

region, having a reported k_{obsd} of $7.0 \pm 3.0 \times 10^{-6} \text{ s}^{-1}$.²⁹ By way of comparison, the k_{obsd} value for hydrolysis of **3** in the plateau region is $1.44 \times 10^{-3} \text{ s}^{-1}$. The acceleration of 100–200-fold is quite reasonable for general-base catalysis of imidazole over a similar role for carboxylate in such hydrolyses^{27a} and argues against a nucleophilic role for either species.

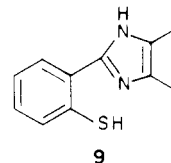
If our results can be accurately transposed to the case of the deacylation of papain, it is likely that the active site imidazole can indeed function as a general base. It is somewhat difficult to determine the magnitude of the rate enhancement to thiol ester hydrolysis which is attributable to the intramolecular general-base role for imidazole since the H_2O term for thiol esters is undetectably small. Some estimate for the rate enhancement in **3** relative to the attack of OH^- can be made by extrapolating the $k_3(\text{OH}^-)$ term (Table I) for **3** to a given pH. Hence at pH 7–8, the imidazole unit affords some 10^3 acceleration over the pseudo-first-order rate constant for attack of OH^- on **3**. The overall rate of deacylation for **3** is quite slow relative to that for the fastest deacylations of various acylpapains ($3\text{--}46 \text{ s}^{-1}$)³⁰ but compared favorably with that reported for *trans*-cinnamoylpapain ($k_{\text{deacylation}} = 3.68 \times 10^{-3} \text{ s}^{-1}$).^{27a} It might be that the slow deacylation of **3** is a consequence of a nonideal fit of H_2O between the imidazole N and acyl C=O group, a problem which might be overcome by a suitable structural change.³⁰ However, insofar as we are aware, the hydrolysis of **3** represents the only well-defined chemical precedent for imidazole acting as an intramolecular general base in promoting the hydrolysis of a thiol ester. The observed solvent isotope effect of 3.75 for **3** is consistent with this interpretation

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and compares favorably with those observed for the deacylation of α -*N*-benzoyl-L-arginylpapain and *trans*-cinnamoylpapain (2.75 and 3.35, respectively).^{1d,27a}

Finally it is of note that **3** and its free mercaptan hydrolysis product **9** were designed as models for the acylated and free forms



of the active site of papain. Accordingly, **9** does indeed act as a true nucleophilic catalyst in promoting the hydrolysis of *p*-nitrophenylacetate.^{18b,30}

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Registry No. **3**, 97878-91-6; **3**·HCl, 97879-00-0; **3** (mercaptan), 97878-97-2; **3** (disulfide), 97878-98-3; **4**, 97878-92-7; **5**, 934-87-2; *S*-benzylthiosalicylamide, 54705-18-9; 2-(benzylthio)benzylamine, 97878-93-8; ethyl oximinoacetoacetate, 5447-76-7; (2-(benzylthio)phenyl)-4-carbomethoxy-5-methylimidazole, 97878-94-9; 2-(2-(benzylthio)phenyl)-4,5-dimethylimidazole, 97878-95-0; 2-(2-(benzylthio)phenyl)-4,5-dimethylimidazole picrate, 97878-96-1; 2-(2-mercaptophenyl)-4,5-dimethylimidazole hydrochloride, 97878-99-4; 4-carbomethoxy-5-methyl-2-phenylimidazole, 77335-93-4; 4,5-dimethyl-2-phenylimidazole, 13682-20-7; 5,5'-dithiobis(2-nitrobenzoic acid), 74959-07-2; cysteine protease, 37353-41-6; benzenethiol, 108-98-5; 2-mercaptoethanol, 60-24-2.

Halomethylenes: Effects of Halogen Substitution on Absolute Heats of Formation

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Abstract: New values for the heats of formation of CF_2 , CCl_2 , CClF , CFH , and CClH have been derived from estimations of the thermochemistry of the reaction(s) $\text{CXYH}^+ + \text{B} \rightarrow \text{CXY} + \text{BH}^+$ where X and Y are F and/or Cl and B is a molecule for which an absolute value of the gas-phase basicity (or proton affinity) is available. The experiments, carried out in an ion cyclotron resonance spectrometer, lead to the following values for the heats of formation (in kcal/mol) of the ground-state singlet carbenes: CF_2 , -49 ± 3 ; CCl_2 , 39 ± 3 ; CFCl , -2 ± 7 ; CFH , 26 ± 3 ; CClH , 71 ± 5 . The value for CF_2 is lower by about 5 kcal/mol than the previously accepted value, but in good agreement with values derived from previous "bracketing" results and also in agreement with values derived from the observed threshold energies for ionic dissociation processes. The value for CCl_2 is significantly lower than the 1976 value of 47 ± 3 kcal/mol recommended by S. W. Benson, but in good agreement with an earlier value (40 ± 5 kcal/mol) recommended by this author and with more recent experimental results on the onset energy for the formation of Cl_2^- from CCl_4 . The values for CFH , CClH , and CFCl are all approximately equal to the averages of the heats of formation of the corresponding CX_2 and CY_2 species, in agreement with assumptions made in previous estimates of these quantities. Values for the C–X bond energies in the halomethylenes, the heats of formation of the corresponding CXY^+ ions, and the ionization potentials of the CXY species are derived from the results. From the most recent calculations of the energy differences between the ground-state singlet halomethylenes and the first triplet state, values for the heats of formation of the triplet halomethylenes are obtained; an analysis of trends in these values indicates that $^3\text{CF}_2$ is substantially destabilized.

There has been considerable interest in carbene chemistry in recent years.^{2,3} Theoretical³ and experimental² examinations of

the properties of halogenated carbenes have provided information about the nature of the ground and first excited electronic states,

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Table I. Heats of Formation of Halomethylenes

species	ΔH_f , kcal/mol	method	ref
CF ₂	<-34.0	photoionization of C ₂ F ₄ (AP(CF ₂ ⁺) = 15.26 eV)	5, 7
	<-34.7	photoionization of C ₂ F ₄ (AP(CF ₂) = 15.2 eV)	6, 7
	-39.7	analysis of data on CF ₂ HCl → CF ₂ + HCl	25b
	-41.2 ± 2	thermal equilibrium: C ₂ F ₄ ⇌ CF ₂ + CF ₂	8
	<-41.6 ± 2	photoionization of C ₂ F ₄ (AP(CF ₂ ⁺) = 14.63 eV)	9, 7
	-42 ± 4	thermal equilibrium: CHF ₂ Cl ⇌ CF ₂ + HCl	10
	-44.1 ± 2	thermal decomposition of CF ₃ H, CHClF ₂ , C ₂ F ₄	11
	<-44.2 ± 1	photoionization of C ₃ F ₆ (AP(C ₂ F ₄ ⁺) = 13.04 eV)	12
	-44.5 ± 1	analysis of thermal equilibrium data	13
	-44.6	analysis of thermal equilibrium data	20
	-45.4 ± 2	thermal equilibrium: C ₂ F ₄ ⇌ CF ₂ + CF ₂	14
	<-45.9 ± 3	photoionization of CF ₃ Cl	15, 7
	-46.4	analysis of data on: CHF ₂ Br ⇌ CF ₂ + HBr	16
	<-47.1 ± 3	photoionization of CF ₂ Cl ₂	15, 7
	-48.0 ± 1	bracketing: CF ₂ H ⁺ + B → BH ⁺	19
	-49.0 ± 3	bracketing: CF ₂ H ⁺ + B → BH ⁺	this work
	-50.8 ± 2	bracketing: CF ₂ H ⁺ + B → BH ⁺ + CF ₂	17
	-56.0 ± 3	onset for CF ₂ Cl ₂ → CF ₂ + Cl ₂ ⁻	18
CCl ₂	<59	threshold for CCl ₃ F → CCl ₂ ⁺ + Cl + F	15, 21 ^a
	<57	threshold for C ₂ Cl ₄ → CCl ₂ ⁺ + CCl ₂ (IP(CCl ₂) = 9.76 eV)	13, 21
	55	bracketing: CCl ₂ H ⁺ + B → BH ⁺ + CCl ₂	22
	<54	threshold for CCl ₄ → CCl ₂ + Cl ₂ ⁻ (2.3 eV)	24 ^b
	<54	threshold for CCl ₃ H → CCl ₂ ⁺ + HCl (IP(CCl ₂) = 9.76 eV)	21
	<53	threshold for CCl ₄ → CCl ₂ + Cl ₂ (IP(CCl ₂) = 9.76 eV)	21
	<50	threshold for CCl ₃ H → CCl ₂ ⁺ + HCl (EA = 41.5)	24
	48	bracketing: CCl ₂ H ⁺ + B → BH ⁺ + CCl ₂	19a
	47 ± 3	recommended value: source of data unspecified	25a
	<46	bracketing: CCl ₂ H ⁺ + B → BH ⁺ + CCl ₂	19b
	<42	threshold for CCl ₄ → CCl ₂ + Cl ₂ ⁻ (0.5 ± 0.1 eV)	24
	40 ± 5	analysis of data (ref 25c) on CCl ₃ H → CCl ₂ + HCl	25b
	39 ± 3	bracketing: CCl ₂ H ⁺ + B → BH ⁺ + CCl ₂	this work
	<30	threshold for CCl ₂ H ₂ → CCl ₂ ⁻ + H ₂ (EA = 41.5)	24
	<30	threshold for CCl ₄ → CCl ₂ + Cl ₂ ⁻ (0 eV)	26
CFCl	<32 ± 10	threshold for CFCICFCl → CFCl ⁺ + CFCl (15.3 eV)	6 ^c
	<3 ± 6	threshold for CCl ₃ F → CFCl + Cl ₂ ⁻ (0.6 eV)	18
	-2 ± 7	bracketing: CFCIH ⁺ + B → BH ⁺ + CFCl	this work
CFH	39	bracketing: CFH ₂ disproportionation reactions	45
	39	estimate (averaging data for ¹ CH ₂ , ¹ CF ₂)	43
	30	estimate (averaging data for ¹ CH ₂ , ¹ CF ₂)	13
	26 ± 3	bracketing: CFH ₂ ⁺ + B → BH ⁺ + CFH	this work
	25	estimate (averaging data for ³ CH ₂ , ¹ CF ₂)	42
CClH	80 ± 10	estimate	13
	71 ± 5	bracketing: CClH ₂ ⁺ + B → BH ⁺ + CClH	this work

^a $\Delta H_f(\text{CCl}_3\text{F})_{0\text{K}}$, -63.3 kcal/mol. ^b Ion formed with 29.5 kcal/mol kinetic energy. ^c Takes $\Delta H_f(\text{CFCl}^+) = 243$ from ref 15.

as well as the structures and vibrational frequencies of the CX₂, CXY, and CHX species (where X and Y are F or Cl).⁴ For instance, it has been established^{3a} that the ground states of CF₂ and CCl₂, as well as CHF and CHCl, are singlets, while CH₂ has a triplet ground state. Even so, the heats of formation of most of the halocarbons are not well established. Experimental determinations of these heats of formation, primarily those of CF₂ and CCl₂, have been carried out with a number of diverse ap-

proaches.⁵⁻²⁷ Available experimental results, summarized in Table I, show that there is appreciable scatter in the reported values for

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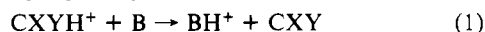
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heats of formation of halocarbenes.

In this paper, we report new determinations of the heats of formation of CF_2 , CCl_2 , CFCl , CFH , and CClH based on observations of the gas-phase proton transfer reactions:



(where X and Y are F and/or Cl). Information about the enthalpy changes of these reactions is derived in experiments in which the CXYH^+ ions (with known heats of formation) are reacted with a series of proton-acceptor molecules for which the proton affinities (and gas basicities) are established. The proton affinity is defined as the enthalpy change for the hypothetical process



while the gas basicity is the Gibbs free energy change for the same process. In the technique used here, which is known as "bracketing", it is generally assumed that if process 1 is observed with a particular base, B, then the gas basicity (or approximately, the proton affinity) of CXYH^+ is below that of B, and if process 1 does not occur, then the gas basicity is probably above that of B.

The success and reliability of this procedure of course depend on (a) the availability of a well-established and accurate scale of gas-phase basicities of molecules as well as (b) accurate values for the heats of formation of the CXYH^+ ions and (c) the validity of the criteria used to estimate the point at which reaction 1 turns from exothermic to endothermic. Although this technique has been applied before to determine the heats of formation of CF_2 ^{17,19} and CCl_2 ,^{19,22,25} variations in the assignments of absolute values to the proton affinity scale during the years when these determinations were made (1975–1978) resulted in large apparent discrepancies in reported heats of formation of the carbenes. This problem is now obviated by a recent comprehensive evaluation²⁹ of the data comprising an extensive interlocking scale of relative gas-phase basicities and of heats of formation of certain relevant BH^+ ions. As a result, the assignment of absolute values to the enthalpy changes associated with process 2 (that is, the proton affinities of the molecules, B) are firmly established for that part of the proton affinity scale which lies below approximately 190 kcal/mol (i.e., that part of the scale which applies to the determinations to be presented here, as will be shown below).

The most difficult aspect of establishing heats of formation of carbenes by this so-called "bracketing" technique lies in pinpointing the bases (B) for which the proton transfer reaction 1 turns from endothermic to exothermic, since, as pointed out before,²⁵ the simple observation that reaction 1 does not occur for a particular reactant pair does not in itself constitute evidence that the reaction is endothermic. Highly exothermic proton-transfer reactions may not occur if other energetically or sterically more favorable reaction

paths are available to the pair. The cutoff point can only be unequivocally established by an examination of the reactions of CXYH^+ with several chemically different bases having similar proton affinities in the vicinity of the cutoff point. One may fail to observe an exothermic proton-transfer reaction, but the observation in the ion cyclotron resonance spectrometer of a BH^+ ion unequivocally originating in a single step from a reaction of CXYH^+ (as evidenced by experiments in which CXYH^+ and other possible precursor ions are ejected from the system with double resonance) is indicative that reaction 1 for the particular reactant pair is exothermic or near thermoneutral.

Experimental Section

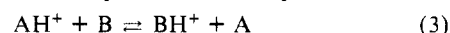
The experiments were carried out by using the NBS pulsed ion cyclotron resonance spectrometer, which has been described previously.³⁰ The inlet system of the spectrometer was improved prior to the initiation of this work by the installation of two leak valves and one servo-motor controlled leak valve, so that better control of the pressures of the reactant gases could be achieved. The pressures of the reactant compounds were monitored during an experiment by an ionization gauge which was calibrated separately for each individual compound against a capacitance manometer.

The appropriate halomethyl ions were generated in halomethanes as follows: CF_2H^+ in CF_3H , CCl_2H^+ in CCl_3H , CFClH^+ in CFCl_2H , CFH_2^+ in CFH_3 , CClH_2^+ in CH_2Cl_2 , and CCl_2H^+ in CCl_3H . The CF_2H^+ , CCl_2H^+ , CCl_2H_2^+ , and CCl_2H_2^+ ions do not undergo reactions with the corresponding precursor compounds. The CFH_2^+ and CFClH^+ ions reacted slowly with their respective precursor halomethanes.

Results and Discussion

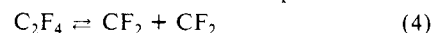
Assignment of Absolute Values to the Proton Affinity Scale.

The proton affinities of the reference bases used in this investigation are based on a proton affinity scale which was mainly derived from numerous studies²⁹ which reported equilibrium constant determinations for proton-transfer equilibria:



The resulting relative scale has been put on an absolute basis²⁹ taking as reference standards species imbedded in the scale for which heats of formation of BH^+ at 298 K are well established from appearance potential measurements. For that portion of the scale of interest for the experiments to be described here (i.e., proton affinities between 190 and 165 kcal/mol) appropriate comparison standards are ethylene and propylene, with proton affinities of 162.6 and 179.5 kcal/mol, respectively. The 298 K heats of formation of C_2H_5^+ (215.6 kcal/mol)³¹ and $i\text{-C}_3\text{H}_7^+$ (191.0 kcal/mol)^{31,32} on which the assignment of the proton affinities is based are well established. The correctness of the assignment of the overall scale in this region has been further confirmed by a recent evaluation³³ of high-level ab initio calculations of proton affinities, which confirmed the proton affinity values cited for PH_3 (188.6 kcal/mol) and H_2S (170.2 kcal/mol), and obtained a value for the proton affinity of H_2O within 1–2 kcal/mol of the experimental value.

CF_2 . The thermochemistry of difluoromethylene has been studied much more extensively than that of any other halomethylene.^{5–20} The values for the heat of formation of CF_2 derived from a variety of experimental approaches are summarized in Table I. Studies of the kinetics of the thermal equilibria lead to



values for $\Delta H_f(\text{CF}_2)$ which vary between –41.2 and –46.4

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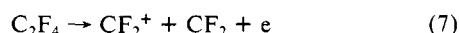
Table II. Thermochemical Data Used in This Study

species	ΔH_f° (298 K), kcal/mol	ref	species	ΔH_f° (298 K), kcal/mol	ref
CH ₃ F	-59.0	45	CF ₂ H ⁺	143.4 ^a	38
CH ₂ F ₂	-108.2	13, 28b	CCl ₂ H ⁺	212 ^a	39
CHF ₃	-165.7	36	CFClH ⁺	178 ^a	37
CF ₄	-223.4	13, 28b, 36	CFH ₂ ⁺	199 ^a	38
CH ₃ Cl	-19.3	28b, 36	CClH ₂ ⁺	229.2 ^a	39
CH ₂ Cl ₂	-22.8	28b, 36	CH	141.7	13, 21, 40
CHCl ₃	-24.7	28b, 36	CF	57.6	40
CCl ₃ F	-64.1	28b	CCl	104	see discussion
CCl ₂ F ₂	-114.1	28b	CH ₅ ⁺	216 ^a	29
CF ₃ Cl	-166	28b		219 ^{a,b}	33
CCl ₄	-22.9	13, 36	H ⁺	365.7 ^a	13
CH ₄	-17.9	28			
CF ₂ HCl	-115.6 ± 3	13, 28b			
CFHCl ₂	-67.7 ± 3	13			
C ₂ F ₄	-157.9	28			

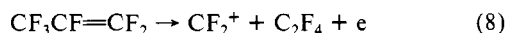
^aAll heats of formation of positive ions given with use of the stationary electron convention; values as given in ref 13 and 28a are 1.48 kcal/mol higher due to inclusion of heat capacity of electron, here defined to be zero. Values for halomethyl ions given here have been derived from appearance potentials in the cited references, using 0 K heats of formation of neutral halomethanes and correcting the resulting 0 K heats of formation of halomethyl ions to 298 using vibrational frequencies reported in ref 4 and/or ref 46. ^bTheoretical value.

kcal/mol. Evaluations of these data have led to recommendations for the value for the 298 K heat of formation of CF₂ of -43.5 ± 1.5,¹³ -44.6,²⁰ or -43.8 ± 2 kcal/mol,¹² all in essential agreement.

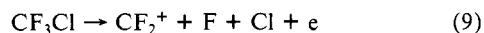
A value for the adiabatic ionization energy of CF₂ of 11.42 ± 0.01 eV has been reported.⁷ Accepting this value, it is also possible to derive values for the heat of formation of CF₂ from measurements of appearance energies of processes in which CF₂⁺ is formed. For example, from the appearance energy,^{5,6,9} 14.63 eV, of the process



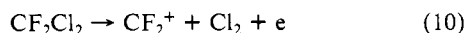
an upper limit for $\Delta H_f^\circ(\text{CF}_2)$ of -41.6 kcal/mol can be estimated. Similarly, the appearance energy¹² of 13.04 eV reported for



leads to an upper limit of -44.2 kcal/mol for the heat of formation of CF₂ (based on a value of -268.9 kcal/mol for the heat of formation of CF₃CF=CF₂³⁵), while the appearance energies of the processes¹⁵

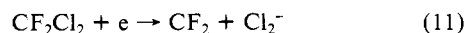


and



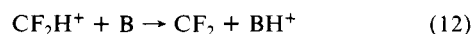
of 18.84 and 16.98 eV, respectively, lead to values of -45.9 and -47.1 kcal/mol, respectively. Since all values derived from appearance potential measurements must be considered as upper limits (because of the possible existence of kinetic shifts or barriers in the dissociation channel), we use the internally consistent (within experimental error) latter two results to assign an upper limit of approximately -47 kcal/mol to the heat of formation of CF₂.

A measurement¹⁸ of the onset energy for the process



leads to a much lower value for $\Delta H_f^\circ(\text{CF}_2)$, -56.0 ± 5 kcal/mol.

Table III summarizes results from earlier studies, as well as the experiments performed as part of this study concerning the observation of the reaction



for a number of bases of varying gas basicity. The results reported

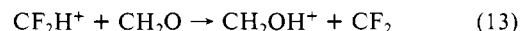
Table III. Rate Constants and Probabilities of Proton Transfer for the Reaction CF₂H⁺ + B → BH⁺ + CF₂

B	proton affinity, ^a kcal/mol	$k_{\text{pn}} \times$ 10 ¹⁰ , cm ³ / (molecule s)	% proton transfer	ref
HCOOCH ₃	188.9		91	19
PH ₃	188.6		100	19
CH ₃ CN	188.4	14.6	not observed	17
CH ₃ CH ₂ OH	188.3		5	19
CH ₃ CHO	186.6		92	19
		16.6	not observed	17
C ₆ H ₅ F	182.6	14.9 ± 0.8	observed	this work
CH ₃ OH	181.9		69	19
		10.4	not observed	17
CH ₃ NO ₂	179.2	14.1 ± 0.7	observed	this work
AsH ₃	179.2		9	19
		2.2	not observed	17
HCOOH	178.8		30	19
C ₆ F ₆	177.7	0.38 ± 0.02	observed	this work
CCl ₃ CH ₂ OH	177.4		observed	this work
CH ₂ =CF ₂	176		observed	this work
CH ₂ (CN) ₂	175.6		observed	this work
H ₂ CO	171.7	0.73	observed	17
HCN	171.4	<0.01	not observed	17
			not observed	this work
H ₂ Se	171.3	0.69	not observed	this work
H ₂ S	170.2		not observed	19
			not observed	this work
H ₂ O	166.5	<0.01		17

^aAll proton affinity values from ref 29.

here on the proton-transfer reactions of CF₂H⁺ are in good agreement with results from the earlier studies, specifically confirming the previously reported¹⁷ bracketing of proton transfer from CF₂H⁺ between formaldehyde and hydrogen cyanide, and providing additional confirming brackets between hydrogen selenide and CH₂(CN)₂. Accepting the evaluated heats of formation for the halomethyl ions given in Table II, the proton-transfer bracketing experiments previously reported in the literature^{17,19a} lead to values for the heat of formation of CF₂ of -50.8 or -48.0 kcal/mol (Table I).

Vogt and Beauchamp¹⁷ concluded that the proton transfer from CF₂H⁺ to formaldehyde was approximately thermoneutral. Lias and Ausloos^{19a} bracketed the gas basicity of CF₂ between those of hydrogen sulfide and formic acid and suggested that the inefficient proton transfer



observed by Vogt and Beauchamp¹⁷ was possibly endothermic by as much as 2 kcal/mol. If the proton-transfer reaction 13 to formaldehyde is considered to be thermoneutral (that is, if the gas basicity of CF₂ is taken as 164.0 kcal/mol), one obtains a value of 172.0 for the proton affinity of CF₂. However, considering the inefficiency of the reaction with formaldehyde, and the total lack of proton transfer to hydrogen cyanide and hydrogen selenide (which have gas basicities which are lower by only about 0.5 kcal/mol), it is reasonable to assume that the proton transfer to formaldehyde is slightly endothermic (by 0.5 to 1 kcal/mol) and assign a value of 173 ± 1 kcal/mol to the proton affinity of CF₂. This leads to a value of -49 kcal/mol for the heat of formation (taking the 298 K heat of formation of CF₂H⁺ to be 143.4 ± 3 kcal/mol³⁸).

This result is in good agreement with the values derived from the appearance energies for processes 9 and 10 (Table I) but indicates that the heat of formation of CF₂ is lower by 4–5 kcal/mol than the value derived from thermal dissociation data.^{8,10,11,13,14,16,20} Vogt and Beauchamp¹⁷ have pointed out that there is a discrepancy between the accepted^{13,20} heat of formation of CF₂ (-44.6 kcal/mol) and the value derived from proton affinity

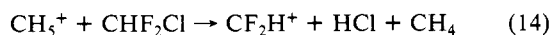
(36) Rodgers, A. S.; Chao, J.; Wilhoit, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1974**, *3*, 117.

(37) Lias, S. G.; Ausloos, P. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *23*, 273.

(38) Lossing, F. P. *Bull. Soc. Chim. Belg.* **1972**, *81*, 125.

(35) Bryant, W. M. D. *J. Polym. Sci.* **1962**, *56*, 272.

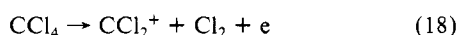
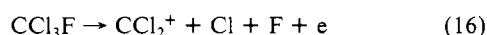
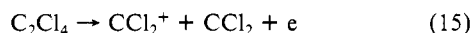
bracketing experiments;^{17,19a} they attributed the problem to a lack of accurate thermochemical data on the halomethanes, resulting in the assignment of an incorrect value for the heat of formation of the CF_2H^+ ion. However, a re-examination of evaluated data on the heats of formation of halomethanes^{13,28,36} (Table II) does not indicate the existence of discrepancies or inconsistencies which could account for a difference as large as 4–5 kcal/mol in the heat of formation of CF_2H^+ . Indeed, since the reaction



occurs with a high efficiency,³⁷ the maximum value for the heat of formation of CF_2H^+ must lie in the region 141–144 kcal/mol (depending on which value one accepts for the 298 K heat of formation of CH_5^+ , Table II), which limits the value for the heat of formation of CF_2 to be more negative than –48 to –51 kcal/mol. The 4–5 kcal/mol discrepancy between the heat of formation of CF_2 emerging from these experiments and the value derived from thermal equilibrium results remains unexplained, although a careful re-examination of the internal consistencies and the error limits associated with the heats of formation of the various relevant neutral molecules seems to be warranted.

Accepting the value for the heat of formation of CF_2 indicated by the results of the present study, –49 kcal/mol, it appears that the thermodynamic threshold for process 7 is 14.02 eV, significantly lower than any of the reported values for onset of this process.^{5,6,9} Similarly, the thermodynamic threshold for process 8 would be estimated to be 12.79 eV, lower than the observed¹² threshold of 13.04 eV.

CCl_2 . Literature values^{15,21–26} for the heat of formation of CCl_2 , summarized in Table I, range from <30 to <59 kcal/mol, with most values falling in the range 46–59 kcal/mol. However, most of the reported determinations involve the observation of the onsets of such processes as

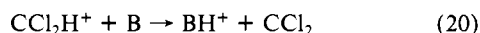


Because of the possibility of energy barriers in the dissociation channels of ionic fragmentations, such determinations give upper limits for the heat of formation of CCl_2 . One previous evaluation^{25b} of data^{25c} on the process



led to a much lower value for the heat of formation, 40 ± 5 kcal/mol.

Results of three previous studies^{19,22} of the proton-transfer reaction



provide a striking illustration of the difficulties which may be associated with the determination of heats of formation of unstable species through bracketing experiments. Lias and Ausloos^{19a} observed proton transfer from CCl_2H^+ to ammonia (proton affinity, 204.0 kcal/mol) but not to dimethyl sulfide (proton affinity, 200.6 kcal/mol) and concluded that the proton affinity of CCl_2 lay between these two values. Levi et al.²² on the other hand, concluded that since they did not observe proton transfer from CCl_2H^+ to diisopropyl sulfide (proton affinity, 209.6 kcal/mol), the proton affinity of CCl_2 , must be higher than this value. Ausloos and Lias^{19b} later noted that CCl_2H^+ preferentially reacts with dialkyl sulfides and ethers through hydride transfer or displacement mechanisms even when proton transfer is exothermic. For this reason, both previous determinations^{19,22} of the proton affinity of CCl_2 through bracketing were in error because of the assumption that the nonoccurrence of a proton transfer to a sulfide indicated endothermicity. Ausloos and Lias^{19b} concluded that the proton affinity of CCl_2 was lower than that of diethyl ether (200.2 kcal/mol) but did not provide a lower bracket for the proton affinity of this species.

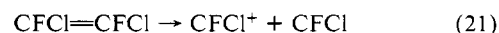
Table IV. Observation of the Reaction $\text{CCl}_2\text{H}^+ + \text{B} \rightarrow \text{BH}^+ + \text{CCl}_2$ for Bases (B) of Varying Proton Affinity

B	proton affinity, ^h kcal/mol	% proton transfer	ref
methylamine	214.1	63	19a
		observed	22
2-(trifluoromethyl)pyridine	211.5	observed	22
$\text{CF}_3\text{CH}_2\text{CH}_2\text{NH}_2$	210.6	observed	22
diisopropyl sulfide	209.6	not observed	22
aniline	209.5	not observed	22
		1	19b
isopropyl ether	206.0	not observed	22
		not observed ^a	19b
ammonia	204.0	46	19a
		57	19b
$\text{C}_2\text{H}_5\text{SCH}_3$	203.5	not observed ^b	19b
di- <i>n</i> -propyl ether	202.3	not observed ^c	19b
dimethyl sulfide	200.6	<1	19a
		not observed ^d	19b
diethyl ether	200.2	22	19b
$\text{C}_6\text{H}_5\text{CN}$	195.9	observed ^f	this work
<i>i</i> - $\text{C}_3\text{H}_7\text{CN}$	194.3	observed ^f	this work
<i>n</i> - $\text{C}_3\text{H}_7\text{CN}$	193.7	observed ^f	this work
$\text{C}_2\text{H}_5\text{CN}$	192.6	not observed ^f	this work
dimethyl ether	192.1	not observed ^e	19
phosphine	188.6	not observed ^f	this work
1,2-difluorobenzene	181.8	not observed ^{f,g}	this work
1,3,5-trifluorobenzene	181.	not observed	this work
arsine	179.2	not observed	this work
hexafluorobenzene	177.7	not observed	this work

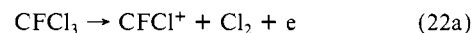
^a Reaction products: $\text{C}_3\text{H}_7^+ + i\text{-C}_3\text{H}_7\text{OCCl}_2\text{H}$. ^b Reaction products: $\text{CH}_3\text{SCH}_2\text{H}^+ + \text{CCl}_2\text{H}_2$. ^c Reaction products: $\text{C}_3\text{H}_7^+ + \text{C}_3\text{H}_7\text{OCCl}_2\text{H}$. ^d Reaction products: $\text{CH}_3\text{SCH}_2^+ + \text{CCl}_2\text{H}_2$. ^e Reaction products: $\text{CH}_3\text{OCH}_2^+ + \text{CCl}_2\text{H}_2$. ^f Reactant ion: CCl_2D^+ . ^g Reaction products: $\text{C}_6\text{F}_5\text{H}_4^+ + \text{CCl}_2\text{D}$. ^h All proton affinities from ref 29.

The results of the present study (Table IV) indicate that the gas basicity of CCl_2 lies between that of $\text{C}_2\text{H}_5\text{CN}$ and that of *n*- $\text{C}_3\text{H}_7\text{CN}$, i.e., that the proton affinity of CCl_2 is 193 ± 1 kcal/mol. Accepting a value of 212 kcal/mol³⁹ for the 298 K heat of formation of CCl_2H^+ , this leads to a value of 39 kcal/mol for the heat of formation of CCl_2 , in good agreement with the earlier estimate of 40 ± 5 kcal/mol.²⁵

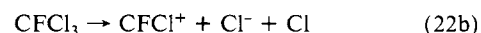
CFCl. An upper limit to the value for the heat of formation of CFCl can, in principle, be derived from the reported⁶ appearance energy (15.3 eV) of the process



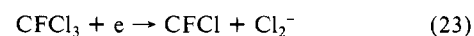
However, the result cannot be interpreted without a reliable value for the heat of formation of CFCl^+ (or a value for the ionization potential of CFCl). The literature provides conflicting evidence about the value of this heat of formation; however, consistent results have been reported^{15,27} for the appearance potential of the CFCl^+ ion from CFCl_3



or



(15.94 and 16.04 eV). The assumption of the formation of a Cl_2 product gives a value of 243 kcal/mol for $\Delta H_f(\text{CFCl}^+)$, while a value of 331 is obtained assuming $(\text{Cl}^- + \text{Cl})$ products. These would correspond respectively to values for the heat of formation of CFCl of 32 or –57 kcal/mol if the measured onset for process 21 (15.3 eV) is the thermodynamic threshold. On the other hand, the reported onset of 0.6 eV for the process



(39) Werner, A. S.; Tsai, B. P.; Baer, T. *J. Chem. Phys.* **1974**, *60*, 3650.
(40) Huber, K. P.; Herzberg, G. "Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules"; Van Nostrand Reinhold Co.: New York, 1979.

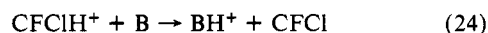
Table V. Observation of the Reaction $\text{CFClH}^+ + \text{B} \rightarrow \text{BH}^+ + \text{CFCl}$ for Bases (B) of Varying Proton Affinity

B	proton affinity, ^a kcal/mol	proton transfer
CD_3CN	188.4	observed
<i>o</i> - $\text{FC}_6\text{H}_4\text{CH}_3$	186.6	observed
<i>p</i> - $\text{FC}_6\text{H}_4\text{CH}_3$	185.8	not observed
$\text{C}_6\text{H}_5\text{F}$	182.6	not observed
HCN	171.4	not observed
H_2Se	171.3	not observed
H_2S	170.2	not observed

^aAll proton affinities from ref 29.

would correspond to an approximate value for $\Delta H_f(\text{CFCl})$ of 3 kcal/mol.

The process



was examined for several bases of varying gas-phase basicity. The results (Table V) indicate that the proton affinity of CFCl is bracketed between that of *p*-fluorotoluene (185.8 kcal/mol) and *o*-fluorotoluene (186.6 kcal/mol). A proton affinity of 186 kcal/mol corresponds to a value for the heat of formation of CFCl of -2 kcal/mol, accepting a value of 178 ± 3 kcal/mol for the heat of formation of CFClH^+ . The latter heat of formation is itself based on results of bracketing experiments, namely the observation of the reactions³⁷

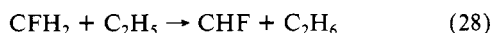


which indicate a value for the heat of formation of <180 kcal/mol, and the nonoccurrence of the reaction

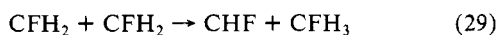


which would indicate a value for the heat of formation of >175 kcal/mol.

CFH. A recent paper⁴¹ reported a value for the heat of formation of CFH of 39 kcal/mol, based on the observations that the reaction:



occurs and must therefore be exothermic, while the reaction



does not occur and was therefore assumed to be endothermic. Taking the heat of formation of CFH_2 to be -7.6 ± 2.0 kcal/mol, these results lead to assigned limits on the heat of formation of CFH of $<38.8 \pm 2.0$ and $>41.6 \pm 6.0$ kcal/mol. The only other published values for the heat of formation of CFH are a MINDO calculation^{3d} and estimates^{13,42} based on (a) averaging the heats of formation of CF_2 and CH_2 and (b) modifying that average by a consideration of the bond energies HC-F and FC-H , assuming that these would fall within normal bounds ($\text{C-F} < 135$ kcal/mol and $\text{C-H} > 80$ kcal/mol). The estimates led to values of 30 ± 7 ¹³ and 25 kcal/mol⁴² for $\Delta H_f(\text{CFH})$. Hsu et al.⁴³ pointed out that such an averaging procedure should use the heat of formation of $^1\text{CH}_2$ rather than that of $^3\text{CH}_2$ and on that basis recommended a value of 39 kcal/mol for the heat of formation of CFH . The MINDO calculation gave a value of 14.5 kcal/mol for a triplet ground state, 21.5 kcal/mol for the $^1\text{A}_1$ state (incorrectly predicting, as the authors pointed out,^{3d} that the triplet state is lower than the singlet). Staemmler^{3h} has calculated the bond-dissociation energies, $D(\text{HC-F})$ and $D(\text{FC-H})$, to be 120 and 83 kcal/mol, respectively, which would correspond to heats of formation of CFH of 40 or 30 kcal/mol, respectively, taking recommended^{13,28,40} values for the heats of formation of CH and CF (Table II).

(41) Pritchard, G. O.; Nilsson, W. B.; Kirtman, B. *Int. J. Chem. Kinet.* **1984**, *16*, 1637.

(42) Tang, Y.-N.; Smail, T.; Rowland, F. S. *J. Am. Chem. Soc.* **1969**, *91*, 2130.

(43) Hsu, D. S. Y.; Umstead, M. E.; Lin, M. C. In "Fluorine-Containing Free Radicals: Kinetics and Dynamics of Reactions"; American Chemical Society: Washington, D.C. 1978; ACS Symp. Ser. 66, p 128.

Table VI. Observation of the Reaction $\text{CFH}_2^+ + \text{B} \rightarrow \text{BH}^+ + \text{CFH}$ for Bases (B) of Varying Proton Affinity

B	proton affinity, ^a kcal/mol	proton transfer
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	195.9	observed
$\text{C}_6\text{H}_5\text{CN}$	195.9	observed
<i>n</i> - $\text{C}_3\text{H}_7\text{CN}$	193.7	observed
HCOOC_2H_5	193.1	observed
$\text{C}_2\text{H}_5\text{CN}$	192.6	observed
CH_3SCN	192.6	not observed
$(\text{CH}_3)_2\text{O}$	192.1	not observed
$\text{C}_2\text{H}_5\text{NO}_2$	184.8	not observed
$\text{C}_6\text{H}_5\text{F}$	182.6	not observed
1,3,5- $\text{C}_6\text{F}_3\text{H}_3$	181.	not observed
C_6F_6	177.7	not observed
CF_3COCH_3	174.2	not observed
HCN	171.4	not observed
H_2Se	171.3	not observed

^aProton affinities from ref 29 except the value for CH_3SCN from the following: Karpas, Z.; Stevens, W. J.; Buckley, T. J.; Metz, R. *J. Phys. Chem.*, in press.

Table VII. Observation of the Reaction $\text{CClH}_2^+ + \text{B} \rightarrow \text{BH}^+ + \text{CClH}$ for Bases (B) of Varying Proton Affinity

B	proton affinity, ^a kcal/mol	proton transfer
$\text{C}_6\text{H}_5\text{NH}_2$	209.5	observed
$\text{CH}_3\text{COC}_6\text{H}_5$	205.4	not observed
NH_3	204.0	not observed ^b
<i>t</i> - $\text{C}_4\text{H}_9\text{OCH}_3$	202.2	not observed ^c
$\text{CH}_3\text{COC}_2\text{H}_5$	199.8	not observed
CH_3COCH_3	196.7	not observed
$\text{C}_2\text{H}_5\text{CN}$	192.6	not observed
HCN	171.4	not observed
H_2Se	171.3	not observed

^aAll proton affinities from ref 29. ^b NH_4^+ formed through two-step mechanism: $\text{CClH}_2^+ + \text{NH}_3 \rightarrow \text{CH}_2\text{NH}_2^+ + \text{HCl}$, $\text{CH}_2\text{NH}_2^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{CH}_2\text{NH}$. ^c MH^+ formed by proton transfer from *t*- C_4H_9^+ .

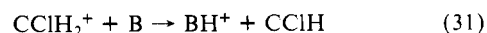
Table VI shows the results of experiments in which the occurrence or nonoccurrence of the reaction



was examined for a series of bases of varying gas-phase basicity. These results indicate that CFH_2^+ transfers a proton to $\text{C}_2\text{H}_5\text{CN}$ (proton affinity, 192.6 kcal/mol) and HCOOC_2H_5 (proton affinity, 193.1 kcal/mol) but not to CH_3SCN (proton affinity, 192.6 kcal/mol) or $(\text{CH}_3)_2\text{O}$ (proton affinity, 192.1 kcal/mol). Thus, the proton affinity of CFH must be 193 kcal/mol. A value of 199 kcal/mol is derived for the 298 K heat of formation of CFH_2^+ from the appearance potential of this ion from CH_2F_2 (14.06 eV),³⁸ in good agreement with limits which can be assigned to the heat of formation from observed ion-molecule reactions.³⁷ On this basis, a value of 26 ± 3 kcal/mol can be assigned to the heat of formation of CHF . This value is in good agreement with previous estimates^{13,42} based on averaging the heats of formation of CH_2 and CF_2 , and indeed it agrees well with such an average taking the heats of formation of these species reported in this paper, as will be discussed below. The estimate of 39 kcal/mol recently reported⁴¹ for $\Delta H_f(\text{CFH})$ assumed that a lower limit could be assigned on the basis of the nonoccurrence of reaction 29; the results obtained here do not conflict with the upper limit of <39 kcal/mol assumed in that study from the observation of reaction 26 but indicate that reaction 29 is exothermic, even though it does not occur at a measurable rate.

CClH. A published estimate of the heat of formation of CClH gave a value of 80 ± 10 kcal/mol,¹³ based on an average of the heats of formation of CH_2 and CCl_2 , modified by assigning "reasonable" values to the HC-Cl and ClC-H bond strengths.

Table VII shows the results of experiments in which the occurrence or nonoccurrence of the reaction



was examined for a series of bases of varying gas-phase basicity. These results indicate that the gas basicity of CClH lies between

Table VIII. Proton Affinities and Heats of Formation (kcal/mol) of Substituted Methylenes

CXY	proton affinity	$\Delta H_f(\text{CXYH}^+)$	$\Delta H_f(\text{CXY})$	
			(exptl)	av (CX ₂ , CY ₂)
¹ CH ₂	(207)	262	(103)	
CHF	193	199	26	27
CF ₂	173	143	-49	
CHCl	207	229	71	71
CCl ₂	193	212	39	
CFCI	186	178	-2	-5

Table IX. Hydrogen Affinities of CXY⁺ Ions and Derived Ionization Energies of CXY Species

CXY	$\Delta H_f(\text{CXY}^+)$, kcal/mol		hydrogen affinity, ^a kcal/mol	ionization energy, ^b eV	
		ref		¹ CXY ^b	³ CXY ^c
¹ CH ₂	334	47	124	10.02	10.45
CHF	268	this work	121 ^d	10.49	10.10
CF ₂	214	7	123	11.42 ^d	9.24
CHCl	322	47	145		
	298	this work	121 ^e	9.84	9.76
CCl ₂	278	15	118	10.36	9.84
CFCI	243	15	117	10.62	

^aHydrogen affinity = $-\Delta H_f(\text{CXYH}^+) + \Delta H_f(\text{H}) + \Delta H_f(\text{CXY}^+)$.

^bExcept where otherwise indicated, cited ionization energy derived from $\Delta H_f(\text{CXY}^+) - \Delta H_f^1(\text{CXY})$. ^c $\Delta H_f(\text{CXY}^+) - \Delta H_f^3(\text{CXY})$, see Table XI. ^dExperimental ionization potential from ref 7. ^eAssumed; see Discussion.

that of CH₃COC₆H₅ (proton affinity, 205.4 kcal/mol) and C₆H₅NH₂ (proton affinity, 209.5 kcal/mol). The appearance potential of CClH₂⁺ from CH₂Cl₂ (12.14 eV)³⁹ leads to an upper limit value for the 0 K heat of formation of the ion of 229.95 kcal/mol, which corresponds to a 298 K value of 229.2 kcal/mol. A value for the 298 K heat of formation of CClH₂⁺ from ion-molecule reaction bracketing experiments³⁷ is in good agreement, leading to an estimate for the maximum value for this quantity of 233 ± 3 kcal/mol. The proton transfer bracketing results summarized in Table VII then correspond to a 298 K heat of formation of CClH of 71 ± 5 kcal/mol.

Heats of Formation of Halomethylenes: C-X and C-H Bond Strengths. The results obtained from the proton transfer bracketing experiments described above are summarized in Table VIII. The experimentally derived values for the heats of formation of methylene and the halogenated methylenes vary in a completely regular way, with the heat of formation for CClH falling half-way between those of ¹CH₂ and CCl₂ and the heat of formation of CFH falling within 1 kcal/mol of the value one would obtain by averaging the values for ¹CH₂ and CF₂. Similarly, the heat of formation of CFCI is within 3 kcal/mol of the value one would obtain by averaging the heats of formation of CF₂ and CCl₂.

Accepting these heats of formation for the carbenes, one can derive information about heats of formation of related ionic species. For example, one can examine (Table IX) the hydrogen affinities of the CXY⁺ ions, i.e., the enthalpy changes associated with the reactions



Where reliable information about the heats of formation of the relevant CXY⁺ ions is available, the hydrogen affinities of the ions are seen to be (Table IX), as expected,⁴⁴ fairly constant. The values of all the relevant hydrogen affinities (except that of CHCl⁺ for which $\Delta H_f(\text{CHCl}^+)$ is not well established) are 121 ± 4 kcal/mol. In fact, the compatible value for the hydrogen affinity of CFCI⁺ serves as a confirmation of the value used here for the heat of formation of CFCIH⁺, which was estimated from ion-molecule bracketing experiments³⁷ (reactions 25, 26, and 27).

(44) See, for example: (a) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527. (b) Lias, S. G.; Ausloos, P. In "Ion-Molecule Reactions: Their Role in Radiation Chemistry"; American Chemical Society, Washington, D.C., 1975; pp 91-95.

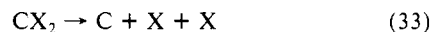
Table X. C-X and C-H Bond Strengths (kcal/mol) in Singlet Halomethylenes

	H	Cl	F
HC-	90	100 ± 5	135 ± 3
ClC-	84 ± 5	94 ± 3	124 ± 7
FC-	85 ± 3	89 ± 7	126 ± 5

Assuming, therefore, that the values for the hydrogen affinities of CHF⁺ and CHCl⁺ will be ~121 kcal/mol, it is possible to estimate the heats of formation of these ions from the known heats of formation of CFH₂⁺ and CClH₂⁺ (Table IX).

Table IX summarizes heats of formation of the CXY⁺ ions and ionization potentials for the CXY species derived from the results of the present study. The ionization potentials reported here are simply taken as the differences between the heats of formation of CXY⁺ and the values reported here for $\Delta H_f(\text{CXY})$, i.e., the "ionization potentials" correspond to differences between 298 K heats of formation and therefore represent 298 K "enthalpies of ionization". The ordering of the derived ionization energies (CF₂ > CFCI > CFH ~ CCl₂ > CHCl ~ CH₂) is reasonable. The experimentally determined value of the ionization potential of CCl₂ (9.76 eV)²¹ appears to be too low. Acceptance of that value and $\Delta H_f(\text{CCl}_2)$ from this study would lead to an unreasonably low value for the hydrogen affinity of CCl₂⁺. On the other hand, use of the derived ionization potential for CCl₂ (10.36 eV) with the appearance potential data^{13,15,21} for CCl₂⁺ summarized in Table I leads to derived upper limits on the heat of formation of CCl₂ in rather good agreement with the value reported here.

The question arises of whether the values recommended here for halomethylene heats of formation lead to "reasonable" carbon-halogen and carbon-hydrogen bond strengths. Table X summarizes the bond strengths derived from the results reported here. The values for the heats of formation of CH and CF used in calculating the bond strengths are taken from the literature.^{13,40} It is seen that a straightforward use of the recommended¹³ value for the heat of formation of CCl leads to values for bond strengths which are obviously much too high (107, 98, and 140 kcal/mol respectively for ClC-H, -Cl, and -F bonds, respectively). In fact, the heat of formation of CCl is poorly established.⁴⁰ Therefore, it appears to be necessary to estimate a value for this quantity in order to obtain bond strengths for ClC-X species. Since, for ¹CH₂ and ¹CF₂, the "average" bond strengths associated with C-X bonds estimated from the reaction



are similar (±5 kcal/mol) to the C-H and C-F bond strengths estimated from



we make the assumption that the same will be true for CCl₂. This leads to an estimate that the heat of formation of CCl is ~104 kcal/mol (rather than 120 kcal/mol).¹³ This is the value used in the calculations of bond strengths given in Table X.

As with the thermochemical properties listed in Table VIII, the bond energies given in Table X conform to reasonable expectations for C-H, C-Cl, and C-F bond energies, i.e., C-H bonds have strengths of about 85-90 kcal/mol, C-Cl bonds lie between 89 and 100 kcal/mol, and C-F bonds are about 125-134 kcal/mol.

(45) The onset energy for the process CH₃F → CH₂F⁺ + H + e has been determined by photoionization mass spectrometry (Krauss, M.; Walker, J. A.; Dibeler, V. H. *J. Res. Natl. Bur. Stand.* **1968**, *72A*, 281) to be 13.37 eV. Accepting the value for the heat of formation of CH₂F⁺ given in Table 2, this leads to an estimate that the heat of formation of CH₃F is -57 kcal/mol at 0 K and -59 kcal/mol at 298 K. This value is preferable to that cited in ref 13, which was based on the same reasoning, but used less accurate appearance potential data.

(46) Shimanouchi, T. "Tables of Molecular Vibrational Frequencies: Consolidated Volume I"; National Bureau of Standards: Washington, D.C., 1972; NSRDS-NBS 39.

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Table XI. Heats of Formation of Singlet and Triplet Methylene

	singlet ^a	triplet ^b	$\Delta E(S-T)^c$
CH ₂	103	93	10
CHCl	71 ± 5 [71] ^d	73 [72] ^d	-2
CCl ₂	39 ± 3	51	-12
CHF	26 ± 3 [27] ^d	35 [47] ^d	-9
CF ₂	-49 ± 3	1	-50
CFCl	-2 ± 7 [-5] ^d		

^a Except for CH₂, from this study. ^b From the theoretical singlet-triplet separation energies given in the third column and the experimental heats of formation of the singlet methylenes in the first column. ^c Singlet-triplet splits for halomethylenes from ref 2b and for CH₂ from ref 2b, 48, and 49. ^d Values in brackets are values for the heat of formation of CXY species which would be obtained by averaging heats of formation of the relevant CX₂ and CY₂ species.

Considerable attention has been given to calculations of singlet-triplet energy separations in halogenated methylenes³ and to experimental⁴⁸ and theoretical⁴⁹ determinations of this energy difference in CH₂. Heats of formation which can be assigned to the triplet halocarbenes based on the most recent calculations of the singlet-triplet split energies and the results presented here for the singlet carbenes are summarized in Table XI. Here, it is seen that the derived heat of formation of ³CHCl lies exactly between the heats of formation of ³CH₂ and ³CCl₂, but the heat of formation of ³CHF is lower by 12 kcal/mol than the value predicted by averaging the heats of formation of ³CH₂ and ³CF₂.

To examine in more detail the relative stabilization energies effected in a methylene species by fluorine substitution, it is instructive to further compare the heats of formation of the singlet and triplet fluorinated methylene species with trends in the heats of formation of corresponding fluoromethanes. In the methanes the substitution of one F for one H lowers the heat of formation by respectively 41, 49, 58, and 57 kcal/mol in the series CH₄, CH₃F, CH₂F₂, CF₄; the significantly larger degree of stabilization effected by the substitution of the second F atom has been termed

the "gem-difluoro effect"⁵⁰ and is interpreted in terms of resonance structures available to a species with two fluorine atoms on a single carbon atom. In the singlet carbenes the same substitution leads to a lowering of the heat of formation by 77 and 76 kcal/mol in the series CH₂, CHF, CF₂, i.e., fluorine substitution in a methylene effects a much greater stabilization than in an alkane, but in the singlet species, no gem-difluoro effect is operative. In the corresponding triplet fluoromethylenes, the respective lowering of the heat of formation upon substitution is 58 and 34 kcal/mol. The anomalously small stabilization effected upon substitution of F for H in CHF suggests that the lack of additivity in the heats of formation of the triplet fluoromethylenes may be due to a relative destabilization of ³CF₂ species.

Additional evidence in favor of this interpretation comes from an examination of the ionization potentials derived in Table IX for the triplet halogenated methylenes. These ionization energies, which correspond to the difference between the heat of formation of the CXY⁺ ion and the ³CXY methylene, can be equated to the energy required for the removal of a π electron. Thus, it would be expected⁵¹ that these ionization energies should remain unchanged or increase slightly with increasing fluorine substitution. Instead, these π -ionization energies decrease from 10.10 to 9.24 eV in going from ³CHF to ³CF₂. This result again indicates a relative destabilization of the ³CF₂ species, indicating that the unusually large singlet-triplet gap associated with CF₂ reflects both the stabilization of ¹CF₂ and the destabilization of ³CF₂ by the fluorine substituents.

Note Added in Proof. A new determination of the heat of formation of CCl₂⁺ (265 kcal/mol) and the adiabatic ionization potential of CCl₂ (9.10 eV) have been reported.⁵² These values cannot be reconciled with the data reported here, and would lead to unreasonable values for both the ClC-Cl bond-dissociation energy (Table X) and the hydrogen affinity of CCl₂⁺ (Table IX).

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Registry No. C₆H₅F, 462-06-6; CH₃NO₂, 75-52-5; C₆F₆, 392-56-3; H₂Se, 7783-07-5; CH₂, 2465-56-7; CHF, 13453-52-6; CF₂, 2154-59-8; CHCl, 2108-20-5; CCl₂, 1605-72-7; CFCl, 1691-88-9.

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