

A computational study of the enthalpies of formation of halomethylidyne

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(Received 2 September 1998; accepted 22 October 1998)

The halomethylidyne CH, CF, CCl, CBr, and CI have been investigated using GAUSSIAN-2 theory and calculations up to QCISD(T)/6-311+G(3df,2p). At the latter level of theory bond lengths, harmonic frequencies, and anharmonicity corrections have been derived and compare well with experimental measurements where these are available. GAUSSIAN-2 and QCISD(T)/6-311+G(3df,2p) energies were employed in isodesmic reactions to obtain the following recommended enthalpies of formation ($\Delta_f H_{298}$) in kJ mol^{-1} : CF, 248.6; CCl, 436.9; CBr, 497.1; CI, 557.6. Estimated error limits are $\pm 6 \text{ kJ mol}^{-1}$. © 1999 American Institute of Physics.
[S0021-9606(99)30804-7]

I. INTRODUCTION

A widely employed mechanism for the combustion chemistry of fluorinated hydrocarbons, which are employed as fire suppressants, includes reactions that form and consume fluoromethylidyne, CF.¹ The thermochemistry of this molecule is not well established: Two reviews arrived at heats of formation that differ by 19 kJ mol^{-1} .^{2,3} A similar remark applies to the other halomethylidynes (halocarbynes), CCl, CBr, and CI, whose roles in the incineration of chlorine-containing organic molecules and in flame inhibition by agents such as CF_3Br and CF_3I have yet to be determined, where discrepancies in reported values of $\Delta_f H_{298}$ are up to 60 kJ mol^{-1} .^{2,3} In order to assist kinetic modeling of the combustion of halogen-containing compounds, the main aim of this study is to employ *ab initio* methods to derive accurate thermochemistry for the series of halocarbynes. In addition, bond lengths, harmonic frequencies, and vibrational anharmonicities are obtained. For the earlier members of the series, comparison with spectroscopic measurements validates the calculations, while our results fill gaps in the data available for CBr and CI.^{4,5}

II. COMPUTATIONAL METHODS

All computations were performed using the GAUSSIAN 94 suite of programs.⁶ Calculations on bromine and iodine-containing species utilized basis sets developed recently.^{7,8} The all-electron (AE) forms of these basis sets were employed in nonrelativistic calculations, and we note that earlier good accord with experimental results suggests that relativistic effects are either small or cancel.⁸ In the case of iodine-containing molecules we also employed basis sets incorporating Hay-Wadt relativistic effective core potentials (ECPs).⁸ Three levels of calculations were performed.

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First, the GAUSSIAN-2 (G2) procedure⁹ was used to obtain approximate QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G(d) energies for the carbynes, CX, X=H, F, Cl, Br, I, and for various reference halomethanes. These data were utilized to compute enthalpies of formation of the four halocarbynes both directly from atomization energies,^{3,10} and via the application of isodesmic reactions.^{11,12}

Second, in order to ascertain the effect of improving the geometries and removing the additivity approximations of the G2 method, nonapproximate QCISD(T)/6-311+G(3df,2p) energies were computed at geometries optimized at the QCISD/6-311G(d,p) level, and used to compute enthalpies of formation.

Finally, in order to obtain very accurate bond lengths, harmonic frequencies, and vibrational anharmonicities, QCISD(T)/6-311+G(3df,2p) energies of the carbynes were computed at increments of 0.01 \AA ($1 \text{ \AA} = 10^{-10} \text{ m}$) in the vicinity of the equilibrium bond lengths (a total of 10–15 points were obtained for each species).

In all calculations, empirical spin-orbit corrections were applied to the energies of the carbynes^{2,13} and halogen atoms.¹⁴

III. RESULTS AND DISCUSSION

A. Bond lengths, harmonic frequencies, and vibrational anharmonicities

The calculated and experimental² equilibrium bond lengths R for CH and the halocarbynes are listed in Table I. Quantities in parentheses represent the percent deviations from experiment;² no error is given for CI since the reported value is only an empirical estimate.²

One observes that for CF, CCl, and CBr, computed MP2(full)/6-31G(d) bond lengths are greater than experiment by as much as 1.4%. One sees further that, except for the CF radical, improving the level to QCISD/6-311G(d,p) increases bond distances, exacerbating the disagreement with experiment.

The most accurate method utilized in this study was to

TABLE I. Equilibrium bond lengths of the carbynes.^a

	CH	CF	CCl	CBr	CI [AE]	CI [ECP]
R [MP2] ^b	1.120 (0.0%)	1.289 (1.4%)	1.662 (1.2%)	1.838 (1.1%)	2.064	2.049
R [QCISD] ^c	1.128 (0.7%)	1.279 (0.6%)	1.674 (1.9%)	1.843 (1.4%)	2.076	2.055
R [QCISD(T)] ^d	1.124 (0.4%)	1.276 (0.3%)	1.655 (0.7%)	1.828 (0.5%)	2.048 [2.036] ^e	2.023
R (expt) ^f	1.120	1.2718	1.643	1.818	2.10 ^g	

^aBond lengths in angstroms. Quantities in parentheses represent percent deviations from experiment.

^bOptimized MP2(full)/6-31G(*d*) bond length.

^cOptimized QCISD/6-311G(*d,p*) bond length.

^dOptimized QCISD(T)/6-311+G(3*df,2p*) bond length (from fit of PED; see the text).

^eMean value.

^fReference 2.

^gEmpirical estimate.

compute equilibrium bond lengths via parabolic interpolation of QCISD(T)/6-311+G(3*df,2p*) energies in the immediate vicinity of the minimum. One finds from Table I that this higher level treatment diminishes computed values of R (by as much as 0.028 Å in the case of CI), and yields the best agreement with experiment, except for CH, where R (MP2) agrees fortuitously with the measured bond length.

It is seen in Table I that the 2.10 Å empirical estimate of the CI bond length² is significantly greater than values computed at all levels. Since the calculated values of R for all other carbynes are somewhat greater than experiment, it is quite likely that the empirical CI bond length is too high. The results obtained with AE and ECP basis sets are similar, with R (CI) being slightly smaller with the ECP basis. In order to

arrive at a more realistic value for R (CI), we have averaged the R [QCISD(T)] bond lengths obtained with the AE and ECP basis sets, which we recommend as a best estimate of the CI bond length.

The first four rows of Table II summarize the calculated and experimental *harmonic* vibrational frequencies of the carbynes. Quantities in parentheses represent percent deviations from experiment; errors are not given for CBr or for CI, for which the values of ω_e are empirical estimates.

The first row in Table II contains unscaled HF/6-31G(*d*) frequencies, obtained from simple harmonic force constant analysis at the optimized bond length. Although ω_e (CCl) is very close to experiment, computed frequencies for CH and CF exhibit large positive deviations (7%–8%). There is a general improvement when frequencies are calculated at the QCISD/6-311G(*d,p*) level, where results are seen to agree to within 1% or better for the three carbynes where accurate data are available.

In order to improve still further the level of calculation to the QCISD(T)/6-311+G(3*df,2p*) level, as well as to compute vibrational anharmonicities, $\omega_e x_e$, we utilized the fact that the potential energy functions of diatomic molecules in the vicinity of the equilibrium bond length, R_e , are well represented by a Morse potential,¹⁵ given by

$$V(R) = D_e [1 - e^{-\alpha(R-R_e)}]^2 + V(R_e). \quad (1)$$

The harmonic frequency and vibrational anharmonicity are related to the dissociation energy, D_e , and exponential factor, α , by¹⁶

$$\omega_e = \alpha \left(\frac{\hbar D_e}{\pi c \mu} \right)^2, \quad \omega_e x_e = \frac{\hbar \alpha^2}{4 \pi c \mu}, \quad (2)$$

where μ is the oscillator's reduced mass and π , c , and \hbar have their usual meanings. For each carbyne, a series of 10–15 QCISD(T)/6-311+G(3*df,2p*) energies at 0.01 Å increments

TABLE II. Vibrational harmonic frequencies and anharmonicities of the carbynes.^a

	CH	CF	CCl	CBr	CI [AE]	CI [ECP]
ω_e [HF] ^b	3057 (6.9%)	1411 (7.9%)	873 (−0.4%)	705	589	584
ω_e [QCISD] ^c	2843 (0.5%)	1315 (0.5%)	868 (−1.0%)	711	598	602
ω_e [QCISD(T)] ^d	2856 (1.0%)	1301 (−0.6%)	877 (0.0%)	725	627 632 ^e	636
ω_e [expt] ^f	2858.5	1308.1	876.4	730 ^g	630 ^g	
$\omega_e x_e$ [QCISD(T)] ^d	64.3 (2.1%)	12.3 (11.8%)	6.3 (2.4%)	4.2	4.0 3.9 ^e	3.7
$\omega_e x_e$ [expt] ^f	63	11	6.15	4.8 ^g	5 ^g	

^aFrequencies and anharmonicities in cm^{-1} . Quantities in parentheses represent percent deviations from experiment.

^bUnscaled HF/6-31G(*d*) frequencies.

^cUnscaled QCISD/6-311G(*d,p*) frequencies.

^dFrequencies and anharmonicities obtained from fit of QCISD(T)/6-311+G(3*df,2p*) energies. See the text.

^eMean value.

^fReference 2.

^gEmpirical estimate.

TABLE III. *Ab initio* energies and enthalpies of formation of halocarbynes.^a

Method	Reaction	CF	CCl	CBr	CI [AE]	CI [ECP]
E_0 [G2]		-137.627 19	-497.614 07	-2610.445 34	-6954.880 29	-49.219 69
E_0 [QCISD(T)] ^b		-137.601 54	-497.589 08	-2610.420 33	-6954.854 91	-49.195 28
$\Delta_f H_{298}$ [G2]	CX→C+X	242.2	436.1	497.8	561.2	554.0
	CH ₃ X+CH→CH ₄ +CX	...	436.7	496.3	559.1	555.0
	CH ₂ X ₂ +2CH→CH ₄ +2CX	248.3	436.1
$\Delta_f H_{298}$ [QCISD(T)] ^b	CH ₃ X+CH→CH ₄ +CX	...	438.2	497.3	560.1	556.0
	CH ₂ X ₂ +2CH→CH ₄ +2CX	248.9	437.4
	Average	248.6 ^c ±6	436.9±6	497.1±6	560.1±6	555.0±6
					557.6±6 ^d	
$\Delta_f H_{298}$ [expt]		236.3±11.5 ^e	440±40 ^e	490±35 ^e	570±35 ^e	
		255.2±8 ^f	502.1±20 ^f	510±63 ^f	...	

^aEnergies are in a.u. and enthalpies are in kJ mol⁻¹.

^bQCISD(T)/6-311+G(3df,2p)//QCISD/6-311G(d,p) energies and enthalpies.

^cExcluding value from G2 atomization reaction.

^dMean of AE and ECP values.

^eReference 2.

^fReference 3.

on both sides of the minimum were fit by Eq. (1) to yield values for R_e , $V(R_e)$, D_e , and α . ω_e and $\omega_e x_e$ were then computed from Eq. (2) using the values of μ corresponding to the most abundant isotopes.

From Table II, one sees that both the high level harmonic frequencies and anharmonicities are in excellent agreement with the accurate experimental data available for CH, CF, and CCl, which indicates that the QCISD(T)/6-311+G(3df,2p) calculations furnish an accurate depiction of the shape of the electronic potential in the vicinity of the equilibrium for CH and the halocarbynes. The fact that the computed frequencies and anharmonicities also agree well with the approximate values reported for CBr and CI provide evidence that the empirical estimates of ω_e and $\omega_e x_e$ for these species are fairly accurate.

After this work was completed we became aware of very recent measurements by Marr *et al.*,¹⁷ who employed high-resolution IR diode laser absorption to derive spectroscopic parameters for CBr, including $\omega_e = 727.99$ cm⁻¹ and $\omega_e x_e = 3.95$ cm⁻¹. Our computed values in Table II are very close to these results.

B. Enthalpies of formation

Shown in Table III are *ab initio* G2 and QCISD(T)/6-311+G(3df,2p) energies as well as calculated and experimental values of $\Delta_f H_{298}$ of the four halocarbynes. The "standard" procedure for calculation of enthalpies of formation is first to compute *ab initio* energy differences, ΔE_0 , for the gas phase atomization reaction, which for the halocarbynes is given by CX(g)→C(g)+X(g). As detailed elsewhere,¹⁸ ΔE_0 is combined with experimental atomic heats of formation and thermal enthalpy contributions $H_{298} - H_0$ of the atoms and molecular species to obtain $\Delta_f H_{298}$. The results of this calculation using G2 energies are shown in Table III. Values of $\Delta_f H_{298}$ [QCISD(T)] (not shown) ranged from 10 to 15 kJ mol⁻¹ higher than $\Delta_f H_{298}$ (G2). This discrepancy can be attributed almost entirely to the in-

clusion of high level corrections (HLC) in the G2 method⁹ which, for the halocarbyne atomization reactions, has the effect of lowering the calculated heat of formation by approximately 12 kJ mol⁻¹.

It has been well documented that *ab initio* heats of formation computed from atomization energies often exhibit relatively large systematic errors from experiment, proportional to the number of each type of bond.¹⁹ It has been demonstrated that the systematic errors are particularly large in G2 heats of formation of the fluoromethanes.^{10,18} A common procedure developed to minimize these systematic errors is to use *isodesmic* reactions,^{11,12} in which the numbers of each type of bond are preserved. The principle is that systematic errors in individual bond energies will in large part cancel during computation of the energy difference, ΔE_0 . If accurate values of $\Delta_f H_{298}$ (expt) are known for all components of the reaction except for the target species, it is then straightforward to extract its heat of formation.

Two useful isodesmic reactions for the accurate calculation of halocarbyne heats of formation are CH₃X+CH→CH₄+CX and CH₂X₂+2CH→CH₄+2CX, since experimental values of $\Delta_f H_{298}$ for CH, CH₄, and many of the mono- and dihalomethanes are known very accurately. *Ab initio* energies and experimental enthalpies of formation of the various reference compounds required for these calculations are given in Table IV. Reported errors in $\Delta_f H_{298}$ [expt] of CH₃F, CH₂Br₂, and CH₂I₂ were relatively large (± 15 , ± 15 , and ± 4 kJ mol⁻¹, respectively).² Hence, these three halomethanes were not used in the calculations.

Calculated enthalpies of formation of the four halocarbynes computed from isodesmic reactions at both the G2 and QCISD(T)/6-311+G(3df,2p) levels are contained in Table III. As noted above, the absence of high level corrections at the latter level introduced large errors in computation of $\Delta_f H_{298}$ from atomization energies. However, the HLCs cancel in the isodesmic reactions and, therefore, one would expect comparable accuracy in computed heats of formation

TABLE IV. *Ab initio* energies and enthalpies of formation of reference compounds.^a

Species	E_0 [G2]	E_0 [QCISD(T)] ^b	$\Delta_f H_{298}(\text{expt})$ ^c	$\Delta_f H_{298}$ [G2]	$\frac{\Delta_f H_{298}[\text{G2}]}{-\Delta_f H_{298}(\text{expt})}$
CH	-38.412 66	-38.402 22	597.4±1.3	593.6	-3.8
CH ₄	-40.410 89	-40.387 91	-74.6±0.3	-77.7	-3.1
CH ₂ F ₂	-238.717 97	-238.664 97	-452.2±1.7	-460.5	-8.3
CH ₃ Cl	-499.553 82	-499.516 84	-81.9±0.6	-82.1	-0.2
CH ₂ Cl ₂	-958.698 92	-958.647 74	-95.0±0.3	-91.1	3.9
CH ₃ Br	-2612.390 46	-2612.353 26	-36.4±0.5	-34.4	2.0
CH ₃ I[AE]	-6956.829 99	-6956.792 51	14.4±0.5	17.0	2.6
CH ₃ I[ECP]	-51.167 83	-51.131 32	14.4±0.5	13.9	-0.5
				MAD: ^d	3.0
				Avg dev:	0.9

^aEnergies are in a.u. and enthalpies are in kJ mol⁻¹.

^bQCISD(T)/6-311+G(3df,2p)//QCISD/6-311G(d,p) energies.

^cReference 2.

^dMean absolute deviation.

from the two methods using this procedure. Indeed, it is satisfying to note that values of $\Delta_f H_{298}$ obtained from the two bases are rather close to each other for all four carbynes; $\Delta_f H_{298}[\text{QCISD(T)}]-\Delta_f H_{298}[\text{G2}]$ ranges from 0.6 to 1.4 kJ mol⁻¹. A check on the consistency of isodesmic reactions involving mono- and dihalomethanes is the close agreement of $\Delta_f H_{298}[\text{CCl}]$ obtained from CH₃Cl and CH₂Cl₂ isodesmic reactions. The AE and ECP results for CI differ by about 5 kJ mol⁻¹; our best estimate for the thermochemistry is the average of the results from the two basis sets.

It is of interest to observe in Table III that for CCl, CBr, and CI, G2 heats of formation obtained from the atomization energies are in excellent agreement with values computed from the isodesmic reactions, indicating that there is little, if any, systematic error in the calculated bond energies of these species. This is in contrast to the results for CF, where it is seen that $\Delta_f H_{298}[\text{G2}]$ calculated from the atomization energy is 6.6 kJ mol⁻¹ lower than the value obtained from the CH₂F₂ isodesmic reaction. This discrepancy is quite close to the average CF bond error of -6.5 kJ mol⁻¹ obtained in a recent investigation of G2 heats of formation in a series of fluoro-, chloro-, and chlorofluoromethanes.^{18,20}

In their initial G2 paper, Curtiss *et al.*⁹ reported dissociation energies for CF and CCl. These dissociation energies (combined with small spin-orbit corrections) yield the $\Delta_f H_{298}$ values found in Table III for the direct dissociation reactions. As part of a comprehensive study of small carbon-fluorine-chlorine species, Rodriguez *et al.*^{21,22} derived $\Delta_f H_{298}=237.2$ kJ mol⁻¹ for CF at the MP4/6-311++G(3df,3pd) level of theory and $\Delta_f H_{298}=436.4$ kJ mol⁻¹ for CCl at QCISD(T) with this basis set. They used isogyric reactions apparently of the form CX+2H→C+X+H₂ together with experimental information about the atoms. Because such isogyric reactions do not remove systematic bond errors, their CF heat of formation is more negative than our proposed value. The lack of bond errors for carbon-chlorine bonds leads to close accord between our heat of formation for CCl and that derived by Rodriguez *et al.*²²

As discussed in Sec. I and observed in Table III, reported uncertainties in $\Delta_f H_{298}[\text{expt}]$ of the halocarbynes are

large and a principal goal of this investigation is to provide more reliable estimates of the heats of formation of these species. Table III contains the average calculated heats of formation of the four halocarbynes obtained by the various methods, which we believe to be more accurate than the discordant evaluations of experimental data.^{2,3} We have excluded the G2 heat of formation of CF from the atomization reaction due to its demonstrated systematic error.

The scatter between the various computed enthalpies of formation for each species is quite small, but would give unrealistically low error estimates in the recommended heats of formation. In order to arrive at an appropriately conservative error estimate for the recommended values of $\Delta_f H_{298}$ for the halocarbynes, we have computed the G2 heats of formation of the reference compounds, for which there are accurate experimental data, via atomization reactions. These values and the deviations from experiment are displayed in the last two columns of Table IV.²³ Even including the rather large deviation of -8.3 for CH₂F₂, which is known to exhibit systematic CF bond errors,^{10,18,20} the mean absolute deviation (MAD) in the G2 enthalpies is 3.0 kJ mol⁻¹. We have conservatively doubled the MAD for the reference compounds to yield an estimated error limit of ±6 kJ mol⁻¹ for the recommended heats of formation of the halocarbynes.

Our proposed value of $\Delta_f H_{298}$ for CF falls between the evaluations of Gurvich *et al.*² and Chase *et al.*³ (Table III), and is also near a recent BAC-MP4 calculation of 236.3 kJ mol⁻¹.¹ Interestingly, a new measurement by Asher and Ruscic based on the appearance potential of CF⁺ from C₂F₄ yields $\Delta_f H_{298}=261.5\pm 4.6$ kJ mol⁻¹,²⁴ which is 6 kJ mol⁻¹ more positive than the higher of the two previous evaluations. These significant deviations indicate that further studies of the thermochemistry of C-F bonds may be warranted. The calculated $\Delta_f H_{298}$ for CCl lies more than 60 kJ mol⁻¹ below the JANAF evaluation,³ but is very close (with a considerably reduced uncertainty) to the Gurvich *et al.* evaluation.² The $\Delta_f H_{298}$ for CBr lies between the two literature evaluations, again with a significantly reduced uncer-

tainty. In the case of CI our result for $\Delta_f H_{298}$ is close to the Gurvich *et al.* evaluation,² but with a higher precision.

IV. CONCLUSIONS

Equilibrium bond lengths, harmonic frequencies, and vibrational anharmonicities computed at up to the QCISD(T)/6-311+G(3df,2p) level are in good agreement with experimental data for CH, CF, and CCl. For CBr earlier empirical estimates appear to be accurate, as do the vibrational data for CI. However, the CI bond length appears to need revision. The methylidyne thermochemistry derived via isodesmic reactions is (except for CF) consistent with atomization calculations, and provides $\Delta_f H_{298}$ values with significantly reduced uncertainty compared to the discordant evaluations available in the literature.

ACKNOWLEDGMENTS

We thank the R. A. Welch Foundation (Grant Nos. B-657 and B-1174), the Air Force Office of Scientific Research, the Air Force Research Laboratory, Wright-Patterson AFB, and the UNT Faculty Research Fund for support.

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¹⁴From Ref. 2, the spin-orbit corrections [in brackets] of the halogen atoms are one-third the $^2P_{1/2}$ - $^2P_{3/2}$ gap: F [-6.14×10^{-4} a.u.], Cl [-1.340×10^{-3} a.u.], Br [-5.596×10^{-3} a.u.], I [-1.155×10^{-2} a.u.].

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