may display enhanced or even diminished acidities. Benzyl derivatives are analogous to the corresponding propenes,[40] but calculated deprotonation energies for substituted ethylenes and cyclopropanes are distinct, i.e. F < OH < NH_2 < H (Table V).[41] The enhanced acidities can be accounted for simply by the electronegativity or field effect of the substituents. This contrasts with the propene data, and presumably is a result of the ions being localized and somewhat less flexible and having less repulsive electron–electron interactions. There is little experimental data, however, to compare the calculations to and consequently further discussion will be deferred until a later date.

Conclusions

Fragile anions which are weakly bound can be prepared at low temperatures under the unique conditions available in a flowing afterglow device. This makes it possible to study a series of 3-substituted propenes. The reactivity of the conjugate bases is generally in keeping with previous reports but occasionally leads to the formation of additional ions of interest, e.g. OHF^-. 3-Fluoropropene, 3-methoxypropene, and 3-(dimethylamino)propene have the same acidities, within experimental error, as the parent compound. Electron-withdrawing and π-donating substituents therefore do not destabilize an ion with respect to its basicity, but they do lead to a decrease in electron-binding energies. There is, however, an empirical correlation between acidity and electron affinity. Molecular orbital calculations reveal that the allylic anions (**4a**, **7a**, and **1a**) have different geometries as a result of a number of compensating factors. This explains why linear free energy relationships are not applicable in this case and suggests that different substrates may behave very differently. Ab initio computations support this latter notion and additional results will be reported in due course.

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Carbene Thermochemistry from Collision-Induced Dissociation Threshold Energy Measurements. The Heats of Formation of $\tilde{X}\,^1A_1$ CF_2 and $\tilde{X}\,^1A_1$ CCl_2

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Abstract: The heats of formation of $\tilde{X}\,^1A_1$ CF_2 and $\tilde{X}\,^1A_1$ CCl_2 have been determined from measurements of the threshold energies for collision-induced halide ion dissociation from CF_3^- and CCl_3^- in a flowing afterglow–triple quadrupole apparatus. The derived values $\Delta H^\circ_{f,298}(CF_2, g) = -39.4 \pm 3.4$ kcal/mol and $\Delta H^\circ_{f,298}(CCl_2, g) = 52.1 \pm 3.4$ kcal/mol are significantly higher than the heats of formation recently obtained for these carbenes from proton affinity bracketing experiments by Lias, Karpas, and Liebman (*J. Am. Chem. Soc.* **1985**, *107*, 6089) but are in good agreement with measurements from other laboratories and with ab initio molecular orbital calculations. The gas-phase acidity (ΔH_{acid}) of $CHCl_3$ has also been determined from a proton-transfer bracketing procedure to be 357.6 ± 2.0 kcal/mol, from which $EA(CCl_3) = 2.25 \pm 0.10$ eV is obtained. The carbon–carbon bond energies in $CF_2{=}CF_2$ (79.1 ± 3.8 kcal/mol) and $Cl_2C{=}CCl_2$ (106.3 ± 4.9 kcal/mol) are derived from the present results and critically compared with the predicted values obtained from the proposed relationship between C=C bond strengths and carbene singlet–triplet energy gaps.

The modern era of carbene chemistry, according to Skell,[1] marks its beginnings with the pioneering kinetic studies by Hine and co-workers of CCl_2 intermediates in the alkaline hydrolysis of chloroform.[2] In the intervening 40 years since these seminal studies, interest in carbenes has grown across diverse chemical disciplines. The prodigious research activity devoted to carbenes is motivated not only by their practical utility in organic synthetic

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procedures for producing cyclopropanes,[3] but also by the recognition that carbenes and carbenoid intermediates intercede in numerous organic and organometallic reaction mechanisms.[4] Moreover, divalent carbon species are proposed to play significant roles in combustion chemistry[5] and interstellar organic synthesis,[6] and they have been advantageously employed in materials science,[7] catalysis,[8] and photoaffinity labeling procedures in biochemistry.[9]

Determination of the fundamental physical properties of carbenes continues to be a vital and challenging task. Among the major classes of reactive organic intermediates such as carbocations, radicals and carbanions, carbenes have the dubious distinction of being the least well characterized thermodynamically.[10] This is due, in part, to their extreme bimolecular reactivity in solution and their proclivity for fast unimolecular rearrangements that preclude the usual calorimetric or equilibrium-based methods for obtaining thermochemical information. Moreover, carbenes do not possess the convenience of a net molecular charge that would enable their direct mass spectrometric characterization, nor do they have a simple chemical relationship with thermodynamically well characterized neutral molecules such as is the case with conjugate acid–base pairs or redox couples. The archetypal carbene, CH_2, has well-established heats of formation for its triplet ground state ($\Delta H^\circ_{f,298}(\tilde{X}^3B_1\ CH_2, g) = 92.6 \pm 0.6$ kcal/mol) and for its first excited singlet state ($\Delta H^\circ_{f,298}(\tilde{a}^1A_1\ CH_2, g) = 101.9 \pm 0.5$ kcal/mol) that have been determined by various experimental methods[11] and confirmed by the highest level quantum mechanical calculations.[12] The halocarbenes likewise have been subjects of numerous direct and indirect thermochemical measurements, although for some of them there remain significant discrepancies among the reported heats of formation.[13] Moreover, for some of the monohalocarbenes, there are still uncertainties about the multiplicities of the ground states.[14] A recent review of the available halocarbene thermochemistry through 1985 by Lias, Karpas, and Liebman (LKL)[13] exposes a surprisingly wide range of measured heats of formation for both $\tilde{X}^1A_1$ CF_2 (−39.7 to −56.0 kcal/mol) and $\tilde{X}^1A_1$ CCl_2 (55 to <30 kcal/mol) as determined from photoionization and electron ionization onsets, gas-phase thermal equilibrium studies, and carbene proton affinity bracketing measurements. In these latter experiments, one determines how strong a neutral base is required to affect thermal energy proton abstraction from a halogenated methyl cation in the gas phase (eq 1).[15] If the heat of formation of the reactant

$$CHX_2^+ + B \rightarrow BH^+ + CX_2 \qquad (1)$$

cation is known independently, then the heat of formation of the singlet carbene product can be determined from the bracketed proton affinity, $PA(CX_2)$. From measurements of this type carried out in an ion cyclotron resonance (ICR) spectrometer, LKL recommend heats of formation for singlet CF_2 and CCl_2 of −49 ± 3 kcal/mol and 39 ± 3 kcal/mol, respectively—values that are at the lower ends of the ranges reported for these species in the literature.[13]

In recent reports from this laboratory, we have shown how collision-induced dissociation (CID) threshold energy measurements with a flowing afterglow–triple quadrupole instrument[16] can provide an excellent source of thermochemical data for gas phase ions.[17] The method relies on the precise determination of an activation energy for the direct cleavage of a thermalized reactant ion to a single product ion and a stable neutral fragment. If the heat of formation of either the reactant ion or product ion is known independently, then the other can be determined from the measured activation energy, provided the dissociation is rapid and does not involve a reverse activation energy. We have employed this technique to determine, inter alia, carbanion heats of formation and hydrocarbon acidities from the decarboxylation onsets for collisionally activated RCO_2^- ions,[18] sequential solvation energies of atomic transition-metal cations with H_2O and NH_3,[19] negative ion binding energies of BH_3,[20] and Me_3Si^+ cation affinities of alkenes.[21] In each of these applications, the focus is on the thermochemistry of the *ionic* product or reactant of the CID reaction. An obvious extension is to use this methodology for determining unknown heats of formation for *neutral* products of well-behaved dissociation reactions involving thermodynamically well characterized reactant and product ions. We introduce here an application of this latter approach to the determination of heats of formation for the singlet dihalocarbene products from dissociation of collisionally activated trihalomethyl anions (eq 2). This

$$CX_3^- \rightarrow CX_2 + X^- \qquad X = F, Cl \qquad (2)$$

reaction is, in principle, well-suited for CID threshold energy measurements because it is a direct bond cleavage from a structurally simple precursor ion that produces a single stable product ion. Moreover, dissociation of the carbanion correlates directly with the singlet ground state of the dihalocarbene.[14,22] The needed heats of formation for the trihalomethyl anions are either known or can be determined accurately from gas-phase acidity measurements, and for the halide ion products the thermochemical data is well-established.[10] In this paper, we present the details of our experimental measurements for CF_2 and CCl_2, along with supplemental results from high-level ab initio molecular

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orbital calculations that bear on the energetics of these carbenes. The combined experimental and theoretical results are critically compared with other recent measurements and calculations for CF_2 and CCl_2 in the literature, and the relevance of our new data to current interests in the C═C bond strengths in C_2F_4 and C_2Cl_4 is discussed.

Experimental Section

All experiments were performed with a flowing afterglow–triple quadrupole apparatus that has been described previously.[16,18-21] The standard operating conditions in the 7.6-cm i.d. × 100 cm helium flow reactor were $P(\mathrm{He}) = 0.400$ Torr, $F(\mathrm{He}) = 190$ STP cm^3/s; $\nu(\mathrm{He}) = 9400$ cm/s, and $T = 298$ K. The negative ions generated in the flow tube are thermalized by ca. 10^7 collisions/s with the helium bath gas and other added neutral compounds and then extracted through a 1-mm orifice in a nose cone into an EXTREL triple quadrupole mass analyzer. The desired reactant ion is selected with the first quadrupole (Q1) and injected into the rf-only, gas-tight central quadrupole (Q2) with an axial kinetic energy determined by the Q2 rod offset voltage. Argon collision gas is maintained in Q2 at a static pressure of $<5 \times 10^{-5}$ Torr, corresponding to single ion/atom collisions.[18] Fragment ions resulting from collision-induced dissociation are efficiently contained in Q2 and extracted by a low-voltage exit lens into Q3, which is maintained at a constant attractive voltage (ca. 5 V) with respect to the variable Q2 rod voltage. Ion detection is carried out with a conversion dynode and electron multiplier operating in pulse-counting mode.

The primary reagent ions used for generating trihalomethyl anions were OH^- (from electron ionization of a mixture of N_2O and CH_4) or NH_2^- (from ionization of NH_3). Proton abstraction from CHF_3 or $CHCl_3$ by either OH^- or NH_2^- produces intense signals of CF_3^- and CCl_3^-, respectively. Alternatively, these ions can be made by direct electron ionization of CF_4 and CCl_4. The measured CID threshold energies displayed no dependence on the particular source of the trihalomethyl anion that was used.

Materials. Gas purities were as follows: He (99.995%), Ar (99.955%), N_2O (99.0%), and CH_4 (99.0%). Liquid samples were obtained from commercial sources and used as supplied except for multiple freeze–pump–thaw cycles prior to use. The negative ion mass spectra from $CHCl_3$, CHF_3, and each of the neutral reference acids used in the acidity bracketing experiments showed these materials to be free of significant impurities.

CID Threshold Measurement and Analysis. A detailed account of the data collection procedures and analysis method for CID threshold energy measurements with the flowing afterglow–triple quadrupole instrument was provided in a recent publication from this laboratory.[18] Briefly, the axial kinetic energy of the mass-selected reactant ion is scanned while the intensity of the CID fragment ion formed in Q2 under single-collision conditions is monitored. The center-of-mass collision energy $E_{\mathrm{c.m.}}$ for the system is given by eq 3, where E_{lab} is the nominal lab energy and M and

$$E_{\mathrm{c.m.}} = E_{\mathrm{lab}}\,[m/(M + m)] \qquad (3)$$

m represent the masses of the reactant ion and neutral target, respectively. The energy axis origin is located by retarding potential analysis with Q2 serving as the retarding field element. The reactant ion kinetic energy distribution, as given by the simple first derivative of the retarding curve, is typically found to have a Lorentzian or near-Gaussian shape with a full width at half-maximum of 1–2 eV (lab frame). Under single collision conditions in Q2, the normalized intensity of the CID fragment ion is directly proportional to the dissociation partial cross section.[18] A plot of the product ion yield versus the center-of-mass collision energy gives rise to an ion appearance curve from which the activation energy for the dissociation may be deconvoluted by means of a fitting procedure based on the assumed model function given by eq 4.[23] Here, $I(E)$ is the

$$I(E) = I_0[(E - E_{\mathrm{T}})^n/E^m] \qquad (4)$$

normalized intensity of the product ion at center-of-mass collision energy E, E_{T} is the desired threshold energy, I_0 is a scaling factor, and n and m are adjustable parameters. For the present studies, we have found $n = 1.5$, $m = 1.5$ and $n = 1.5$, $m = 1.0$ to provide the best fits of the experimental halide ion appearance curves from trihalomethyl anions.[24] Use of linear models ($n = 1$, $m = 0$) or higher values than 1.5 for n and m were found to give significantly poorer fits. Optimization is carried out by an iterative procedure in which n and m are held constant and I_0 and E_{T} are varied so as to minimize the deviations between the experimental and calculated appearance curves in the vicinity of the reaction onset and up to the point where the product ion yield begins to decay.[18] Convoluted into this fit are the reactant ion kinetic energy distribution approximated by a Gaussian function with a 1.5-eV (lab) half-width and a Doppler broadening function developed by Chantry to account for the random thermal motion of the argon target.[25] The CID threshold, E_{T}, derived in this way is considered to correspond to a *thermal* activation energy for production of room temperature (298 K) products from thermalized, room temperature reactants. Therefore, unlike photoionization and electron ionization thresholds, a temperature correction for the products is unnecessary.[26] In order to convert E_{T} to a bond dissociation enthalpy term for use in deriving heats of formation, an expansion work factor ΔnRT must be added.[27] Thus, for the present systems at 298 K (eq 2, $\Delta n = 1$), $DH_{298}[CX_2\text{–}X^-] = E_{\mathrm{T}} + 0.59$ kcal/mol.

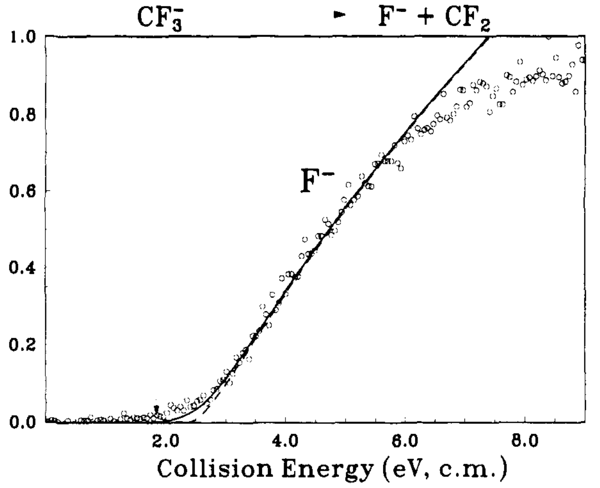

Figure 1. Appearance curve for F^- from collisional activation of CF_3^- with argon at 5.0×10^{-5} Torr. The solid line is the optimized, fully convoluted model appearance curve calculated by using eq 4 with $n = 1.5$ and $m = 1.0$, and the dashed line represents the unconvoluted excitation function. The arrow indicates the electron binding energy of the CF_3^- reactant ion (ref 10).

Calculations. The energetics for various reactions involving $^1A_1$ CF_2 and $^1A_1$ CCl_2 were evaluated at different levels of theory by using the GAUSSIAN 86 package of ab initio MO programs[28] on a VAXstation 3200. Complete geometry optimizations were carried out by using analytically evaluated energy gradients, and all stationary points were verified to be true minima by the absence of any negative force constants in the Hessian matrix. For all of the negative ion calculations, the geometries and vibrational frequencies were obtained with a diffuse-function augmented 6-31+G(d) basis set,[29] and correlation-corrected single-point energies were computed by using third-order Møller–Plesset perturbation theory (frozen core) (i.e., MP3/6-31+G(d)//6-31+G(d)). For the CF_2, CCl_2, and CH_2 proton affinity calculations, we employed fourth-order Møller–Plesset corrections (frozen core) including all quadruple, triple, double, and single excitations with a 6-311G(2d) basis set (i.e., MP4SDTQ/6-311G(2d)//6-311G(2d)). The calculated energy changes (ΔE_{TOT}) for all reactions were converted to 298 K enthalpies by including the standard zero-point energy, temperature, and work terms given in eq 5.[30] The calculated vibrational frequencies were scaled by a factor of 0.9,[29] and those falling below 500 cm^{-1} were omitted from the analysis.

$$\Delta H_{298} = \Delta E_{\mathrm{TOT}} + \Delta E_{\mathrm{vib}} + \Delta(\Delta E_{\mathrm{vib}})_{298} + \Delta E_{\mathrm{rot}} + \Delta E_{\mathrm{trans}} + \Delta PV \quad (5)$$

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Table I. Supplemental Thermochemical Data[a]

	$\Delta H^\circ_{f,298}$(g), kcal/mol	ref	ΔH_{acid}, kcal/mol	ref
HF	−64.8 ± 0.2	32	371.0 ± 0.2	10
CHF_3	−166.1 ± 0.3	33	377.0 ± 2.1	34
CH_2F_2	−108.2 ± 0.2	36		
$F_2C{=}CF_2$	−157.9 ± 0.4	36		
CF_4	−223.4 ± 0.1	36		
CF_3	−112.4 ± 1.3	63		
CHF_2	−57.1 ± 1.2	64		
F	18.9 ± 0.1	39		
CHF_2^+	143.4 ± 3.0	42		
HCl	−22.1 ± 0.1	32	333.4 ± 0.2	10
$CHCl_3$	−25.0 ± 0.5	36	357.6 ± 2.0	this work
CH_2Cl_2	−22.9 ± 0.2	36		
$Cl_2C{=}CCl_2$	−2.1 ± 1.2	36		
CCl_4	−23.2 ± 0.7	36		
CCl_3	18.7 ± 1.5	47		
$CHCl_2$	22.3 ± 1.0	65		
Cl	29.1 ± 0.1	39		
$CHCl_2^+$	212 ± 3	42, 43		
CH_4	−17.8 ± 0.1	36		
$^1A_1$ CH_2	101.9 ± 0.5	11	$PA(CH_2)$ =	
CH_3^+	261.3 ± 0.4	26	206.3 ± 0.8	10
H	52.1	39		
H^+	365.7	10		

[a] All data taken from ref 10 with the primary references indicated. The stationary electron convention is employed in this work.

Results

CF_2. Reaction between CHF_3 and either OH^- or NH_2^- in the helium flow reactor produces a clean mass spectrum with CF_3^- (*m/z* 69) as the only significant product ion. Low energy (<50 eV, lab) collisional activation of CF_3^- in the triple quadrupole yields F^- as the sole ionic product (eq 6). Dissociation to the singlet

$$CF_3^- \rightarrow CF_2 + F^- \tag{6}$$

$^1A_1$ state of CF_2 is the spin-allowed process. This state is well-separated energetically from the lowest triplet $^3B_1$ by ca. 57 kcal/mol.[31] Careful monitoring of the F^- yield as a function of the center-of-mass collision energy with argon target gas at 5 × 10^{-5} Torr in Q2 gives rise to the appearance plot illustrated in Figure 1. An estimate of the maximum cross section (σ_{max}) for the dissociation observed at 8 eV (center-of-mass frame) can be computed from eq 7, where N is the target gas number density

$$\sigma_{max} = [I_{max}/I_0]/Nl \tag{7}$$

(<1.6 × 10^{12} molecules/cm^3), l is the corrected collision path length in the middle quadrupole (23 cm at 8 eV), and I_{max} and I_0 are the product ion and initial reactant ion intensities, respectively. The calculated value for these conditions is 1–2 Å^2. The optimized fit of the n = 1.5, m = 1.0 model function (eq 4) convoluted together with the CF_3^- ion beam and Doppler broadening distributions described in the Experimental Section is shown as the solid curve in Figure 1, and the dashed line represents the unconvoluted function. Most of the threshold behavior can be satisfactorily modeled with this composite function within fairly strict limits on the adjustable parameters. The optimal value of the threshold energy, E_T, derived for this data set is 2.41 eV. Several replicate measurements carried out with a range of conditions over a period of several months give an average value of 2.40 ± 0.12 eV (55.3 ± 2.7 kcal/mol). The uncertainty quoted is larger than the actual precision (±1.5 kcal/mol) and reflects the minor variation in the final value of E_T that results from use of slightly different values of n and m in the model excitation function. Thus, at room temperature, the bond dissociation enthalpy, $DH_{298}[CF_2{-}F^-]$, is 55.9 ± 2.7 kcal/mol.

The enthalpy change for reaction 6 can be expressed in terms of the measured bond dissociation enthalpy and the heats of formation for CF_3^- and F^-, the latter two quantities being derived from the heats of formation and gas-phase acidities of CHF_3 and HF, respectively. Rearranging this equation in terms of the gas-phase heat of formation for CF_2 gives eq 8. The absolute

$$\Delta H^\circ_{f,298}(^1A_1\ CF_2) = DH_{298}[CF_2{-}F^-] + \Delta H_{acid}(CHF_3) - \Delta H_{acid}(HF) + \Delta H^\circ_{f,298}(CHF_3) - \Delta H^\circ_{f,298}(HF) \tag{8}$$

acidity and heat of formation of HF are accurately known to be 371.0 ± 0.3[10] and −64.8 ± 0.2 kcal/mol,[32] respectively (Table I). Fluoroform has a measured heat of formation of −166.1 ± 0.3 kcal/mol[33] and a gas-phase acidity of 377.0 ± 2.1 kcal/mol,[10] the latter determined from proton transfer equilibrium studies with ethanol and 2-propanol in an ICR.[34] Combining these quantities with the bond dissociation enthalpy for CF_3^- according to eq 8 gives a final value for $\Delta H^\circ_{f,298}(^1A_1\ CF_2,\ g)$ of −39.4 ± 3.4 kcal/mol, where the quoted uncertainty represents the square root of the sum of squares of the component uncertainties.

The nature and magnitude of the carbon–carbon bonding in $CF_2{=}CF_2$ are of current interest because of its extraordinary weakness.[35] Our new value for $\Delta H_f(CF_2)$ can be combined with the measured heat of formation for $CF_2{=}CF_2$ ($\Delta H^\circ_{f,298}[C_2F_4, g]$ = −157.9 ± 0.4 kcal/mol)[36] to yield a total C=C bond energy in C_2F_4, $DH_{298}[CF_2{=}CF_2]$, of 79.1 ± 3.8 kcal/mol.

CCl_2. Reaction between $CHCl_3$ and OH^- or electron ionization of CCl_4 at the ion source produces intense signals of CCl_3^- along with even greater amounts of Cl^- from S_N2 displacement and dissociative electron capture processes. CID of the *m/z* 117 (all ^{35}Cl) isotopomer of CCl_3^- under single collision conditions yields Cl^- as the only fragment ion (eq 9) with the energy dependence

$$CCl_3^- \rightarrow CCl_2 + Cl^- \tag{9}$$

illustrated in Figure 2. As with CF_2, the singlet-state product is the ground state of the carbene.[14,22] The maximum cross section for the dissociation of CCl_3^- at 5.0 eV (center-of-mass) with 4.6 × 10^{-5} Torr Ar collision target is calculated from eq 7 to be ca. 5 Å^2. Analysis of the Cl^- appearance curve in Figure 2 with the

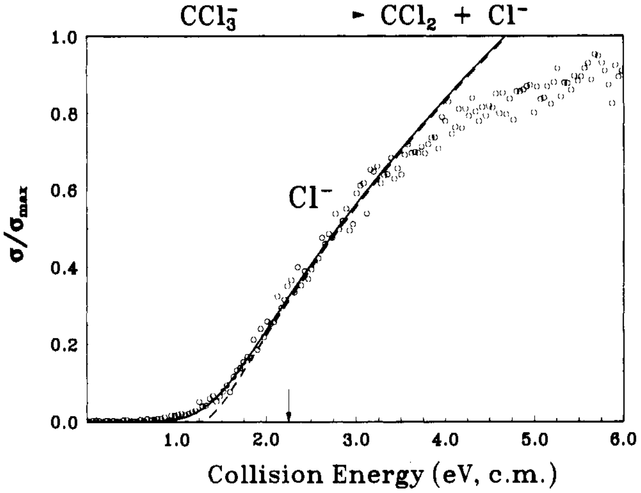

Figure 2. Appearance curve for Cl^- from collisional activation of CCl_3^- with argon at 4.6 × 10^{-5} Torr. The solid line is the optimized, fully convoluted model appearance curve calculated by using eq 4 with n = 1.5 and m = 1.0, and the dashed line represents the unconvoluted excitation function. The arrow indicates the electron binding energy of the CCl_3^- reactant ion (ref 47).

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Table II. Summary of Acid–Base Bracketing Experiments for $CCl_3^-/CHCl_3$[a]

$$CCl_3^- + HA \underset{\text{reverse}}{\overset{\text{forward}}{\rightleftharpoons}} CHCl_3 + A^-$$

HA	$\Delta G_{acid}(HA)$[b]	forward[c,d]	reverse
$PhCOCH_3$	354.5 ± 2.0	−	
CF_3CH_2OH	354.1 ± 2.0	−	+
$CF_3C(CH_3)_2OH$	353.5 ± 2.0	−	+
$((CH_3)_3Si)_2NH$	352.9 ± 2.0	−	+
$HCONH_2$	352.8 ± 2.0	−	
$(CH_3CH_2)_3SiOH$	351.5 ± 2.0		+
pyrrolidine	350.9 ± 2.0	+ (slow)	+ (fast)
$(CH_3)_2CHNO_2$	350.0 ± 2.0	+ (slow)	+ (fast)
CH_3NO_2	349.7 ± 2.0	+ (fast)	+ (slow)
CH_3CH_2SH	348.9 ± 2.0	+	−
$CH_3CH_2CH_2SH$	347.9 ± 2.0	+	−
1,3-cyclopentadiene	347.7 ± 2.0	+[e]	
$(CH_3)_2CHSH$	347.1 ± 2.0	+	−

[a] All reactions carried out in the helium flow reactor at 298 K. [b] Gas-phase acidity in kcal/mol, ref 10. [c] + and − correspond to observing and not observing proton transfer, respectively. [d] By slow it is meant that while some proton transfer takes place, it does so with an apparent rate that is less than that for the reverse proton transfer under conditions of comparable neutral flow rate (ca. 0.1 STP cm^3/s). [e] Reference 37.

same model as was used for CF_3^- yields a value of 1.29 eV for the threshold energy. Many replicate measurements carried out over an extended period provide a final value for E_T (eq 9) of 1.31 ± 0.12 eV (30.2 ± 2.7 kcal/mol). Therefore, the heterolytic bond dissociation enthalpy for the trichloromethyl anion, $DH_{298}[CCl_2{-}Cl^-]$, is 30.8 ± 2.7 kcal/mol. Equation 10 provides the expression for obtaining $\Delta H^\circ_{f,298}(^1A_1\ CCl_2, g)$ from the measured Cl^- dissociation enthalpy and supplemental thermochemical data.

$$\Delta H^\circ_{f,298}(^1A_1\ CCl_2) = DH_{298}[CCl_2{-}Cl^-] + \Delta H_{acid}(CHCl_3) - \Delta H_{acid}(HCl) + \Delta H^\circ_{f,298}(CHCl_3) - \Delta H^\circ_{f,298}(HCl) \quad (10)$$

In eq 10, all but $\Delta H_{acid}(CHCl_3)$ are well-known quantities.[10] The gas-phase acidity of chloroform has been reported by Bohme and co-workers to be between that of cyclopentadiene (ΔG_{acid} = 347.7 ± 2.0 kcal/mol) and acetone (ΔG_{acid} = 361.9 ± 2.0 kcal/mol).[37] We have carried out a more detailed proton transfer bracketing procedure in the helium flow reactor using an extended series of reference acids and bases, with the results summarized in Table II. The CCl_3^- ion rapidly abstracts a proton from CH_3NO_2, alkyl thiols, and other compounds of greater acidity but fails to deprotonate formamide, hexamethyldisilazane, β-fluoroalcohols, and all weaker acids. Further, $CHCl_3$ transfers its proton to $CF_3CH_2O^-$, $CF_3C(CH_3)_2O^-$, $(Me_3Si)_2N^-$, and Et_3SiO^- but not to any thiolate ions. These observations locate $\Delta G_{acid}(CHCl_3)$ in the vicinity of 350 kcal/mol.[10] Pyrrolidine, nitromethane, and 2-nitropropane (and their conjugate base anions) are all observed to undergo *reversible* proton transfer with the $CHCl_3/CCl_3^-$ conjugate acid–base pair. Qualitative observations of the relative rates of the forward and reverse proton transfers with each of these species leads us to assign a final value to $\Delta G_{acid}(CHCl_3)$ of 349.9 ± 2.0 kcal/mol. In order to derive $\Delta H_{acid}(CHCl_3)$ from these results, the entropy of chloroform ionization (ΔS_{acid}) is required.[38] Because the rotational symmetries of CCl_3^- and $CHCl_3$ are the same and the translational, vibrational, and electronic entropy differences are neglibly small, $\Delta S_{acid}(CHCl_3)$ is reliably given by the absolute entropy of the proton, 26.0 eu.[39] Thus, at 298 K, $\Delta H_{acid}(CHCl_3)$ = 357.6 ± 2.0 kcal/mol.

With the gas-phase acidity of $CHCl_3$ in hand, we can now derive the heat of formation for CCl_2 from the CCl_3^- bond dissociation enthalpy and eq 10 using $\Delta H_{acid}(HCl)$ = 333.4 ± 0.2,[10] $\Delta H^\circ_{f,298}(CHCl_3)$ = −25.0 ± 0.5,[36] and $\Delta H^\circ_{f,298}(HCl)$ = −22.1 ± 0.1 kcal/mol[32] (Table I). The final value is $\Delta H^\circ_{f,298}(^1A_1\ CCl_2, g)$ = 52.1 ± 3.4 kcal/mol, with the quoted uncertainty representing the square root of the sum of squares of the component uncertainty intervals. From this value for $\Delta H_f(CCl_2)$ and the literature value for the heat of formation of $Cl_2C{=}CCl_2$ (−2.1 ± 1.2 kcal/mol),[36] we derive a total C=C bond energy in C_2Cl_4 ($DH_{298}[Cl_2C{=}CCl_2]$) of 106.3 ± 4.9 kcal/mol.

Table III. Total Energies (au) for Ions and Molecules Related to Carbene Thermochemistry

species		$-E_{TOT}$(MP3/ 6-31+G(d)// 6-31+G(d))	ZPE[a]	$-E_{TOT}$(MP4SDTQ/ 6-311G(2d)// 6-311G(2d))	ZPE[a]
$^1A_1$ CF_2	C_{2v}	237.129 104	4.32	237.332 315	4.38
CF_3^-	C_{3v}	336.820 891	4.58		
CHF_3	C_{3v}	337.430 714	14.3		
CH_2F_2	C_{2v}	238.391 923	20.2		
F^-		99.613 630			
CHF_2^+	C_{2v}			237.623 773	12.9
$^1A_1$ CCl_2	C_{2v}	957.121 692	2.11	957.268 844	2.05
CCl_3^-	C_{3v}	1416.848 918	0.73		
$CHCl_3$	C_{3v}	1417.438 139	11.2		
CH_2Cl_2	C_{2v}	958.411 839	17.7		
Cl^-		459.682 380			
$CHCl_2^+$	C_{2v}			957.608 194	10.0
$^1A_1$ CH_2	C_{2v}	38.993 238	10.2	39.022 449	10.0
CH_4	T_d	40.349 991	26.9		
CH_3^+	D_{3h}			39.362 874	18.8

[a] Zero-point energies in kcal/mol. All frequencies scaled by 0.9; frequencies less than 500 cm^{-1} ignored.

Table IV. Calculated Reaction Enthalpies[a] for CX_2, CX_3^-, CHX_3^+, and CHX_2^+

carbene, CX_2	ΔH_{diss} (eq 11)	ΔH_{acid} (eq 12)	ΔH_{stab} (eq 13)	ΔPA (eq 14)
$^1A_1$ CF_2	50.2	374.5	58.2	−30.5
$^1A_1$ CCl_2	30.9	360.7	40.7	0.15

[a] All data in kcal/mol; see text for discussion of theoretical levels and defining equations.

Computational Results. In order to obtain a theoretical perspective for our experimental results, we have carried out ab initio MO calculations on a series of ions and neutral compounds related to the thermochemistry for CF_2 and CCl_2. Total energies for the optimized geometries of the various species are listed in Table III. The energetics for selected reactions have been computed from the differences in total energies and corrected to ΔH_{298} in order to make direct comparisons with experimental data; these data are summarized in Table IV. ΔH_{diss} is the enthalpy of halide dissociation from CX_3^- to the singlet carbene (eq 11), and ΔH_{acid}

$$CX_3^- \xrightarrow{\Delta H_{diss}} {}^1A_1\ CX_2 + X^- \quad (11)$$

$$CHX_3 \xrightarrow{\Delta H_{acid}} CX_3^- + H^+ \quad (12)$$

is the computed gas-phase acidity of the corresponding neutral haloform molecule (eq 12). A theoretical estimate of the heats of formation for the dihalocarbenes can be derived from the singlet carbene stabilization energy, ΔH_{stab}, which is given by the computed enthalpy of the isodesmic reaction shown in eq 13.[40] For

$$^1A_1\ CX_2 + CH_4 \xrightarrow{\Delta H_{stab}} {}^1A_1\ CH_2 + CH_2X_2 \quad (13)$$

CF_2 and CCl_2, stabilization energies of 58.2 and 40.7 kcal/mol, respectively, are calculated at the MP3/6-31+G(d)//6-31+G(d) level of theory. By combining the computed stabilization enthalpies with the experimental heats of formation for $^1A_1$ CH_2, CH_4, and CH_2X_2,[11,36] we calculate heats of formation for $^1A_1$ CF_2

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and ${}^1A_1$ CCl_2 of −46.4 and 56.2 kcal/mol, respectively.

Because much of the earlier thermochemical data for CF_2 and CCl_2 is based on measurements of their gas-phase proton affinities,[13,15] we have calculated $PA(CF_2)$ and $PA(CCl_2)$ relative to $PA(CH_2)$ (eq 14) at the MP4SDTQ/6-311G(2d)//6-311G(2d)

$$\mathrm{CHX_2^+} + {}^1\mathrm{A_1}\ \mathrm{CH_2} \xrightarrow{\Delta \mathrm{PA}} {}^1\mathrm{A_1}\ \mathrm{CX_2} + \mathrm{CH_3^+} \tag{14}$$

level of theory, corrected to ΔH_{298}.[41] For CF_2, ΔPA is calculated to be −30.5 kcal/mol, while for CCl_2 a value of 0.15 kcal/mol is obtained. Combining these differences with the absolute experimental proton affinity of ${}^1A_1$ CH_2 (206.3 ± 0.8 kcal/mol)[10] gives $PA(CF_2)$ = 175.8 kcal/mol and $PA(CCl_2)$ = 206.5 kcal/mol. It is worthwhile to note that the directly calculated value for $PA(CH_2)$ at this level of theory (206.3 kcal/mol) is in excellent agreement with the experimental value. The computed proton affinities for CF_2 and CCl_2 can be combined with the experimental heats of formation for CHF_2^+ (143.4 ± 3.0 kcal/mol),[42] $CHCl_2^+$ (212.0 ± 3.0 kcal/mol),[42,43] and the proton (365.7 kcal/mol)[10] to yield heats of formation for CF_2 and CCl_2 of −46.5 and 52.9 kcal/mol, respectively.

Discussion

General Considerations. Unimolecular dissociation of a halide ion from α-halocarbanions such as CF_3^- or CCl_3^- formally represents the second stage of a stepwise, base-catalyzed α-elimination of HX from the corresponding haloform molecule. α-Eliminations have been extensively studied in solution and are frequently used to generate carbene intermediates in practical synthetic procedures.[3,4] In polar, protic media, or in the presence of strongly ion pairing countercations, trihalomethyl carbanions and other α-halocarbanions are often unstable with respect to halide dissociation and formation of the corresponding carbene.[4] In the gas phase, stable CX_3^- ions are easily generated in abundance and halide ion dissociation from them requires thermal or photochemical activation.

Collision-induced halide ion dissociation from a trihalomethyl anion has several desireable features for appearance energy measurements and the derivation of thermochemical data. The dissociation is a prototype direct-cleavage process involving structurally simple reactants that produce stable products. The reverse process, nucleophilic addition to a singlet carbene, has been examined computationally for simple cases and has been shown to proceed without a barrier.[44] Moreover, gas-phase flash photolysis studies of the reaction between ${}^1A_1$ CH_2 and H_2O at 298 K give an overall reaction rate that is close to the gas-kinetic limit.[45] For these reasons, we assume that halide ion loss from CX_3^- ions proceeds without any reverse activation energy. Furthermore, the sharply rising halide ion appearance plots (Figures 1 and 2) and normal dissociation cross sections (1–5 Å^2) suggest that these are relatively efficient CID processes and do not suffer from kinetic shifts.

For negative ion CID studies, competitive shifts[46] in the observed dissociation onsets are possible from competing electron detachment from the activated reactant ion. In the case of CCl_3^-, the electron binding energy (2.25 ± 0.10 eV) derived from our $CHCl_3$ acidity measurements[47] is significantly greater than the observed Cl^- dissociation energy (1.31 eV), so collision-induced electron loss is not competitive at threshold (cf. Figure 2). For CF_3^-, however, the electron binding energy $EA(CF_3)$ = 1.84 eV[10] is less than our measured F^- dissociation energy of 2.4 eV (Figure 1) so, in principle, electron detachment can occur in competition with F^- loss at threshold and this could result in a shift in the F^- appearance curve to higher collision energies. The smaller cross sections observed for F^- dissociation from CF_3^- (1 Å^2) compared to Cl^- dissociation from CCl_3^- (5 Å^2) and the difference between the experimental dissociation energy and the calculated one (Table IV) may indicate the occurrence of a small competitive shift in the measured onset. However, we note that electron detachment from CF_3^- has been reported to be a relatively inefficient process due to poor Franck–Condon overlap between the carbanion and radical surfaces. A 1.6-eV difference between the vertical and adiabatic electron affinities of CF_3 was found from photodetachment studies in an ICR.[48] If collision-induced detachment from CF_3^- is similarly slow, then a competitive shift in the F^- dissociation onset becomes less likely. Unfortunately, unambiguous electron scavenging experiments that might clarify the role of electron detachment during CID of CF_3^- are not practical with a triple quadrupole analyzer.

Comparison with Earlier Results. Lias, Karpas, and Liebman (LKL) recently compiled the available thermochemical data for fluoro- and chlorocarbenes and presented a critical evaluation of these data for comparison with their own estimates obtained from proton affinity bracketing in an ICR.[13] Difluorocarbene has been investigated by a variety of experimental methods over a period of 25 years. Analysis of gas-phase thermal dissociation equilibria in which CF_2 is involved leads to values for $\Delta H^\circ_{f,298}({}^1A_1\ CF_2)$ of ca. −44 kcal/mol.[39,49] Slightly lower values (−46 to −47 kcal/mol) are obtained from combinations of the measured value for $IP(CF_2)$ (11.42 ± 0.01 eV)[50] with CF_2^+ appearance energy measurements from various fluorocarbons.[51] Berman et al. recommend a value for $\Delta H^\circ_{f,298}(CF_2)$ of −44.2 ± 1.0 kcal/mol on the basis of measurements of the photoionization onsets for production of ions formed by loss of CF_2 from $CF_2{=}CFCF_3$, c-C_3F_6, and $C_6H_5CF_3$.[52] Their measured value is close to the weighted average (−43.8 ± 2.0 kcal/mol) derived from a compilation of several other measurements in the literature that were adjusted for updated thermochemical data. From analysis of the occurrence of reaction 15 with various reference bases in the gas

$$\mathrm{CHF_2^+} + \mathrm{B} \rightarrow \mathrm{BH^+} + \mathrm{CF_2} \tag{15}$$

phase, LKL assign a proton affinity to CF_2 of 173 ± 1 kcal/mol,[13] which is essentially the same as that obtained earlier from PA bracketing in an ICR by Vogt and Beauchamp (172 ± 2 kcal/mol).[15] The heat of formation of CHF_2^+ has been determined to be 143.4 ± 3.0 kcal/mol by its appearance potential from CH_2F_2.[42] Combining this with $PA(CF_2)$ leads to $\Delta H^\circ_{f,298}({}^1A_1\ CF_2)$ = −49 ± 3 kcal/mol, as reported by LKL.[13]

The present value for $\Delta H_f(CF_2)$ of −39.4 ± 3.4 kcal/mol is nearly 10 kcal/mol higher than the LKL value but within the error limits of the average value recommended by Berman et al.[52] In attempting to understand the discrepancy, it is important to recognize that the present value and the LKL value are both ultimately based on the same three types of experimental data: an ion appearance measurement, a gas-phase acid–base measurement, and a measured combustion enthalpy and heat of va-

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porization for a halogenated methane. If −49 kcal/mol is the true value for $\Delta H_f(CF_2)$, then either an F^- appearance energy of 2.04 eV (47 kcal/mol) would be required from our CF_3^- CID experiments or the reference acidity and/or heat of formation for CHF_3 must be in error by about 10 kcal/mol. Alternatively, for our value to be correct, either the bracketed $PA(CF_2)$ is too low by ca. 10 kcal/mol or the reference data for CHF_2^+ and/or CH_2F_2 are inaccurate.

The MO calculations provide only limited arbitration here. The values for $\Delta H_f(CF_2)$ obtained from the computed enthalpies for isodesmic reaction 13 (−46.4 kcal/mol) and reaction 14 (−46.3 kcal/mol) are both nearly halfway between our measured value and the LKL value. Carter and Goddard recommend a similar value for $\Delta H^\circ_{f,298}(CF_2, g)$ of −46.5 ± 1.6 kcal/mol on the basis of correlation-consistent CI (CCCI) calculations of the $^1A_1$ CF_2 dimerization energy combined with the experimental heat of formation of C_2F_4.[53] The computed F^- dissociation enthalpy of CF_3^- (eq 11) at the MP3/6-31+G(d) level (50.2 kcal/mol) is also nearly halfway between our measured value and that predicted from the LKL value for $\Delta H_f(CF_2)$. However, it is likely that the total correlation energy contribution to this (nonisodesmic) reaction energy is incompletely accounted for. It is significant that the computed gas-phase acidity of CHF_3, 374.5 kcal/mol, is 2.5 kcal/mol *lower* than the experimental value of 377.0 ± 2.1 kcal/mol.[10,34] Gas-phase acidities calculated with double-ζ quality basis sets including zero-point energy and limited correlation corrections (such as in the present case) are almost always *higher* than the true values.[54] Indeed, the calculated gas-phase acidity of $CHCl_3$ (360.7 kcal/mol, Table IV) is 3.1 kcal/mol higher than the experimental value determined in the present study. Thus, it is entirely possible that the fluoroform acidity in the literature is too high. A lower value for $\Delta H_{acid}(CHF_3)$ would lead to a lower (more negative) heat of formation for CF_2 derived from our measured F^- dissociation energy (eq 8). In view of the good agreement among the theoretical values for $\Delta H_f(CF_2)$, as well as the possibilities for error in the fluoroform acidity and/or a small competitive shift in our F^- appearance energy, we suggest that −39.4 kcal/mol represents an accurate upper limit for $\Delta H^\circ_{f,298}(CF_2, g)$, with the true value being closer to −44 kcal/mol, as recommended by Berman et al.

From their proton transfer bracketing experiments, LKL assign the proton affinity of $^1A_1$ CCl_2 to be between that of n-C_3H_7CN and C_2H_5CN, or 193 ± 2 kcal/mol.[13] The heat of formation of $CHCl_2^+$ is reported to be 212 ± 2 kcal/mol from its appearance energy from $CHCl_3$.[42,43] Combining this with $PA(CCl_2)$ led LKL to assign an absolute heat of formation to $^1A_1$ CCl_2 of 39 ± 3 kcal/mol. It was noted by these investigators that their proton affinity and heat of formation for CCl_2 differed significantly from the values derived earlier from PA bracketing by Levi et al. ($PA(CCl_2)$ = 209.6 ± 2.0 kcal/mol, $\Delta H_f(CCl_2)$ = 56 ± 2 kcal/mol).[55] They argued that the earlier measurements were complicated by the occurrence of fast, competing side reactions of $CHCl_2^+$ with the reference bases that obscured the thermochemical threshold for proton transfer. Ironically, in the same year as the LKL investigation, a photoionization study of CF_2CCl_2 and CCl_2 appeared in which the heat of formation and adiabatic ionization potential for $^1A_1$ CCl_2 were determined.[56] The derived value for $\Delta H^\circ_{f,298}(^1A_1\ CCl_2)$ of 54.9 ± 2.0 kcal/mol is in excellent agreement with earlier ICR measurements criticized by LKL. It is noteworthy that these investigators chose to use a value for $\Delta H_f(CF_2)$ of −43.5 ± 1.5 kcal/mol in deriving the heat of formation of CCl_2 from the measured CCl_2^+ appearance energy.

Cheng and Grabowski reported a redetermination of $\Delta H_f(CCl_2)$ based on measurements of the gas-phase acidity of the dichloromethyl radical, $CHCl_2$ (eq 16).[57] From their bracketed acidity (ΔH_{acid}) of 362.4 ± 3.0 kcal/mol and auxilliary thermochemical data for $CHCl_2$ and CCl_2, they assign the heat of formation of $^1A_1$ CCl_2 to be 57.2 ± 4.0 kcal/mol.

$$CCl_2^- + HA \rightarrow A^- + CHCl_2 \qquad (16)$$

The calculated heats of formation for CCl_2 derived from the ab initio results for reaction 13 (56.2 kcal/mol) and reaction 14 (52.9 kcal/mol), as well as the computed Cl^- binding energy of CCl_3^- (30.9 kcal/mol), are all in good agreement with the experimental results. The computed gas-phase acidity for $CHCl_3$ is slightly high, as expected. The calculated *difference* in acidities between $CHCl_3$ and CHF_3, which should be more reliably estimated from the ab initio calculations,[54] is 13.8 kcal/mol, compared to the experimental difference of 19.4 kcal/mol. This again suggests that the literature value for $\Delta H_{acid}(CHF_3)$ is probably too high.

In view of the good general agreement among the values for $\Delta H_f(CCl_2)$ derived from such diverse experimental approaches as CCl_2 photoionization (54.9 ± 2.0 kcal/mol),[56] $CHCl_2$ acidity bracketing (57.2 ± 4.0 kcal/mol),[57] CCl_2 proton affinity bracketing (56 ± 2 kcal/mol),[55] and CCl_3^- collision-induced dissociation (52.1 ± 3.4 kcal/mol), it seems likely that the LKL value (39 ± 3 kcal/mol) is in error. Our ab initio calculations suggest that the proton affinity of $^1A_1$ CCl_2 is close to 207 kcal/mol—some 13 kcal/mol higher than that obtained by the LKL. Possible sources of error in the PA bracketing experiments include residual vibrational or translational excitation in the $CHCl_2^+$ reactant ion that could lead to a lower apparent basicity for CCl_2 and/or the occurence of fast secondary reactions or reactions with impurity ions in the ICR that leads to protonation of reference bases with proton affinities below 207 kcal/mol.

Carbon–Carbon Bond Strengths in C_2F_4 and C_2Cl_4. Discrepancies among any measured or calculated values for $\Delta H_f(CX_2)$ are amplified by a factor of 2 in comparing the corresponding derived values for $DH_{298}[X_2C{=}CX_2]$. Using $\Delta H_f(CF_2)$ = −39.4 ± 3.4 kcal/mol from our CID measurements, we obtain $DH_{298}[F_2C{=}CF_2]$ = 79.1 ± 3.8 kcal/mol. This bond strength is in fair agreement with the equilibrium $CF_2{=}CF_2$ bond dissociation enthalpy of 76.3 ± 3.0 kcal/mol obtained by Margrave and coworkers from Knudsen cell experiments at 1200 K[49c] but is significantly higher than the value of 64.5 ± 2.5 calculated by Carter and Goddard.[53] The higher value derived from our CID results probably represents a reliable upper limit, for the reasons cited earlier. Using the recommended value for $\Delta H_f(CF_2)$ of −44 kcal/mol, we obtain $DH_{298}[F_2C{=}CF_2]$ = 70 kcal/mol—a value halfway between the thermal equilibrium value[49c] and the value calculated by Carter and Goddard.[53]

The carbon–carbon bond enthalpy in $Cl_2C{=}CCl_2$ (106.3 ± 4.9 kcal/mol) derived from our CID threshold results is ca. 14 kcal/mol lower than the bond energy predicted by Carter and Goddard (120.4 ± 2.1 kcal/mol) on the basis of CCCI calculations of the singlet–triplet energy gap in CCl_2 (ΔE_{ST} = 25.9 kcal/mol)[58] and a presumed relationship between double bond strengths and carbene singlet–triplet splittings (eq 17).[59] Here, the premise

$$DH_{298}[X_2C{=}CX_2] = DH_{298}[H_2C{=}CH_2] - 2\Delta E_{ST}(CX_2) \qquad (17)$$

is that the C=C bond energy in a halogenated olefin is weakened relative to the C=C bond in ethylene ($DH_{298}[H_2C{=}CH_2]$ = 172.2 ± 2.1 kcal/mol) by an amount equal to the promotion energy ΔE_{ST} required to prepare the halocarbene fragments in their triplet bonding state. Subsequent calculations by Shin et al.[60] using an improved computational method (DCCI) yield a lower value for $\Delta E_{ST}(CCl_2)$ of 20.9 kcal/mol and a correspondingly higher value

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for $DH_{298}[Cl_2C{=}CCl_2]$ of 130.4 kcal/mol. From this bond energy and the experimental heat of formation for C_2Cl_4, the heat of formation of $^1A_1$ CCl_2 is predicted to be 64.2 kcal/mol—a value that is well outside the error limits on any of the experimentally determined values. Similarly, if one uses the present value for $DH_{298}[Cl_2C{=}CCl_2]$ (106.3 ± 4.9 kcal/mol) in conjunction with eq 17, then a singlet–triplet splitting of 33.0 kcal/mol is predicted for CCl_2—a result that is well outside the probable error in the DCCI calculations.[14b,58] We therefore conclude that the relationship described by eq 17, while certainly having qualitative utility, is of limited use for reliable *absolute* predictions of C=C bond energies and carbene singlet–triplet energy gaps, at least for the dihalocarbene systems examined here.

Grev, Schaefer, and Baines recently described an alternative analysis of the C=C bond energies in haloethylenes and related organometallic compounds in terms of the "divalent-state stabilization energy" (DSSE) of the component carbene fragments.[61] The DSSE, originally defined by Walsh for binary SiX_4 compounds,[62] is simply the difference between the first and second C–X bond energies in a CX_4 molecule, i.e., DSSE = $D[X_3C{-}X] - D[X_2C{-}X]$. These parameters were shown by Grev et al. to correlate with the strengths of double bonds in substituted alkenes, disilenes, and digermenes, although for systems with electronegative substituents the quantitative accuracy of the correlations was relatively poor. However, an advantage of DSSE values is that, unlike the Carter and Goddard model, they are independent of the ground-state multiplicity of the carbene fragments. From a consideration of the DSSE values for SiH_2, SiHCl and $SiCl_2$ derived from the sequential dissociation energies of various SiH_nCl_m compounds, Grev et al. concluded that the DSSE is a function of the silylenes only; i.e., it is essentially independent of the tetravalent silane from which it is derived. From the heats of formation for CF_2 and CCl_2 obtained in the present study, we can derive DSSE values for these carbenes and evaluate the proposed independence of DSSE on the precursor. While DSSE is formally defined in terms of bond dissociation energies at 0 K, the errors imposed by using 298 K heats of formation are minor compared to the absolute experimental uncertainties. The first C–X bond energies in CF_4 and CCl_4 are known to be 130 ± 2 and 71 ± 2 kcal/mol, respectively.[10] The second C–X bond energies determined from the heats of formation for CF_2, CCl_2, and the corresponding trihalomethyl radicals (Table I) are $DH_{298}[F_2C{-}F] = 92 \pm 4$ and $DH_{298}[Cl_2C{-}Cl] = 63 \pm 4$ kcal/mol, from which we calculate DSSE values for CF_2 and CCl_2 of 38 ± 4 and 8 ± 4 kcal/mol, respectively. Similarly, the first C–H bond energies in CH_2F_2 and CH_2Cl_2 are 103 ± 1 and 97 ± 1 kcal/mol,[10] while the second C–H bond energies are 70 ± 4 and 82 ± 4 kcal/mol, respectively (Table I). Thus, from CH_2X_2 precursors, the DSSE's are 33 ± 4 kcal/mol for CF_2 and 15 ± 4 kcal/mol for CCl_2. Within error, the DSSE values for each carbene derived from the two different precursors are the same, although just barely so for CCl_2. We note, however, that the first C–Cl and C–H bond energies in CCl_4 and CH_2Cl_2 need only change by 1–2 kcal/mol in order to make the two CCl_2 DSSE's identical. Therefore, this limited data set further supports the notion that DSSE depends only on the divalent species being considered.

Conclusions

We have described here a new experimental strategy for obtaining thermochemical information for gas-phase halocarbenes and an application of this approach to the determination of heats of formation for $^1A_1$ CF_2 and $^1A_1$ CCl_2. Analysis of the threshold dissociation behavior of collisionally activated trihalomethyl anions in a flowing afterglow–triple quadrupole apparatus yields accurate limiting values for the carbon–halide bond dissociation enthalpies, $DH_{298}[CX_2{-}X^-]$. These bond dissociation enthalpies can be combined with known or measurable heats of formation for CX_3^- and X^- ions to yield heats of formation for the corresponding singlet dihalocarbenes. The derived value for CF_2 of −39.4 ± 3.4 kcal/mol is slightly higther than the recommended value of −44 kcal/mol. We suggest that the observed dissociation onset for CF_3^- could be slightly shifted to higher collision energy due to competing electron detachment from this ion at threshold. Also, potential inaccuracies in the gas-phase acidity of CHF_3 that was used to derive $\Delta H_f(CF_2)$ are suggested by our molecular orbital calculations. The value for $\Delta H_f(CCl_2)$ of 52.1 ± 3.4 kcal/mol obtained in the present study is in good agreement with recent measurements by different techniques in other laboratories[55-57] but significantly higher than the value of 39 ± 3 kcal/mol recommended by Lias, Karpas, and Liebman on the basis of proton transfer bracketing experiments with $CHCl_2^+$ in an ICR. The origin of the discrepancy is traced to a misassignment of the proton affinity of CCl_2. High-level ab initio MO calculations suggest a value for $PA(CCl_2)$ of 207 kcal/mol, which leads to a heat of formation for CCl_2 in good agreement with the present experimental results.

The experimental thermochemistry for CF_2 and CCl_2 has been used to evaluate the Carter and Goddard proposal concerning the quanitative relationship between C=C bond energies and triplet excitation energies of singlet carbenes (eq 17).[58,59] It is shown that while fair agreement is obtained between the actual and predicted value for $DH_{298}[F_2C{=}CF_2]$,[53] the predicted C=C bond enthalpy for $Cl_2C{=}CCl_2$ based on the current best estimate for $\Delta E_{ST}(CCl_2)$ = 20.9 kcal/mol[60] is well outside the range of experimentally determined values. Similarly, the recommended value for $DH_{298}[Cl_2C{=}CCl_2]$ of 106.3 ± 4.9 kcal/mol leads to a predicted singlet–triplet splitting for CCl_2 that is inconsistent with the accurately calulated value. The simple relationship shown in eq 17 should therefore be applied with caution.

The CID threshold technique described here should be applicable to other carbenes. In surveying the scope and limitations of this method, we have found that cyclic and acyclic α-halocarbanions bearing a wide variety of different substituents can be formed in the gas phase using standard negative ion synthesis procedures. Moreover, halide ion dissociation from these species appears to be a general and kinetically facile decomposition pathway. We have discussed the potential complicating effects on CID threshold measurements of electron detachment from the collisionally activated halocarbanions. For this reason, dissociations involving α-fluorocarbanions are anticipated to be problematic since the carbene–halide ion binding energies are maximal for fluoride,[66] but the electron affinities of fluorinated radicals are comparatively low.[10] α-Chlorocarbanions probably provide the best compromise here. It should also be noted that while dissociation to the singlet carbene is the spin-conserving process, the halide ion appearance curves reflect the lowest energy, kinetically accessible decomposition route. α-Halocarbanions that produce carbenes with triplet ground states may well dissociate with collision energies less than that of the singlet carbene asymptote if the intersystem crossing rate is competitive with the rate of unimolecular decomposition at threshold. We are presently examining the dissociation behavior of simple monohalomethyl anions, CH_2X^-, X = Cl, Br, I, in order to address this issue.

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