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A redetermination of the heats of formation of chloro- and dichlorocarbene and the deprotonation of methyl cation, a spin forbidden process?

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Dedicated to the memory of Sharon Lias, whose work is timeless and will influence scientists for generations to come.

Abstract

The reactions of CH_3^+, CH_2Cl^+ and $CHCl_2^+$ with standard reference bases were examined in a dual cell Fourier transform mass spectrometer. Deprotonation of methyl cation occurs rapidly via a spin forbidden process to afford triplet methylene even when the reaction is nearly thermoneutral. Bracketing results enable us to assign PA(CHCl) = 209.7 ± 2.2 kcal mol^{-1} and PA(CCl_2) = 205.2 ± 1.9 kcal mol^{-1}, the latter value of which is considerably larger than previous determinations. The resulting heats of formation, however, are in good accord with other measurements and lead to recommended values of ΔH_f°(CHCl) = 74.6 ± 2.4 kcal mol^{-1} and ΔH_f°(CCl_2) = 53.0 ± 2.6 kcal mol^{-1}. These values correspond to a 2–3 kcal mol^{-1} lowering of these quantities and are within 1–2 kcal mol^{-1} of high level G3 and W1 predictions based upon the atomization energies and a series of four isodesmic reactions.

Keywords: Chlorocarbene; Dichlorocarbene; Methyl cation; Spin-forbidden reaction; FTMS

1. Introduction

Carbenes are commonly used intermediates in synthetic transformations and play an important role in combustion, interstellar and technological processes [1]. As a result, they have been studied by a wide variety of means. Singlet (S) and triplet (T) electronic states are routinely encountered and the ground state multiplicity has a significant impact on their structure and reactivity. Energetic determinations of these species have been carried out using a number of techniques but in some cases the values are not well established. For example, in 1985 Lias, Karpas and Liebman (LKL) reported $\Delta H^\circ_{f,298}(CCl_2) = 39 \pm 3$ kcal mol^{-1} [1 cal = 4.184 J] and noted 13 previous measurements which ranged from <30 to <59 kcal mol^{-1} [2]. Subsequently, at least six more values have appeared and they range from 51 to 57 kcal mol^{-1} [3–8]. Recommended heats of formation of 47 ± 3 and 55 ± 2 kcal mol^{-1} also have been given, but no basis was provided for the first of these values [9] and the second is based in part upon the expectation that the computed G2 energy is 2–3 kcal mol^{-1} too small [10].

One approach that has been used to obtain carbene heats of formation is to measure gas phase deprotonation energies of carbenium ions and combine this with ancillary thermochemical data (Eq. (1)). This methodology was employed by LKL and has been used four times for dichlorocarbene [2,11–13].

$$\mathrm{HCXY}^+ + \mathrm{B} \rightarrow \mathrm{CXY} + \mathrm{BH}^+,$$

$$\Delta H_f^\circ(\mathrm{CXY}) = \mathrm{PA(CXY)} - \Delta H_f^\circ(H+) + \Delta H_f^\circ(\mathrm{HCXY}^+) \tag{1}$$

Heats of formation ranging from 39 to 55 kcal mol^{-1} were reported over a 9-year period in this way. If these energies are updated for changes in the basicity scale [14] and a uniform value of $\Delta H^\circ_{f,298}(CHCl_2^+) = 213.2 \pm 0.7$ kcal mol^{-1} is adopted [15], the range becomes somewhat larger (i.e., 38–59 kcal mol^{-1}) and the results generally are in poor accord with more recent determinations (Table 1). A similar situation applies to chlorocarbene (CHCl) in that its heat of formation is not well established and the deprotonation of CH_2Cl^+ leads to $\Delta H^\circ_{f,298}(CHCl) = 71 \pm 5$ kcal mol^{-1},

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Table 1
Reported heats of formation for CHCl and CCl_2 by deprotonation of their conjugate acids or since 1985

Carbene	$\Delta H^{\circ}_{f,\,298}$ (kcal mol^{-1})		Year	Methodology[a]	Ref.
	Literature	Updated[b]			
$^1CCl_2$	$42.8 < x < 45.8$	$46.1 < x < 51.5$	1976	PT ($CHCl_2^+$)	[11]
	53.5 ± 2.0	59.3 ± 2.1	1977	PT ($CHCl_2^+$)	[12]
	$<47.8 \pm 2.0$	$<45.5 \pm 2.1$	1978	PT ($CHCl_2^+$)	[13]
	39 ± 3	38 ± 3	1985	PT ($CHCl_2^+$)	[2]
	55.0 ± 3.0 (est.)[c]	49.2 ± 3.0	1990	Thermokinetic	[3]
	52.1 ± 3.4	52.5 ± 3.4	1991	CID	[4]
	57.2 ± 4.0	55.0 ± 3.1	1992	PT ($CCl_2^{\bullet-}$)	[5]
	51.0 ± 2.0	51.0 ± 2.0	1993	IP	[6]
	54.0 ± 6.0	56.8 ± 2.5	2000	PT ($CCl_2^{\bullet-}$)	[7]
^1CHCl	71 ± 5	72.1 ± 3.0	1985	PT (CH_2Cl^+)	[2]
	80.4 ± 2.8	80.5 ± 2.8	1993	CID	[10]
	75.8 ± 4.8	75.3 ± 2.4	1994	PT ($CHCl^{\bullet-}$)	[16]

[a] PT = Proton transfer, CID = collision-induced dissociation and IP = ionization potential.

[b] These values were derived based upon changes in the acidity scale (see Ref. [14]) and ancillary thermochemical data (see Ref. [15]).

[c] Based in part on an estimate of the heat of formation of *trans*-1,1-dichloro-2,3-dimethylcyclopropane (−12.8 kcal mol^{-1}). If one uses Benson's group equivalents as given in Ref. [9], a value of −18.5 kcal mol^{-1} is obtained and this is the basis for the updated result.

whereas other gas phase approaches led to reports of 75.8 ± 4.8 and 80.4 ± 2.8 kcal mol^{-1} [2,10,16].

Chloro- and dichlorocarbene both are ground state singlets [17,18]; consequently, the deprotonation of their conjugate acids is a spin allowed transformation. For a ground state, triplet carbene this process is spin forbidden if it is formed in its lowest energy state. This raises the question, what multiplicity (singlet versus triplet) will be formed? To our surprise, this question does not appear to have been addressed [19], but methyl cation is a good substrate to explore this issue. This is because it readily can be generated and proton abstraction unambiguously affords methylene (CH_2). Moreover, this carbene is a ground state triplet with a relatively large S–T gap of 9.00 ± 0.09 kcal mol^{-1} [20], which should enable the two possibilities (singlet versus triplet formation) to be differentiated since all of the relevant thermochemistry is well-established. In this work, we show that the deprotonation of CH_3^+ is a rare example of a spin forbidden reaction [21–23], and the heat of formation of CHCl and CCl_2 are redetermined.

2. Experimental

Gas phase experiments were carried out in a dual cell model 2001 Finnigan Fourier transform mass spectrometer (FTMS) equipped with a 3 T superconducting magnet which has been retrofitted with IonSpec electronics and the Omega version 8.0.309 data system. Methyl cation was produced by electron ionization (EI, 65 eV) of a constant pressure of methane ($\sim 1 \times 10^{-7}$ Torr) in the source cell, and after a short (1 ms) −10 V pulse on the trapping plate of the analyzer cell to remove any trapped ions, all of the ions were transferred to the analyzer cell. One or more pulses of argon up to a pressure of approximately 10^{-5} Torr were used to cool the ions, and after an additional delay of about 1 s to enable the argon to be pumped away, CH_3^+ was carefully isolated using a stored-waveform inverse Fourier transform (SWIFT) excitation typically with a 20 amu window to avoid depositing energy into the ion during the isolation process [24]. Alternatively, chirp excitations were used to remove unwanted ions from the cell [25]. Proton transfer reactions subsequently were carried out with a variety of bases, which were added at constant pressures via leak valves on the analyzer side of the instrument. Control experiments were carried out by continually ejecting methyl cation and by simply not transferring it to the analyzer cell. In addition, branching ratio measurements were carried out to ascertain whether the observed products were due to primary or secondary reactions. Rate measurements also were carried out by monitoring reactions as a function of time. Chloro- and dichloromethyl cations (CH_2Cl^+ and $CHCl_2^+$, respectively) were generated by 30 eV EI of dichloromethane or chloromethane and were studied in a similar manner to methyl cation.

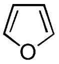
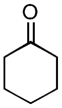
G3 [26] and W1 [27,28] computations were carried out as described in the literature using Gaussian 03 [29] on workstations at the University of Minnesota Supercomputer Institute. Heats of formation of neutral compounds were computed via atomization energies, and those for cations were obtained from their corresponding radicals and the calculated ionization energy. Reaction energies also were calculated and all of the resulting energetic quantities are reported at 298 K. In carrying out the temperature correction from 0 to 298 K, low frequency modes were found to contribute more than $1/2RT$ in a few instances and in these cases $1/2RT$ was substituted for these terms [30].

3. Results and discussion

3.1. Methyl cation

A series of standard bases of increasing strength were allowed to react with methyl cation (Table 2) [15]. In each case, a

Table 2
Bracketing experiment results for the reactions of CH_3^+ with standard reference bases

Base	PA ($kcal\ mol^{-1}$)	Proton transfer[a]
t-BuOH	191.8 ± 2.0	No[b]
	192.0 ± 2.0	No[c]
CH_3COCH_3	194.4 ± 2.0	No[d]
$CH_3CO_2CH_3$	196.4 ± 2.0	No[d]
p-FC_6H_4CHO	197.7 ± 2.0	Yes/no[e]
Et_2O	198.0 ± 2.0	Yes
CH_3CO_2Et	199.7 ± 2.0	Yes[f]
C_6H_5CHO	199.3 ± 2.0	No[g]
$C_6H_5OCH_3$	200.7 ± 2.0	No[c]
	201.0 ± 2.0	No[h]

[a] Proton transfer (PT) is a primary product in those reactions where a yes is listed and a secondary product where a no is given.

[b] t-Bu^+ is formed.

[c] Electron transfer takes place.

[d] CH_3CO^+ is observed.

[e] $C_7H_6F^+$ (adduct- CH_2O, ~90%) and PT (~10%) are the primary products.

[f] CH_3CO^+ (~90%) and PT (~10%) are observed.

[g] $C_7H_7^+$ (adduct- CH_2O, ~60%) and $C_6H_5^+$ (adduct- C_2H_4O, ~40%) are formed.

[h] $C_2H_5O^+$, which presumably is $CH_3O{=}CH_2^+$, is observed.

fast transformation took place (i.e., $k \approx k_{ADO}$) and a slower secondary process generally was observed. Proton transfer is not an initial (i.e., primary) product with *tert*-butyl alcohol, furan, acetone and methyl acetate but it is with some stronger bases such as p-fluorobenzaldehyde, diethyl ether and ethyl acetate. Other bases such as benzaldehyde, anisole and cyclohexanone react via different pathways. These results enable us to assign $PA(CH_2) = 197.2 \pm 1.6\ kcal\ mol^{-1}$, although strictly speaking this value is an upper limit. More specifically, ethyl ether and methyl acetate were taken to be the limiting reagents since the former compound is the weakest base that was used that cleanly abstracts a proton and the latter reagent is the strongest base, which is weaker than Et_2O and does not react via acid–base chemistry. p-Fluorobenzaldehyde also undergoes proton transfer with CH_3^+, but this pathway only accounts for 10% of the products. This may indicate that proton abstraction is slightly endothermic or it could be a reflection of a more efficient competitive process. As this is an ambiguous situation, this compound was not used as one of the brackets. Our assigned proton affinity is in essentially perfect accord with the literature value derived from the known heats of formation of $^3CH_2$ and CH_3^+ ($197.1 \pm 0.2\ kcal\ mol^{-1}$). It also leads to $\Delta H_f^\circ(^3CH_2) = 93.4 \pm 1.6\ kcal\ mol^{-1}$ (Eq. (2)) which is in excellent agreement with the well-established and more precise literature value of $93.3 \pm 0.2\ kcal\ mol^{-1}$ (Table 3) [15].

$$\Delta H_f^\circ(CH_2) = PA(CH_2) + \Delta H_f^\circ(CH_3^+) - \Delta H_f^\circ(H^+) \qquad (2)$$

The S–T gap for methylene is $9.00 \pm 0.09\ kcal\ mol^{-1}$ and enables one to derive $PA(^1CH_2) = 206.1 \pm 0.2\ kcal\ mol^{-1}$. This value and our observations that CH_3^+ is deprotonated by p-fluorobenzaldehyde, diethyl ether and ethyl acetate, all of which have proton affinities of less than $200\ kcal\ mol^{-1}$, indicates that only $^3CH_2$ is energetically accessible in these reactions. Since the ions and bases are all singlets, the formation of triplet methylene means that these acid–base reactions are a rare example of a spin-forbidden process [21–23]. There also appears to be no significant bottleneck near the threshold in these transformations since diethyl ether reacts at approximately the collision limit even though proton transfer is only exothermic by $1\ kcal\ mol^{-1}$.

Methyl cation is extremely reactive, in part because of the large ionization energy of methyl radical. It also undergoes a spin-forbidden deprotonation, which makes bracketing the acidity of CH_3^+ potentially difficult. The correct thermochemical result was obtained, however, so there is no reason a priori why this methodology should not work for CHCl and CCl_2. These carbenes are ground state singlets and CH_2Cl^+ and $CHCl_2^+$ are more stable and less reactive than CH_3^+. Consequently, we decided to reinvestigate these species.

3.2. Dichlorocarbene

Electron ionization of CH_2Cl_2 primarily affords $CHCl_2^+$ and CH_2Cl^+. The former ion was carefully isolated and vibrationally cooled with one or more pulses of argon to pressures of $\sim 10^{-5}$ Torr, but was not isotopically resolved to avoid inadvertently exciting it. A series of reference bases were allowed to react with dichloromethyl cation and the products were monitored as a function of time (Table 4). Proton transfer was observed in every instance except with ethyl acetate, which did not react, but it is not a primary product with the weaker bases (i.e., benzonitrile, methyl acetate and ammonia). Diethyl sulfide reacts relatively quickly ($k = \sim 1.36 \times 10^{-9}\ cm^3\ molecule^{-1}\ s^{-1}$) and nearly every collision leads to product formation (i.e., $k_{ADO} = 1.50 \times 10^{-9}\ cm^3\ molecule^{-1}\ s^{-1}$ and $k/k_{ADO} = 0.90$). The efficiency for proton transfer is about half of the reaction efficiency, which suggests that the proton affinity of dichlorocarbene is very similar to that for diethyl sulfide. To be conservative, ammonia and acetamide are used as the limiting brackets and $PA(CCl_2) = 205.2 \pm 1.9\ kcal\ mol^{-1}$ is assigned. This result can be combined with $\Delta H_f^\circ(CHCl_2^+) = 213.2 \pm 0.7\ kcal\ mol^{-1}$ and $\Delta H_f^\circ(H^+) = 365.7\ kcal\ mol^{-1}$ as in Eq. (2) to afford $\Delta H_f^\circ(CCl_2) = 52.7 \pm 2.0\ kcal\ mol^{-1}$. This heat of formation is in excellent accord with the most recent determinations based upon a threshold measurement for the collision-induced dissociation of CCl_3^- [4] and the ionization energy of CCl_2 [6]. It also is in agreement with measurements based upon the proton affinity of $CCl_2^{\bullet -}$, but suggests that the earlier study carried out in a flowing afterglow device by Grabowski may be the more accurate [5,7]. Our determination, however, is significantly higher than the 1985 LKL value measured in the same way. It is possible that hot ions or stray electrons could account for the low proton affinity previously measured ($191 \pm 1\ kcal\ mol^{-1}$) but in hindsight a more likely explanation is the presence of fast secondary reactions which can erroneously lead to false positives in double resonance and bracketing experiments.

Table 3
Thermochemical data used in this work[a]

Cmpd	EQ[b]	Expt	Calc		EQ[b]	Expt	Calc	
			G3[c]	W1			G3[c]	W1
CH_4	ΔH_f°	−17.8 ± 0.1	−18.1	−18.3	C–H BDE	104.95 ± 0.1	104.2	104.3
CH_2Cl_2	ΔH_f°	−22.8 ± 0.3[d]	−22.2	−24.5	C–H BDE	96.2 ± 0.8	96.1	
CH_3Cl	ΔH_f°	−19.6 ± 0.2	−19.4	−21.1	C–H BDE	99.7 ± 0.7	99.3	99.6
$CH_3^\bullet$	ΔH_f°	35.05 ± 0.07	34.1	34.6	IE	226.87 ± 0.01[e]	227.3	226.8
	ΔH_{acid}°	408.8 ± 0.3	411.4					
$CH_2Cl^\bullet$	ΔH_f°	28.0 ± 0.7	27.8	26.4	IE	201.8 ± 0.2[f]	200.3	
	ΔH_{acid}°	384.8 ± 2.4[g]	387.7, [387.5]					
$CHCl_2^\bullet$	ΔH_f°	21.3 ± 0.7	21.7	19.7	IE	191.9 ± 0.2[f]	190.0	
	ΔH_{acid}°	363.1 ± 1.9[h]	363.4, [361.4]					
$^3CH_2$	ΔH_f°	93.3 ± 0.2	92.4	93.2	IE	239.74 ± 0.069	239.7	239.3
	EA	15.04 ± 0.14	13.4		S–T	−9.00 ± 0.09	−9.5	−9.2
CHCl	ΔH_f°	74.6 ± 2.4[i]	76.3	75.9				
	EA	27.97 ± 0.12	27.2		S–T	4.2 ± 2.5	6.5	5.9
CCl_2	ΔH_f°	53.0 ± 2.6[i]	54.4	53.8	IE	213.8 ± 0.9		
	EA	37.0 ± 0.2	35.8		S–T	3 ± 3	21.0	19.9
CH_3^+	ΔH_f°	261.9 ± 0.1	261.4	261.4	ΔH_{acid}°	197.1 ± 0.2 (T), 206.1 ± 0.2 (S)	197.5, 207.0	197.7, 206.9
$CHCl_2^+$	ΔH_f°	213.2 ± 0.7	211.7		ΔH_{acid}°	205.2 ± 1.9[i]	209.2, [206.5]	
CH_2Cl^+	ΔH_f°	229.8 ± 0.7	228.1	228.2	ΔH_{acid}°	209.7 ± 2.2[i]	214.7, [213.6]	213.5
H^+	ΔH_f°	365.7						
$H^\bullet$	ΔH_f°	52.103 ± 0.001						

[a] All values are in kcal mol^{-1} and at 298 K. They also come from refs. [14] and [15] unless other-wise noted.
[b] EQ = Energetic quantity.
[c] G2 energies are given in brackets and come from Ref. [10].
[d] Ref. [34].
[e] Ref. [35].
[f] Ref. [36].
[g] Ref. [16].
[h] This value is the average of the two determinations given in Refs. [5,7].
[i] This work, see text for additional details.

3.3. Chlorocarbene

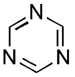
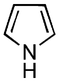
Electron impact on CH_2Cl_2 affords CH_2Cl^+, which was carefully isolated and subjected to one or two pulses of argon to pressures of $\sim 10^{-5}$ Torr in order to vibrationally thermalize the ions. Similar experiments also were carried out using xenon instead of argon, but this did not lead to any changes in the results. Standard reference bases were reacted with chloromethyl cation and as before the reaction products were carefully monitored as a function of time. Weak bases such as benzonitrile, methyl acetate, ammonia and acetophenone do not abstract a proton from CH_2Cl^+, whereas acid–base chemistry does occur with acetamide and ethyl vinyl ether (Table 5). To our surprise, these last two reactions do not take place when the reactant ion is generated from CH_3Cl; proton transfer only is observed as a secondary product in these cases. Presumably, this is because the chloromethyl cation is formed from dichloromethane with excess vibrational energy, which is not efficiently dissipated upon collisions with argon or xenon, whereas it is cooler when produced from methyl chloride. Pyrrole is strong enough to deprotonate CH_2Cl^+ regardless of how it is formed, but electron and $CH_2^{\bullet +}$ transfer products (*m*/*z* 67 and 81) are observed as well. This reaction is very efficient and occurs at roughly the collision rate, but the proton transfer pathway only accounts for ~20% of the product. This suggests that the proton affinity of chlorocarbene

Table 4
Bracketing experiment results for the reactions of $CHCl_2^+$ with standard reference bases

Base	PA (kcal mol^{-1})	Proton transfer
C_6H_5CN	194.0 ± 2.0	No[a]
$CH_3CO_2CH_3$	196.4 ± 2.0	No[b]
CH_3CO_2Et	199.7 ± 2.0	No
NH_3	204.0 ± 2.0	No[c]
Et_2S	204.8 ± 2.0	Yes/no[d]
CH_3CONH_2	206.4 ± 2.0	Yes
$CH_2{=}CHOEt$	208.0 ± 2.0	Yes

[a] Electron transfer is observed and PT is a secondary product.
[b] CH_3CO^+ is formed and PT is a secondary product.
[c] Several ions are produced and PT is a secondary product.
[d] Proton, electron and hydride transfer are all primary products whose relative contributions are ~50%, 20% and 30%, respectively. The overall reaction rate is $\sim 1.36 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} and $k_{ADO} = 1.50 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} so the reaction efficiency for proton transfer is ~45%.

Table 5
Bracketing experiment results for the reactions of CH_2Cl^+ with standard reference bases

Base	PA (kcal mol^{-1})	Proton transfer
C_6H_5CN	194.0 ± 2.0	No
$CH_3CO_2CH_3$	196.4 ± 2.0	No[a]
	202.9 ± 2.0	No
NH_3	204.0 ± 2.0	No[b]
Et_2S	204.8 ± 2.0	No
$C_6H_5COCH_3$	205.8 ± 2.0	No[a]
CH_3CONH_2	206.4 ± 2.0	No[c]
CH_2=CHOEt	208.0 ± 2.0	No[d]
	209.2 ± 2.0	Yes/no[e]
CH_3SOCH_3	211.4 ± 2.0	Yes[f]

[a] CH_3CO^+ is formed and PT is observed as a secondary product.

[b] $H_2C{=}NH_2{}^+$ was observed ($k = 4.45 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}) and PT is a secondary product.

[c] PT is observed when the CH_2Cl^+ is produced by EI of CH_2Cl_2 and the reaction is relatively efficient (k/k_{ADO} = ~0.4) even when xenon is pulsed into the system twice to cool the ion. When the reactant ion is produced from CH_3Cl then CH_3CO^+ is formed and PT is only observed as a secondary product.

[d] The same behavior is observed as for acetamide except $C_2H_5{}^+$ (*m/z* 29), CH_3CHOH^+ (*m/z* 45) and $CH_2{=}CHOCH_2{}^+$ (*m/z* 57) are the reaction products.

[e] Three products are observed at *m/z* 67, 68 and 81 which correspond to electron transfer (~35%), proton transfer (~20%) and $CH_2{}^{\bullet+}$ transfer (~45%).

[f] This reaction occurs rapidly and leads to PT (~50%) and a *m/z* 62 ion.

is similar to that of pyrrole but to be secure in our assignment we take ethyl vinyl ether and dimethylsulfoxide as the brackets. Consequently, we assign PA(CHCl) = 209.7 ± 2.2 kcal mol^{-1}, which is in good accord with the updated 1985 LKL value of 208.4 ± 2.9 kcal mol^{-1}. Upon combining our result with $\Delta H_f^\circ(CH_2Cl^+) = 229.8 \pm 0.7$ kcal mol^{-1} and $\Delta H_f^\circ(H^+) = 365.7$ kcal mol^{-1} in an analogous manner to Eq. (2), $\Delta H_f^\circ(CHCl) = 73.8 \pm 2.3$ kcal mol^{-1} is obtained. This value also is in excellent accord with the updated 1985 LKL determination using the same approach (72.1 ± 3.0 kcal mol^{-1}) [2] as well as Nibbering's report based upon the proton affinity of $CHCl^{\bullet-}$ (75.3 ± 4.5 kcal mol^{-1}) [16], but is significantly smaller than a measurement of 80.5 ± 2.8 based upon a threshold determination for the fragmentation of $CHCl_2{}^-$ [10]. Perhaps the latter result is in error because a larger halide is needed to obtain the correct dissociation onset; such behavior previously has been reported [31].

3.4. Calculations

High level G3 and W1 computations are reported in general to give accurate results within 1–2 kcal mol^{-1} for small molecules [26–28]. Both of these methods, consequently, were used to predict bond dissociation energies, heats of formation, ionization energies and additional quantities as given in Table 3. All of the computed energetics are within 3 kcal mol^{-1} of the experimental values except for the singlet–triplet gap for dichlorocarbene and our acidities for $CHCl_2{}^+$ and CH_2Cl^+. In the first case, the discrepancy is 17–18 kcal mol^{-1} and this strongly suggests that the experimental assignment is in error. A similar conclusion recently was reported based upon different high level computations, and it was suggested that the source of the problem is due to an excited quartet state of the anion in the photoelectron spectrum [32,33]. As for the differences with the acidities, these largely disappear if one uses G2 values instead of G3 energies and are a reflection of the errors in computed heats of formation of $CHCl_2{}^+$ and CH_2Cl^+.

Isodesmic reactions and the atomization of CCl_2 were used to predict the heat of formation of dichlorocarbene at the G3 level (Eqs. (3)–(7) and Table 6). W1 theory also was used in some of these cases and the agreement with the G3 results is excellent. In no case do the two methods deviate from each other by more than 1.1 kcal mol^{-1}. The average of the different approaches leads to $\Delta H_f^\circ(CCl_2) = 55.2 \pm 1.2$ (G3) and 54.6 ± 0.7 (W1) kcal mol^{-1}, both of which are in good accord with a previous G2 estimate of 53.6 kcal mol^{-1} [10] and our measured value of 52.7 ± 2.0 kcal mol^{-1}. To derive a recommended heat of formation, we simply averaged our result with the three other independent determinations since 1991 and obtained 53.0 ± 2.6 kcal mol^{-1}, where the given uncertainty is the mean of the individual error limits. This value is only slightly larger than our determination and also is in accord with the theoretical predictions. Finally, it corresponds to a 2 kcal mol^{-1} downward revision of the most recently recommended heat of formation of dichlorocarbene [10,15].

$$ {}^{\bullet}CHCl_2 + {}^3CH_2 \rightarrow {}^1CCl_2 + CH_3{}^{\bullet}, $$
$$ \Delta H_{Rxn} = -25.7\,(G3),\ -24.6\,(W1)\ kcal\ mol^{-1} \qquad (3) $$

$$ CH_2Cl_2 + {}^3CH_2 \rightarrow {}^1CCl_2 + CH_4, $$
$$ \Delta H_{Rxn} = -33.8\,(G3),\ -33.3\,(W1)\ kcal\ mol^{-1} \qquad (4) $$

Table 6
Predicted heats of formation for CHCl and CCl_2 via isodesmic and atomization reactions

Compound	Rxn	ΔH_f°	
		G3	W1
${}^1CCl_2$	Eq. (3)	53.9	55.0
	Eq. (4)	54.5	55.0
	Eq. (5)	56.3	
	Eq. (6)	56.3[a]	
	Eq. (7)	54.4	53.8
	Avg.	55.2	54.6
	Recommended	53.0 ± 2.6[b]	
${}^1CHCl$	Eq. (8)	76.3	77.1
	Eq. (9)	76.7	77.0
	Eq. (10)	78.3	77.0
	Eq. (11)	75.9	
	Eq. (12)	76.3	75.9
	Avg.	76.7	76.7
	Recommended	74.6 ± 2.4[b]	

[a] See Table 3 for additional details.

[b] This work. See the text for more details.

$$\mathrm{CHCl_2}^{+} + {}^{3}\mathrm{CH_2} \rightarrow {}^{1}\mathrm{CCl_2} + \mathrm{CH_3}^{+},$$
$$\Delta H_{\mathrm{Rxn}} = 11.7\,\mathrm{kcal\,mol^{-1}}\ (\mathrm{G3}) \tag{5}$$

$$\mathrm{CCl_2}^{\bullet -} + {}^{3}\mathrm{CH_2} \rightarrow {}^{1}\mathrm{CCl_2} + \mathrm{CH_2}^{\bullet -},$$
$$\Delta H_{\mathrm{Rxn}} = 22.4\,\mathrm{kcal\,mol^{-1}}\ (\mathrm{G3}) \tag{6}$$

$${}^{1}\mathrm{CCl_2} \rightarrow {}^{3}\mathrm{C} + 2\mathrm{Cl},$$
$$\Delta H_{\mathrm{Rxn}} = 174.8\ (\mathrm{G3}),\ 175.5\ (\mathrm{W1})\,\mathrm{kcal\,mol^{-1}} \tag{7}$$

An analogous approach was employed to derive the heat of formation of chlorocarbene. G3 and W1 computations of the reaction energies for a series of isodesmic reactions and the atomization of CHCl (Eqs. (8)–(12)) leads to $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{CHCl}) = 76.7 \pm 0.9$ (G3) and 76.7 ± 0.6 (W1) kcal mol^{-1}. These values are a little larger but in reasonable accord with a previous G2 estimate of 75.7 kcal mol^{-1} [10] and our measurement of 73.8 ± 2.3 kcal mol^{-1}. We have averaged our result with Nibbering's determination based upon the proton affinity of $\mathrm{CHCl}^{\bullet -}$ [16] to arrive at $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{CHCl}) = 74.6 \pm 2.4$ kcal mol^{-1}, which is our recommended value. This quantity corresponds to a downward revision of 3.4 kcal mol^{-1} for the heat of formation for chlorocarbene [10,15]. It also is in good accord with theoretical predictions and leads to $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{CHCl} - \mathrm{CCl_2}) = 21.6 \pm 3.5$ kcal mol^{-1} based upon our recommended heats of formation and 21.1 ± 3.2 kcal mol^{-1} based upon our measured values, both of which are very accurately reproduced by G3 and W1 computations (i.e., 21.5 and 22.1 kcal mol^{-1}, respectively).

$${}^{\bullet}\mathrm{CH_2Cl} + {}^{3}\mathrm{CH_2} \rightarrow {}^{1}\mathrm{CHCl} + \mathrm{CH_3}^{\bullet},$$
$$\Delta H_{\mathrm{Rxn}} = -9.9\ (\mathrm{G3}),\ -9.2\ (\mathrm{W1})\,\mathrm{kcal\,mol^{-1}} \tag{8}$$

$$\mathrm{CH_3Cl} + {}^{3}\mathrm{CH_2} \rightarrow {}^{1}\mathrm{CHCl_2} + \mathrm{CH_4},$$
$$\Delta H_{\mathrm{Rxn}} = -14.8\ (\mathrm{G3}),\ -14.5\ (\mathrm{W1})\,\mathrm{kcal\,mol^{-1}} \tag{9}$$

$$\mathrm{CH_2Cl}^{+} + {}^{3}\mathrm{CH_2} \rightarrow {}^{1}\mathrm{CHCl} + \mathrm{CH_3}^{+},$$
$$\Delta H_{\mathrm{Rxn}} = 17.1\ (\mathrm{G3}),\ 15.8\ (\mathrm{W1})\,\mathrm{kcal\,mol^{-1}} \tag{10}$$

$$\mathrm{CHCl}^{\bullet -} + {}^{3}\mathrm{CH_2} \rightarrow {}^{1}\mathrm{CHCl} + \mathrm{CH_2}^{\bullet -},$$
$$\Delta H_{\mathrm{Rxn}} = 13.8\,\mathrm{kcal\,mol^{-1}} \tag{11}$$

$${}^{1}\mathrm{CHCl} \rightarrow {}^{3}\mathrm{C} + \mathrm{H} + \mathrm{Cl},$$
$$\Delta H_{\mathrm{Rxn}} = 176.1\ (\mathrm{G3}),\ 176.5\ (\mathrm{W1})\,\mathrm{kcal\,mol^{-1}} \tag{12}$$

4. Conclusions

The proton affinity of ${}^{3}\mathrm{CH_2}$ can be bracketed despite the fact that its formation via the deprotonation of methyl cation is a spin forbidden process and the ionization energy of methyl radical is quite high (i.e., 9.84 eV). This was established since the singlet–triplet gap for methylene is relatively large (9.0 kcal mol^{-1}), the energetics needed to derive the acidity of $\mathrm{CH_3}^{+}$ are well known, and several bases were found to rapidly abstract a proton from methyl cation which can only afford the triplet carbene. This spin forbidden process, presumably, occurs via a facile curve crossing mechanism.

Chloro- and dichlorocarbene were reinvestigated and their proton affinities were measured. Particular care was taken to cool the ions and to ascertain whether the observed proton transfer products are due to primary reaction pathways or result from secondary processes of the first formed ions. For $\mathrm{CH_2Cl}^{+}$, it turns out that the identity of the substrate used to prepare it is significant as several gas pulses of argon or xenon proved to be insufficient to thermalize this small rigid tetra atomic ion. As a result, the proton affinities and heats of formation of these carbenes are larger than previously reported. Our recommended values are $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{CCl_2}) = 53.0 \pm 2.6$ kcal mol^{-1} and $\Delta H_{\mathrm{f}}^{\circ}(\mathrm{CHCl}) = 74.6 \pm 2.4$ kcal mol^{-1}, which are in accord with high level G3 and W1 predictions but correspond to 2–3 kcal mol^{-1} downward revisions of these quantities.

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