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Theoretical Enthalpies of Formation of CH_mCl_n: Neutral Molecules and Cations

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Ab initio molecular orbital calculations have been performed on all possible neutral molecules and cations of the type CH_mCl_n ($m + n = 1-3$). Equilibrium structures were optimized using gradient techniques at HF/6-31G(d,p), MP2/6-311G(d,p), QCISD/6-311G(d,p), and MP2/6-311++G(d,p). Thermochemical properties (standard enthalpies of formation, adiabatic ionization energies, and proton affinities) have been calculated at QCISD(T)/6-311++G(3df,3pd)//MP2/6-311++G(d,p) and QCISD(T)/6-311G(2df,p)//QCISD/6-311G(d,p), both including core-electron correlation, and at MP4SDTQ/6-311G(2df,p)//MP2/6-311G(d,p), frozen core. Calculations at the first level of theory are accurate to ± 1.0 kcal mol^{-1}, and at the second and third levels of theory, to ± 2.3 kcal mol^{-1}. Recent experimental data are critically reviewed against these calculated results, and theory indicates that some experimental values are incorrect. Calculated QCISD(T)/6-311++G(3df,3pd) values for the enthalpies of formation for CCl^+ and $CHCl^+$ are 304.9 and 286.7 kcal mol^{-1}, respectively, and the ionization energies for CCl and CHCl($^1A'$) are 8.70 and 9.10 eV. Recent experimental results for the enthalpies of formation for CCl_2 (56.5 ± 3.0 kcal mol^{-1}) and CCl_3^+ (202.2 ± 0.8 kcal mol^{-1}) are validated. A hydride affinity scale for chlorinated carbocations, calculated at the MP4SDTQ/6-311G(2df,p) level, gives the relative affinity order to be $CCl_3^+ \approx CCl^+ < CHCl_2^+ < CCl_2^+ < CH_2Cl^+ < CHCl^+ < CH_3^+ < CH^+ < CH_2^+$.

Introduction

Halogenated hydrocarbons are important industrial compounds used as solvents, as dry-cleaning agents, as refrigerants, and in the etching of microelectronic chips.[1,2] This widespread usage has led to their existence in the environment as pollutants,[3] and there has been considerable interest over the past decade in the chemistry of small halogenated hydrocarbons, an interest sparked by the discovery of the destruction of the stratospheric ozone layer by chlorine atoms originating primarily from the photolysis of chlorofluorocarbons.[4] Organochloro compounds have also been detected in interstellar space and play a role in the depletion of HCl in the Orion molecular cloud.[5] These discoveries have stimulated interest, both theoretical and experimental, in the chemistries and thermochemical properties of small chlorinated hydrocarbons and cations of the type CH_mCl_n (where $m + n = 1-3$).[6−10] Much of the thermochemical data for these small molecules are not well-established, particularly for CCl and CCl^+,[11−19] CHCl and $CHCl^+$,[10−12,16,20] and CCl_2 and CCl_2^+.[7b,11,13,21−24] For example, for the enthalpy of formation of CCl_2, there are several reported values,[11] ranging from 30 to 59 kcal mol^{-1}. Two values are preferred, but they differ widely (39 ± 3 and 52.4 ± 3.1 kcal mol^{-1}).[11,21] The former is based on proton affinity bracketing techniques using an ICR apparatus, while the latter is derived from the energetics of the collisional induced dissociation of CCl_3^- in a flowing afterglow-triple quadrupole apparatus. The higher value is reinforced by *ab initio* calculations which give 52.9 kcal mol^{-1} (using calculated proton affinities) and 56.2 kcal mol^{-1} (using computed stabilization energies).[21] In addition, two recent results, one derived from $CHCl_2$ acidity bracketing (57.2 ± 4.0 kcal mol^{-1})[22] and the other (51.0 ± 2.0 kcal mol^{-1}) deduced from the enthalpy of formation[13] of CCl_2^+ and an adiabatic ionization energy (9.27 ± 0.04 eV) extracted from the photoelectron spectrum of CCl_2,[7b] lend credibility to a value greater than 50 kcal mol^{-1}. *Ab initio* molecular orbital calculations carried out on chlorine−substituted methylidynes and methylenes have been useful in resolving some of these inconsistencies.[8a,25−31]

The experimental thermochemistries of CH_2Cl and CH_2Cl^+,[32−39] $CHCl_2$ and $CHCl_2^+$,[32,35,36,39,40] and CCl_3 and CCl_3^+,[9,32,35,36,41−44] obtained from a variety of methods are internally consistent, with one major exception, that being the standard enthalpy of formation of CCl_3^+. Prior to 1977, the experimental $\Delta H°_{f,298}$ (CCl_3^+) was bracketed between 192 and 208.8 kcal mol^{-1} based on a series of ion−molecule reactions[43] and on appearance energy measurements.[35] Two recent studies gave values greater than 200 kcal mol^{-1}. One,[9a] based on an adiabatic ionization energy of 8.109 ± 0.005 eV derived from a photoelectron spectroscopy study of CCl_3 and a $\Delta H°_{f,298}(CCl_3)$ of 17.0 ± 0.6 kcal mol^{-1}, determined $\Delta H°_{f,298}(CCl_3^+)$ to be 205.2 ± 0.6 kcal mol^{-1}. The other, from an adiabatic ionization energy of 8.06 ± 0.02 eV,[7a] gave $\Delta H°_{f,298}(CCl_3^+) = 202.2 \pm 0.8$ kcal mol^{-1}. Also, the Lias compilation[44] gives $\Delta H°_{f,298}(CCl_3^+)$ to be 199 kcal mol^{-1}, and Holmes and co-workers,[36] using appearance energy measurements, obtained a value of 195 ± 0.5 kcal mol^{-1}. *Ab initio* calculations (using the method of atom equivalents) have produced satisfactory values for the enthalpies of formation of CH_2Cl, $CHCl_2$, and CCl_3,[39] and the heats of atomization method has been used to obtain $\Delta H°_{f,298}(CH_2Cl)$.[45]

Methylidynes, methylenes, and methyl radicals are highly reactive, making them difficult to isolate and study experimentally. Such molecules are small enough to be amenable to high-level *ab initio* calculations, thereby providing an independent and reliable method of assessing experimental thermochemical values. Theoretical methods which consistently reproduce accurate thermochemical data (to within ± 3.0 kcal mol^{-1}) include the BAC-MP4 approach by Binkley and Melius,[46] the heats of atomization method employing isogyric reactions (in which the number of unpaired electrons are equal on both sides

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of the reaction) by Pople's group,[47] and the G1 and G2 methods also by Pople's group.[48,49] Basis sets used in these procedures are traditionally quite small, and we have found that by using larger basis sets, combined with the heat of atomization method, better accuracies can be attained.[50] For example, for halogenated radicals, we calculated electron affinities, gas-phase acidities, and standard enthalpies of formation to an accuracy of ± 2.4 kcal mol^{-1}.[45]

The objective of the current study is to provide reliable and accurate thermochemical properties (standard enthalpies of formation, ionization energies, and proton affinities) for small chlorinated hydrocarbons and cations, some of which are not yet firmly established from experiment. In order to accomplish this, we have extended our level of theory to the quadratic configuration interaction (QCI) level and have included core-electron correlation and larger basis sets.

Theoretical Methods

Molecular orbital calculations were carried out using the Gaussian 86, Gaussian 90, and Gaussian 92 suite of programs.[51−53] Geometries were optimized at the MP2[54] level, employing the 6-311G(d,p)[55] and 6-311++G(d,p) basis sets and at the QCISD[56] level with the 6-311G(d,p) basis set. All structures obtained at MP2/6-311G(d,p) were characterized by harmonic frequency calculations. Single-point calculations using fourth order Møller−Plesset theory[54] (frozen core) with the 6-311G(2df,p) basis set were performed on the MP2/6-311G(d,p) optimized geometries (denoted MP4/2df,p for brevity). Single-point calculations employing QCISD with a perturbative estimation of the triples[56] (including core correlation) with the 6-311G(2df,p) basis set were also performed on the QCISD/6-311G(d,p) optimized structures (abbreviated to QCI/2df,p). In addition, single-point calculations were carried out at the QCISD(T) levels (including core correlation) with the 6-311++G(3df,3pd) basis set on the MP2/6-311++G(d,p) optimized structures (abbreviated QCI/3df,3pd). These three different levels of theory enabled us to have an internal check on the consistency of the calculated values. The total energies for these calculations are given in Table 1.

In order to obtain satisfactory zero-point energies from harmonic frequency calculations, it is necessary to use a scale factor, the magnitude of which is dependent on the level of theory employed. Some calculated results (G1) underestimate the zero-point energies, and an increase in the HF scale factor has been recommended to rectify this problem.[57] A comparison of 36 experimental and calculated harmonic frequencies for small chlorocarbons yielded an average scale factor of 0.91 for the SCF/6-31G(d,p) frequencies and 0.94 for those at the MP2/6-311G(d,p) level.[50] Consequently we have used these factors in scaling the zero-point energies listed in Table 1.

Results and Discussion

Structural Details. Optimized structures are given in Figures 1 and 2. Geometry optimizations at the MP2(FULL) level, in conjunction with either the 6-311G(d,p) or the 6-311++G(d,p) basis set, provide excellent molecular structures. The mean bond length error for the MP2/6-311G(d,p) optimizations is 0.008 Å, and with the inclusion of diffuse functions, an accuracy of 0.005 Å is produced. The errors in the bond angles are 2.2 and 1.3°, respectively. The QCISD method gives optimized structures which have a mean bond length error of 0.013 Å and a bond angle error of 2.2°; this result may be due to inadequacies in the 6-311G(d,p) basis set, which was optimized for use in MP2 calculations.[55]

Our calculations show CH_2Cl and CCl_3 to be planar and pyramidal, respectively, in agreement with previous experimental and theoretical studies.[9b,39,45,68−72] The situation for $CHCl_2$ is less well-established experimentally, although it is probably pyramidal,[40,73−76] and previous calculations suggest an inversion barrier of less than 1 kcal mol^{-1}.[39,40] Here, we find that, based only on the electronic energy, pyramidal $CHCl_2$ is consistently slightly lower in energy than the planar structure, but, at the highest level of theory (MP4/2df,p), inclusion of zero-point energy is sufficient to reverse this order and the planar structure is preferred by 0.3 kcal mol^{-1}.

Standard Enthalpies of Formation. The method by which the enthalpies of formation in Table 2 have been calculated has been described in detail previously,[27,50] but briefly the procedure was as follows. The atomization energy for a molecule was calculated from the *ab initio* molecular energies in Table 1, and this was combined with experimental enthalpies of formation for the constituent atoms[44] to yield $\Delta H^\circ_{f,0}$. Thermal corrections were then added, using standard heat capacities for the elements[77] and theoretical values from Table 1 for the molecule, to give $\Delta H^\circ_{f,298}$.

For the 24 molecules studied in this investigation the calculated enthalpies of formation of all molecules (Table 2), with the exception of CCl^+, $CHCl^+$, CCl_2, CCl_2^+ amd CCl_3^+, are consistent with experimental results. After removal of the five problem molecules, enthalpies from MP4/2df,p and QCT/2df,p calculations are within ± 2.3 kcal mol^{-1} of the experimental values, and for the most accurate calculations, at QCI/3df,3pd, they are within ± 1 kcal mol^{-1}.

(*a*) *CCl^+*. The calculated $\Delta H^\circ_{f,298}(CCl^+)$ of 304.9 kcal mol^{-1} falls between the experimental values of 297,[44] 311.1 $\pm$ 2.0,[9] and 313 $\pm$ 4 kcal mol^{-1},[14] and, noting that this level of theory generally gives enthalpies within ± 1 kcal mol^{-1}, we suggest that a value of 304.9 $\pm$ 1 kcal mol^{-1} be adopted. In this respect, it is interesting to note that combining an established[11,27] $\Delta H^\circ_{f,298}(CCl)$ of 104.0 kcal mol^{-1} with an experimental adiabatic ionization energy[19] of 8.9 $\pm$ 0.2 eV, gives $\Delta H^\circ_{f,298}(CCl^+) = 309.2 \pm 4.6$ kcal mol^{-1}, and the error limits of this value encompass our theoretical value.

(*b*) *$CHCl^+$*. An experimental $\Delta H^\circ_{f,298}(CHCl^+)$ of ~298 kcal mol^{-1} has been derived from the assumption that the hydrogen atom affinities (121 $\pm$ 4 kcal mol^{-1}) of CHF^+ and $CHCl^+$ are equal.[11] However, calculations show this assumption to be incorrect since the MP4/2df,p hydrogen atom affinity (using isogyric equations) for $CHCl^+$ is 112.8 kcal mol^{-1}. Therefore, we strongly suggest that our QCI/3df,3pd value for $\Delta H^\circ_{f,298}(CHCl^+)$ of 286.7 kcal mol^{-1} is more reliable. Additional theoretical support for this value can be found in the recent literature.[8a]

(*c*) *CCl_2^+*. Recently we have calculated an enthalpy of formation for CF_2 of −51 kcal mol^{-1},[27] in agreement with an experimental value[11] of −49 $\pm$ 3 kcal mol^{-1}. An accurate value for $\Delta H^\circ_{f,298}(CF_2)$ is important as this molecule is frequently produced as a stable neutral in many appearance energy measurements whenever fluorinated-organic compounds are used as a source. For example, Rademann, Jochims, and Baumgartel (RJB)[13a] have determined the appearance energy of CCl_2^+ from the reaction,

$$Cl_2C{=}CF_2 \rightarrow CF_2 + CCl_2^{\ +} + e \tag{1}$$

they deduced $\Delta H^\circ_{f,298}(CCl_2^+)$ from eq 2, where $\Delta H_{cor,298}$ is a correction term for thermal energies.[13b] Using $\Delta H^\circ_{f,298}(CF_2)$

$$AE(CCl_2^{\ +}) = \Delta H^\circ_{f,298}(CCl_2^{\ +}) + \Delta H^\circ_{f,298}(CF_2) - \Delta H^\circ_{f,298}(CF_2CCl_2) - \Delta H_{cor,298} \tag{2}$$

as −49 ± 3 kcal mol^{-1} (instead of an earlier value of −43.5 ± 1.5 kcal mol^{-1})[12] produces a $\Delta H^\circ_{f,298}(CCl_2^+)$ of 270.3 ± 3.0 kcal mol^{-1}, about 3 kcal mol^{-1} higher than the value obtained from MP4/2df,p calculations. Furthermore, $\Delta H^\circ_{f,298}(CCl_2)$, previously derived from RJB's $\Delta H^\circ_{f,298}(CCl_2^+)$ and an adiabatic ionization energy,[7b] now becomes 56.5 ± 3.0 kcal mol^{-1} (the

TABLE 1: Total Energies (hartrees) and Zero-Point and Thermal Energies (All in kcal mol^{-1}) from the Optimized Structures and Single-Point Calculations

	optimized HF/6-31G(d,p) MP2/6-311G(d,p) QCISD/6-311G(d,p) MP2/6-311++G(d,p)			single point MP4/2df,p QCI/2df,p QCI/3df,3pd		optimized HF/6-31G(d,p) MP2/6-311G(d,p) QCISD/6-311G(d,p) MP2/6-311++G(d,p)			single point MP4/2df,p QCI/2df,p QCI/3df,3pd
molecule	total energy	ZPE[a]	thermal correcn	total energy	molecule	total energy	ZPE[a]	thermal correcn	total energy
$CH(^2\Pi)$	−38.266 92	3.8			$CH_2Cl(^2A')$	−498.464 72	14.0		
	−38.379 96	3.9	1.5	−38.401 54		−498.828 77	13.8	2.2	−498.875 17
	−38.405 63			−38.423 79		−498.858 49			−498.958 52
	−38.381 86			−38.431 10		–			–
$CH^+(^1\Sigma^+)$	−37.897 54	4.1			$CH_2Cl^+(^1A_1)$	−498.153 59	15.4		
	−37.995 24	4.0	1.4	−38.012 53		−498.519 60	15.3	1.8	−498.560 16
	−38.026 04			−38.037 22		−498.549 31			−498.644 61
	−37.995 82			−38.042 48		–			–
$CCl(^2\Pi)$	−497.205 54	1.1			$CHCl_2(^2B_1)$	−957.358 41	9.0		
	−497.531 96	1.2	1.5	−497.578 24		−957.929 41	9.0	2.1	−957.998 54
	−497.562 21			−497.661 63		–			–
	−497.537 29			−497.705 37		–			–
$CCl^+(^1\Sigma^+)$	−496.880 71	1.6			$CHCl_2(^2A')$	−957.359 82	9.7		
	−497.223 23	1.7	1.5	−497.262 11		−957.930 56	9.7	2.2	−957.999 14
	−497.250 85			−497.343 88		−957.965 61			–
	−497.227 85			−497.386 42		–			–
$CH_2(^1A_1)$	−38.876 31	10.1			$CHCl_2^+(^1A_1)$	−957.055 42	10.7		
	−39.022 38	10.1	1.8	−39.048 60		−957.640 06	10.7	2.1	−957.701 44
	−39.049 89			−39.072 58		−957.671 11			−957.846 09
	−39.024 64			−39.083 56		–			–
$CH_2(^3B_1)$	−38.925 49	10.5			$CCl_3(^2A_1)$	1416.248 16	4.6		
	−39.051 15	10.5	1.7	−39.069 25		1417.028 06	4.5	2.7	−1417.119 88
	−39.071 41			−39.090 11		–			–
	−39.052 44			−39.099 94		–			–
$CH_2^+(^2A_1)$	−38.570 61	10.0			$CCl_3^+(^1A_1')$	1415.945 76	5.4		
	−38.676 44	10.0	1.8	−38.690 54		1416.746 60	5.4	2.5	−1416.830 70
	−38.697 64			−38.711 66		–			–
	−38.676 86			−38.719 46		–			–
$CHCl(^1A')$	−497.799 20	6.9			CH_4	−40.202 17	26.9[b]	1.8	
	−498.156 24	6.9	1.8	−498.205 79		−40.398 04			−40.424 66
	−498.188 45			−498.290 70		–			–
	−498.161 51			−498.337 90		–			–
$CHCl(^3A'')$	−497.827 75	7.0			CH_3Cl	−499.098 95	23.0[b]	1.9	
	−498.157 40	7.1	1.8	−498.199 10		−499.494 11			−499.541 86
	−498.188 51			−498.283 00		–			–
	−498.161 42			−498.329 51		–			–
$CHCl^+(^2A')$	−497.499 17	7.2			CH_2Cl_2	−957.990 02	18.1[b]	2.2	
	−497.836 94	7.2	1.8	−497.876 37		−958.473 79			−958.659 85
	−497.865 60			−497.959 63		–			–
	−497.841 00			−498.005 51		–			–
$CCl_2(^1A_1)$	−956.712 26	2.6			$CHCl_3$	−1416.873 44	12.5[b]	2.7	
	−957.282 31	2.5	2.1	−957.355 46		−1417.684 45			−1417.775 78
	−957.317 58			−957.500 43		–			–
	–			–		–			–
$CCl_2^+(^2A_1)$	−956.406 61	3.2			$C(^3P)$				
	−956.963 34	3.3	2.0	−957.025 20					−37.775 44
	−956.994 30			−957.168 94					−37.796 42
	–			–					−37.799 10
$CH_3(^2A_1')$	−39.564 46	17.7			$Cl(^2P)$				
	−39.725 67	17.8	2.0	−39.749 99					−459.657 14
	−39.748 35			−39.771 07					−459.717 96
	−39.727 16			−39.784 05					−459.754 90
$CH_3^+(^1A_1')$	−39.236 30	19.0			$H(^2S)$				
	−39.374 32	18.9	1.8	−39.393 59					−0.499 81
	−39.397 86			−39.415 39					−0.499 81
	−39.374 73			−39.425 95					−0.499 82
$CH_2Cl(^2B_1)$	−498.464 51	13.5			$H_2(^1\Sigma_g^+)$				
	−498.828 75	13.5	1.8	−498.875 22					−1.167 73
	−498.858 48			−498.958 52					−1.168 34
	–			–					−1.172 52

[a] HF zero-point energies are scaled by 0.91 and MP2 zero-point energies are scaled by 0.94.[50] [b] HF/6-31++G(d,p) (scaled by 0.91) zero-point energies.[45]

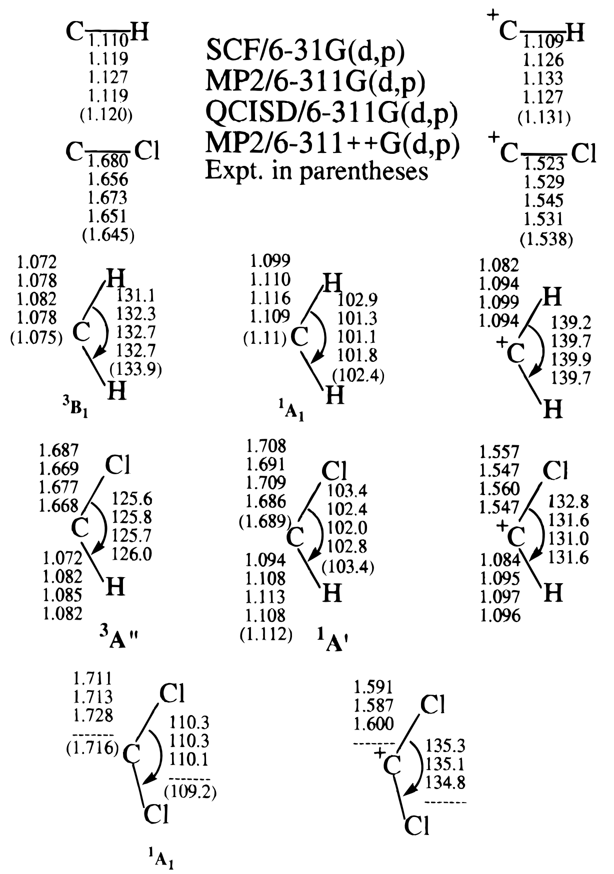

Figure 1. Optimized structures of methylidynes and methylenes and their cations; bond lengths in angstroms and bond angles in degrees. Experimental data can be found in refs 58−66.

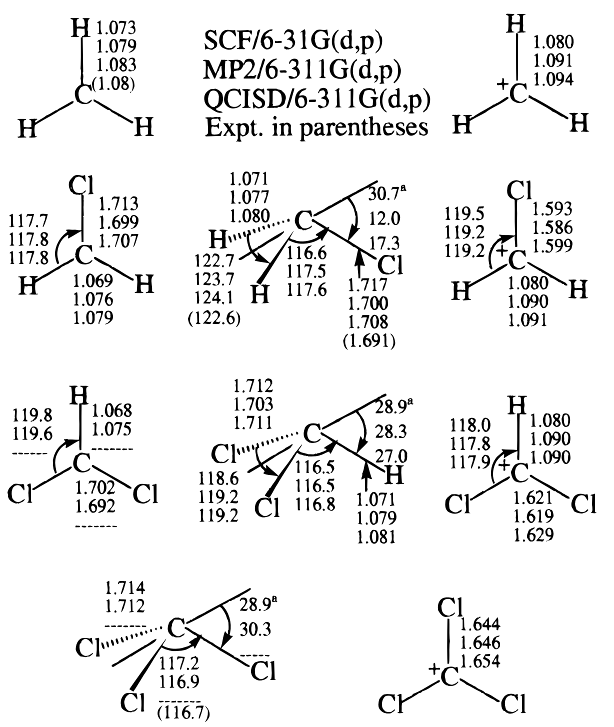

Figure 2. Optimized structures of methyl radicals and their cations: bond lengths in angstroms and bond angles in degrees. Experimental data can be found in refs 9b, 67, and 68. "a" refers to the out-of-plane angle, the angle between the bisector of HCH or ClCCl and the C−Cl or C−H bond.

previous value was 51 ± 2.0 kcal mol^{-1}), a value which compares well with Cheng and Grabowski's value of 57.2 ± 4.0 kcal mol^{-1} (based on bracketed acidities)[22] and with our MP4/2df,p value of 55.3 kcal mol^{-1}.

(*d*) CCl_3^+. All of the MP4/2df,p enthalpies of formation for the methyl radicals and their cations, except that for CCl_3^+, agree to within ±1.2 kcal mol^{-1} with the experimental values. As outlined in the Introduction, there has been considerable controversy over the value of $\Delta H^\circ_{f,298}(CCl_3^+)$, with bracketing methods establishing a range from 192 to 208.8 kcal mol^{-1}. The two most recent[7a,9a] experimental values for $\Delta H^\circ_{f,298}(CCl_3^+)$, 205.2 ± 0.6 and 202.2 ± 0.8 kcal mol^{-1}, disagree by 3 kcal mol^{-1} and our calculated value of 200.2 kcal mol^{-1} favors the lower one, but is outside the error limits.

(*e*) *CHCl*. Inclusion of core electron correlation and use of a larger basis set resulted in a decrease in the calculated enthalpy of formation of $CHCl(^3A')$ from 85.9 kcal mol^{-1} at MP4/2df,p to 83.3 kcal mol^{-1} at QCI/3df,3pd. There was also a decrease in $\Delta H^\circ_{f,298}(CHCl(^1A'))$, but here the change was only 0.8 kcal mol^{-1}. In general, the MP4/2df,p enthalpies of formation are slightly higher than the QCI/3df,3pd values, and calculations with the 6-311G(2df,p) basis set overestimate enthalpies of formation of the two molecules in triplet states. The G1 and G2 methods give results comparable to those at MP4/2df,p, underestimating the atomization energies of triplet states.[48,49] At the QCI/3df,3pd level the singlet−triplet splitting for chloromethylene is 6.5 kcal mol^{-1}, and for methylene it is 8.9 kcal mol^{-1}, results which are in excellent agreement with experimental values[20,78] of 6.4 ± 0.5 and 9.024 ± 0.014 kcal mol^{-1}.

The enthalpy of formation for $CHCl(^1A')$ has proven difficult to measure, with experimental values ranging from 71 to 80 kcal mol^{-1}, and with large uncertainties (±10 kcal mol^{-1}).[10−12] The most recent experimental result,[10] using gas-phase acidity bracketing, the electron affinity of $CHCl(^1A')$, and the bond dissociation energy of H−CHCl, gave $\Delta H^\circ_{f,298}(CHCl(^1A'))$ to be 76 ± 5 kcal mol^{-1}, in excellent agreement with the QCI/3df,3pd calculation (76.8 kcal mol^{-1}). Using this value in combination with the experimental singlet−triplet splitting, an experimental $\Delta H^\circ_{f,298}(CHCl,^3A'')$ of 82.4 ± 5 kcal mol^{-1} is obtained, and this is consistent with the QCI/3df,3pd result of 83.3 kcal mol^{-1}.

(*f*) CH^+. For chlorocarbons the QCI/3df,3pd calculations consistently yield the best correlation with experimental values, but for CH^+ the situation is anomalous with MP4/2df,p calculations being the best and the QCI calculations both underestimating the enthalpy of formation. Extension of the basis set using the Møller−Plesset method to MP4SDTQ/6-311++G(3df,3pd)//MP2/6-311++G(d,p) gave $\Delta H^\circ_{f,298}(CH^+)$ to be 388.2 kcal mol,$^{-1}$ in excellent agreement with the experimental values.

Ionization Energies. The adiabatic ionization energy of a molecule A is defined as the standard enthalpy change in reaction 3, assuming that ion A^+ is allowed to relax to its optimum structure. We have used the calculated enthalpies of formation in Table 2 to calculate ionization energies using eq 3.

$$A \rightarrow A^+ + e \qquad (3)$$

All of the calculated ionization energies in Table 3 are systematically, but only slightly, lower than the experimental results (Figure 3). The calculated ionization energies of the parent hydrocarbons, CH_n, are well-represented at all levels of theory, with a maximum deviation from experiment of 0.12 eV, and with still smaller deviations (0.06 eV) at QCI/3df,3pd.

Calculations at the three levels of theory gave almost identical ionization energies, and this gave us confidence in assessing

TABLE 2: Calculated and Experimental Standard Enthalpies of Formation ($\Delta H^{\circ}_{f,298}$), (kcal mol^{-1})

molecule	MP4/2df,p	QCI/2df,p	QCI/3df,3pd	exptl
$CH(^2\Pi)$	143.1	142.6	142.4	142.5 $\pm$ 0.3,[a] 142.3 $\pm$ 0.3,[b]
$CH^+(^1\Sigma^+)$	387.2	385.2	386.2	387.8 $\pm$ 0.2,[a] 388.0 $\pm$ 0.1,[c]
$CCl(^2\Pi)$	104.9	104.3	104.3	~104,[d] 120 $\pm$ 5[e]
$CCl^+(^1\Sigma^+)$	303.8	304.2	304.9	311.1 $\pm$ 2.0,[f] 313 $\pm$ 4,[g] 297[h]
$CH_2(^1A_1)$	103.8	102.7	102.7	101.7 $\pm$ 0.5,[i] 102.6 $\pm$ 0.6[j]
$CH_2(^3B_1)$	95.2	95.7	93.8	93.6 $\pm$ 0.6,[i] 93.9 $\pm$ 0.7,[k] 94.1 $\pm$ 0.6,[i] 92.8 $\pm$ 0.6[l]
$CH_2^+(^2A_1)$	332.4	332.5	332.1	331,[m] 333.6 $\pm$ 0.7[n]
$CHCl(^1A_1)$	77.6	76.4	76.8	76 $\pm$ 5,[o] 71 $\pm$ 5,[d] 80 $\pm$ 10[e]
$CHCl(^3A'')$	85.9	85.0	83.3	82.4 $\pm$ 5,[o] 73[d]
$CHCl^+(^2A')$	288.6	288.0	286.7	~298,[d] 324 $\pm$ 1[p]
$CCl_2(^1A_1)$	55.3	54.5		52.4 $\pm$ 3.1,[q] 51.0 $\pm$ 2.0,[r] 57.2 $\pm$ 4.00,[s] 39 $\pm$ 3[d]
$CCl_2^+(^2A_1)$	267.3	267.0		264.8 $\pm$ 1.8,[f] 279[t]
$CH_3(^2A_1')$	35.9	36.5	35.3	35.1 $\pm$ 0.1[u]
$CH_3^+(^1A_1')$	260.4	260.6	260.9	261.3 $\pm$ 0.4[m]
$CH_2Cl(^2B_1)$	28.4	28.2		27.7 $\pm$ 2.0[v]
$CH_2Cl^+(^1A_1)$	227.8	226.9		227.0 $\pm$ 0.5,[w] 228.8 $\pm$ 0.4[x]
$CHCl_2(^2B_1)$	22.4			22.3 $\pm$ 2.0[v]
$CHCl_2^+(^1A_1)$	210.1	210.0		211.2 $\pm$ 0.4,[x] 212.0.0 $\pm$ 0.5[w]
$CCl_3(^2A_1)$	18.0			18.0 $\pm$ 2.0,[v] 17.0 $\pm$ 0.6[y]
$CCl_3^+(^1A_1')$	200.2			199,[h] 205.2 $\pm$ 0.6,[y] 202.2 $\pm$ 0.8[z]
CH_4	−18.3			−17.8 $\pm$ 0.1[h]
CH_3Cl	−20.1			−19.6 $\pm$ 0.1[h]
CH_2Cl_2	−23.2			−22.9 $\pm$ 0.2[h]
$CHCl_3$	−25.4			−25.0 $\pm$ 0.5[h]

[a] Reference 57. [b] Reference 80. [c] Reference 81. [d] Reference 11. [e] Reference 12. [f] Reference 13. [g] Reference 14. [h] Reference 44. [i] Reference 82. [j] Reference 83. [k] Reference 84. [l] Reference 85. [m] Reference 86. [n] Calculated using the enthalpy of formation in ref 84 and an ionization energy of 10.396 $\pm$ 0.003 eV from: Herzberg, G. *Can. J. Phys.* **1961**, *39*, 1511. [o] Reference 10, the enthalpy of formation of ($^3A''$) is calculated by using a singlet−triplet splitting of 6.4 kcal. [p] Reference 16. [q] Reference 21. [r] See ref 7b and text. [s] Reference 22. [t] Reference 24. [u] Reference 87. [v] Reference 32. [w] Reference 36. [x] Reference 35. [y] Reference 9a. [z] Reference 7a. mol^{-1} from ref 20.

TABLE 3: Calculated and Experimental Adiabatic Ionization Energies (eV).

molecule	MP4/(2df,p)	QCI/(2df,p)	QCI/(3df,3pd)	exptl
CH	10.58	10.52	10.57	10.64 $\pm$ 0.01[a]
CCl	8.63	8.67	8.70	8.9 $\pm$ 0.2,[b] 10.6[c]
$CH_2(^3B_1)$	10.29	10.27	10.34	10.396 $\pm$ 0.003[d]
$CH_2(^1A_1)$	9.91	9.97	9.95	
$CHCl(^1A')$	9.15	9.18	9.10	9.84 $\pm$ 0.20[e]
CCl_2	9.19	9.21		9.10 $\pm$ 0.10,[f] 9.27 $\pm$ 0.04[g]
CH_3	9.74	9.72	9.78	9.84 $\pm$ 0.01[h]
CH_2Cl	8.65	8.61		8.75 $\pm$ 0.01,[i] 8.64 $\pm$ 0.01[j]
$CHCl_2$	8.14			8.45 $\pm$ 0.05,[k] 8.32 $\pm$ 0.01,[l] 8.23 $\pm$ 0.10[j]
CCl_3	7.90			8.109 $\pm$ 0.005,[m] 8.06 $\pm$ 0.02[n]

[a] Reference 57. [b] Reference 19. [c] Reference 18. [d] Reference 88. [e] Difference in enthalpies of formation of neutral and cation from ref 11. [f] Reference 13. [g] Reference 7b. [h] Reference 89. [i] Reference 38. [j] Calculated from the difference in enthalpies of formation for the neutral from ref 32 and cations from ref 36. [k] Reference 37. [l] Reference 90. [m] Difference in enthalpies of formation of neutral and cation from ref 9a. [n] Reference 7a.

widely differing experimental results for CCl. The most recent ionization energy,[18] based on multiphoton ionization mass spectrometry, is 10.6 eV, and this contrasts with an earlier value of 8.9 $\pm$ 0.2 eV, from multiphoton ionization photoelectron spectroscopy.[19] Clearly then, the theoretical value of 8.70 eV indicates that the larger experimental value is too high and that the lower one is correct. Similarly, the calculated ionization energy of 9.10 eV for $CHCl(^1A')$ is 0.74 eV lower than the experimental value (derived from the enthalpies of formation of the neutral molecule and its cation),[11] thereby casting doubt on the experimental value.

Both the theoretical ionization energies for CCl_2 (9.19 eV at MP4/2df,p and 9.21 eV at QCI/2df,p) are intermediate between the experimental values of 9.10 $\pm$ 0.10 eV (from ionization thresholds)[13] and 9.27 $\pm$ 0.04 (from photoelectron spectroscopy.[7b] However, a recently calculated value of 9.55 eV, based on density functional theory, is substantially larger.[28]

In the methyl series, the experimental ionization energies which correlate best with calculated results are those derived from the differences in the experimental enthalpies of formation of the neutral[36] and cation[37] (as opposed to directly measured values). Using this approach, the MP4/2df,p ionization energies for the chloromethyl and dichloromethyl radicals are within 0.01 and 0.07 eV, respectively, of ionization energies derived from enthalpies of formation. There are two recent values for the ionization energy of the trichloromethyl radical, one experimental (8.06 $\pm$ 0.02 eV),[7a] obtained from a photoelectron spectroscopy study of CCl_3, and the other (7.990 eV) calculated at the CEPA-1 level using a triple-ζ equivalent basis set.[6] Both values are lower than an earlier resonance-enhanced multiphoton ionization energy of 8.109 $\pm$ 0.005 eV,[9a] and all are slightly higher than the MP4/2df,p calculated value of 7.90 eV.

For molecules CCl and CH_mCl_n, where $m + n = 3$, the electron removed in the ionization is from the π-system (assuming that the methyl radicals are planar), and this results in the general trend of the ionization energy decreasing with increased substitution by chlorine. The origin of this effect lies in the ability of the chlorine atoms to carry a large amount of the positive charge in chlorocarbocations. For example, from a Mulliken population analysis at HF/6-31G(d,p) on molecules $CX(^2\Pi)$, where X is Cl or H, both atoms carry essentially zero charge, but in ions CX^+ the charge on H is +0.30, while that on Cl is +0.57. Consequently the ionization energy of CH is much higher than that of CCl (10.58 eV compared with 8.70

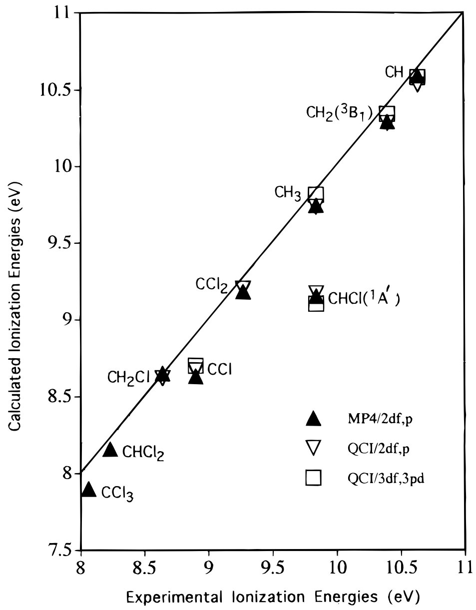

Figure 3. Plot of calculated ionization energy (eV) against experimental values.

TABLE 4: Calculated Proton Affinities (kcal mol^{-1})

molecule	MP4/ 2df,p	QCI/ 2df,p	QCI/ 3df,3pd	exptl
C	149.7	151.6	150.7	149.2 ± 0.2[a]
CH	176.5	175.7	176.0	177.0 ± 0.3[b]
CCl	182.3	182.2	183.5	$\sim$172[c]
$CH_2(^1A_1)$	209.1	207.7	207.4	207.0 ± 1.0[d]
$CHCl(^1A')$	215.5	215.2		207.5 ± 2.0[e]
CCl_2	210.4	210.2		209.6 ± 2.0,[f] 193 ± 1[e]

[a] References 44 and 57. [b] References 44, 86, and 91. [c] References 11 and 44. [d] References 83 and 86. [e] Reference 11. [f] Reference 23.

eV). In the methyl radical series, there is a saturation effect with the first chlorine substituent resulting in a decrease of 1.09 eV, the second 0.49 eV, and the third only 0.26 eV (from MP4/2df,p calculations).

In the singlet methylenes, CH_mCl_n, ionization removes a σ-electron and the stabilization by chlorine is diminished. Substitution by one chlorine decreases the ionization energy by 0.7 eV (at QCI/2df,p), a smaller change than that resulting from monosubstitution in the methylidyne and methyl series, and the second chlorine actually results in a small increase (by 0.03 eV).

Proton Affinities. The proton affinity of a base (B) is defined as the standard enthalpy change for the reaction in eq 4. The calculated proton affinities for carbon, the methylidynes, and the carbenes are listed in Table 4, along with experimental values.

$$BH^+ \rightarrow B + H^+ \qquad (4)$$

The carbon atom has the lowest proton affinity in Table 4, and as the reactant and products have different spin multiplicities ($CH^+(^1\Sigma^+) \rightarrow C(^3P) + H^+$), then the reaction has little physical importance. In all other protonation reactions spin is preserved. The methylidynes have proton affinities which are lower by $\sim$33 kcal mol^{-1} than the similarly substituted methylenes. Substitution of both methylidyne and methylene by Cl atoms results in increases in the proton affinities, but the changes are small, indicating that stabilization of the cation by delocalization of the charge onto chlorine is largely offset by the stabilizing effect of chlorine on the carbene and carbyne.

TABLE 5: Substituent Stabilization Energies[a] (SSE, kcal mol^{-1}) Calculated from Reaction $CH_mCl_n + CH_4 \rightarrow CH_{4-n}Cl_n + CH_{m+n}$

molecule	SSE	molecule	SSE	molecule	SSE
CCl^+	81.6	$CHCl^+$	41.8	CH_2Cl^+	30.8
		CCl_2^+	60.0	$CHCl_2^+$	45.0
				CCl_3^+	53.1
CCl	36.4	CHCl	24.4	CH_2Cl	5.7
		CCl_2	43.6	$CHCl_2$	8.6
				CCl_3	10.8

[a] The MP4/2df,p enthalpies of formation in Table 2 are used to calculate the substituent stabilization energies.

There are two molecules, CCl and $CHCl(^1A')$, for which the theoretical and experimental proton affinities do not agree to within $\pm$1.5 kcal mol^{-1}. For CCl the estimate of the experimental proton affinity was obtained from the enthalpies of formation of CCl (104 kcal mol^{-1}) and $CHCl^+$ ($\sim$298 kcal mol^{-1}), both of which are not firmly established.[11,44] The calculated enthalpies in Table 2 confirm the value for CCl but show $\Delta H^\circ_{f,298}(CHCl^+)$ to be too high by $\sim$11 kcal mol^{-1}. Hence, the experimental proton affinity is underestimated by this amount.

Protonation enthalpy ladders are frequently used to determine proton affinities, but the bracketing experiments[11] that established the proton affinity of $CHCl(^1A')$, to lie between 205.4 and 209.5 kcal mol^{-1}, gave results that are too low when compared to the calculated MP4/2df,p value of 214.9 kcal mol^{-1}. A similar situation exists in the case of CCl_2, where a value of 193 $\pm$ 1 kcal mol^{-1} has been quoted[11] but recent results,[21] including our MP4/2df,p calculations, are in agreement with a value[23] of 209.6 $\pm$ 2.0.kcal mol^{-1}. Possible sources of error in the bracketing experiments leading to low basicities include residual internal excitation of the $CHCl_2^+$ reactant ion, the occurrence of fast secondary reactions, and impurity ions in the ICR.[21]

Substituent Effects. As already discussed above, chloro substituents decrease the ionization energies and slightly increase the proton affinities of small hydrocarbons. These substituent effects result from the ability of chlorine to delocalize the positive charge in carbocations. We now discuss two additional methods of assessing the stabilizing effect of chlorine in hydrocarbons and in carbocations.

The stabilization originating from chloro substitution in CH_mCl_n ($m + n = 1-3$) can be estimated from the enthalpy of the isodesmic reaction in eq 5. Here, molecule CH_mCl_n (or ion

$$CH_mCl_n + CH_4 \rightarrow CH_{4-n}Cl_n + CH_{m+n} \qquad (5)$$

$CH_mCl_n^+$) is compared with the corresponding unsubstituted molecule CH_{m+n} (or CH_{m+n}^+), and it is assumed that there is minimal interaction between chlorine atoms in the methane $CH_{4-n}Cl_n$. A positive energy for reaction 5 indicates that CH_mCl_n (or $CH_mCl_n^+$) is more stable than its CH_{m+n} (or CH_{m+n}^+) analogue.

From the data in Table 5, chloro substitution stabilizes all species, with the effect being larger in carbocations than in the corresponding neutrals. CCl^+ has the highest substituent stabilization energy, and this is consistent with the observation that the chlorine in CCl has the most pronounced effect in decreasing the ionization energy. For the perchloro-substituted carbocations the order of stabilization is $CCl^+ > CCl_2^+ > CCl_3^+$, and along the methyl cation series the one chloro substituent of CH_2Cl^+ is more stabilizing than the second chloro (in $CHCl_2^+$), while the third one of CCl_3^+ has even less effect, i.e., there is a saturation effect with increased substitution. Among the neutral molecules, the methyl radicals have only

TABLE 6: Hydride Affinities (HA, kcal mol^{-1}) Calculated from Equation $CH_{m+1}Cl_n \rightarrow CH_mCl_n^+ + H^-$

molecule	HA	molecule	HA	molecule	HA
CH^+	318.1	CH_2^+	331.0	CH_3^+	313.4 (313)[b]
CCl^+	260.9	$CHCl^+$	294.9	CH_2Cl^+	282.6(281)[c]
		CCl_2^+	279.6	$CHCl_2^+$	268.4 (270)
				CCl_3^+	260.3 (262.3)[c,d]

[a] The hydride affinities are calculated from MP4/2df,p enthalpies of formation in Table 2. The enthalpy of formation for H^- (34.7 kcal mol^{-1}) is taken from ref 44. [b] Reference 36. [c] The hydride affinities of CH_2Cl^+ and CH_3^+ relative to CCl_3^+ have been reported to be 22.3 and 53.1 kcal mol^{-1}, respectively, at MP4(SDTQ)//MP2/6-31G(d): Reynolds, C. H. *J. Chem. Soc., Chem. Commun.* **1991**, 975. [d] References 7a and 44.

small substituent dependence, but there are large stabilization energies in the chlorocarbenes and in CCl.

Hydride affinities, as defined by eq 6, provide an alternate method of assessing the stabilizing effect of Cl atoms in carbocations. For the parent carbocations, the hydride affinities

$$CH_{m+1}Cl_n \rightarrow CH_mCl_n^+ + H^- \qquad (6)$$

are $CH_2^+ > CH^+ > CH_3^+$. All chloro substituents result in a decrease in hydride affinity, again indicating their stabilizing effect in carbocations, and the largest decrease is in the methylidynes, where CCl^+ has an affinity 57.2 kcal mol^{-1} smaller than that of CH^+. The same lack of additivity of substituent effects as observed in the stabilization energies is repeated in the hydride affinities.

Both methods (Tables 5 and 6) show that the order of stabilization for the methyl cations is $CCl_3^+ > CHCl_2^+ > CH_2Cl^+ > CH_3^+$, for the methyliumyl ions $CCl_2^+ > CHCl^+ > CH_2^+$, and for the methyliumylidyne ions $CCl^+ > CH^+$. The hydride affinity scale for the chlorocarbocations as calculated from reaction 6 is $CCl_3^+ \approx CCl^+ < CHCl_2^+ < CCl_2^+ < CH_2Cl^+ < CHCl^+ < CH_3^+ < CH^+ < CH_2^+$.

Conclusions

Extending the level of theory from MP4SDTQ/6-311G(2df,p) to QCISD(T)/6-311++G(3df,3pd) plus the inclusion of core-electron correlation provides significant improvement (from $\pm$2.3 to $\pm$1.2 kcal mol^{-1}) in the accuracy of calculating thermochemical properties of organo-chloro compounds. In particular, standard enthalpies of formation of triplet state species, which are difficult to determine even at such high levels of theory as G1, G2, and MP4SDTQ/6-311(2df,p), can be calculated accurately at QCISD(T)/6-311++G(3df,3pd).

For some CH_nCl_m molecules there are widely varying enthalpies of formation in the literature, and for these species the high level of agreement between the QCISD(T)/6-311++G-(3df,3pd) and experimental values enables us to be confident in choosing which of the values is the most reliable. In the case of CCl^+, $CHCl^+$, and CCl_2 theory indicates that the experimental enthalpies of formation are incorrect, and for CCl_3^+ the most recent experimental value appears to be the best.

Chloro substituents stabilize all carbocations, with the effect being largest in the smallest ion, CCl^+. Multiple substitution by Cl in methyl cations leads to further stabilization than in CH_2Cl^+, but each additional chloro substituent provides smaller increments of stabilization.

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