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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?

Zhixin Tian, Steven R. Kass *

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, USA

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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 $\Delta H_{f,298}^\circ(CCl_2) = 39 \pm 3$ 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]. 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 $\Delta H_{f,298}^\circ(CHCl_2^+) = 213.2 \pm 0.7$ 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 $\Delta H_{f,298}^\circ(CHCl) = 71 \pm 5$ kcal mol^{-1},

$$\mathrm{HCXY^+ + B \rightarrow CXY + BH^+},$$
$$\Delta H_f^\circ(\mathrm{CXY}) = \mathrm{PA(CXY)} - \Delta H_f^\circ(H+) + \Delta H_f^\circ(\mathrm{HCXY^+}) \qquad (1)$$

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* Corresponding author. Tel.: +1 612 625 7513; fax: +1 612 626 7541.
E-mail address: kass@chem.umn.edu (S.R. Kass).

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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 ± 2.0	<45.5 ± 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