Halon Thermochemistry: Calculated Enthalpies of Formation of Chlorofluoromethanes

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The ab initio G2, G2(MP2), CBS-4, CBS-Q, and BAC-MP4 methods have been used to calculate the enthalpies of formation of the series of four chloromethanes and six chlorofluoromethanes \[CH_xF_{4-x}, x = 0−3, y = 0−3\]. Calculated values of \(\Delta H^\circ\) using the first four ab initio methods exhibit comparatively large systematic negative errors compared with experimental values, up to \(-50\) kJ/mol, which are nearly linearly dependent upon the number of C−F and C−Cl bonds in the molecule. It is found for the chlorofluoromethanes that the application of bond additivity corrections (BAC’s) to the ab initio enthalpies effectively removes systematic errors in the calculations and yields values that are in close agreement with experimentally derived heats. The rms deviations of the corrected calculated enthalpies from the experimental values are 2.4, 2.6, 3.4, 4.7, and 3.8 kJ/mol for the G2(MP2), G2, CBS-Q, CBS-4, and BAC-MP4 methods, respectively. These deviations are lower than the rms errors \((6.9\) kJ/mol\) in the experimental enthalpies. Therefore, it is concluded that any of these calculational procedures, together with bond additivity corrections to remove systematic error, may profitably be used to obtain accurate enthalpies of formation in chlorofluorocarbon species.

Introduction

It is well documented that chlorofluorocarbons (CFC’s) and halon fire suppressants (e.g., CF₃Br, CF₂CIBr, CF₂BrCF₂Br) efficiently catalyze the destruction of stratospheric ozone.\(^1,2\) Hence, their commercial use has been increasingly restricted in recent years.\(^2,3\) Partially hydrogenated CFC’s are more efficiently destroyed in the troposphere, which results in a diminished ozone depletion potential. Therefore, these compounds have been proposed as transitional replacements for the perhalogenated CFC’s and halons.\(^2,4\)

Accurate thermochemical data and rate constants are required to study the effectiveness of a proposed fire suppression agent via kinetic modeling. Unfortunately, these data are not currently available for the majority of the CFC’s.

Recently, we investigated the capability of various ab initio quantum mechanical methods to predict accurate enthalpies of formation in the series of fluoromethanes,\(^5\) \(CH_xF_{4-x}, x = 0−4\). Here, we report the extension of these studies to the complete series of chloromethanes and chlorofluoromethanes, \(CH_xF_yCl_{4-x-y}, x = 0−3, y = 0−3\). The results are presented below.

Calculations

The ab initio calculations were performed using the GAUSSIAN code\(^6−8\) on CRAY Y-MP, CRAY X-MP, CONVEX-C3820, SUN-Sparc, HP-PARisk, and SGI Power-Challenge computers.\(^9\) The G2,\(^10\) the related G2(MP2),\(^11\) and the CBS series\(^12−14\) (CBS-4 and CBS-Q) were used in this investigation of ab initio protocols all involve use of a series of lower level calculations that are designed to provide estimates of the molecular energy with large basis sets and a high degree of electron correlation. The procedures are described in detail in the original references. The BAC-MP4 method\(^15,16\) requires determination of electronic energies and, from these, enthalpies of formation, at the MP4/6-31G(d,p)//HF/6-31G(d) basis level, followed by empirical energy corrections dependent upon the numbers, types, and proximities of the various bonds in the molecule.

Displayed in Table 1 are the HF/6-31G(d) and MP2(FU)/6-31G(d) geometries of the 10 molecules investigated here, together with scaled (by 0.8929) HF/6-31G(d) vibrational frequencies. Also shown in the table are the experimental vibrational frequencies.\(^17\) The average difference between the calculated and experimental frequencies is less than 1%. Further examination suggests that calculated vibrational frequencies less than 1000 cm\(^{-1}\) are in the range 1−3% low, frequencies between 1000 and 1500 cm\(^{-1}\) are roughly 1−3% high, and calculated C−H vibrational frequencies near 3000 cm\(^{-1}\) are about 1% low.

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\(^¶\) Sabbatical Leave, Spring 1995, Lawrence Associates, Inc.
Shown in Table 2 are the ground state G2, G2-MP2, CBS-4, CBS-Q, and MP4/6-31G(d,p) electronic energies of the 10 molecules. These quantities, together with calculated atomic energies, enthalpies of formation of the elements, and heat
TABLE 3: Experimental and Calculated Enthalpies of Formation

<table>
<thead>
<tr>
<th>species</th>
<th>expt</th>
<th>G2</th>
<th>G2(MP2)</th>
<th>CBS-4</th>
<th>CBS-Q</th>
<th>CBS-Q'</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4</td>
<td>-74.9(0.4)</td>
<td>-77.7(-2.8)</td>
<td>-75.6(-0.7)</td>
<td>-77.6(-2.7)</td>
<td>-74.0(0.9)</td>
<td>-74.8(0.1)</td>
</tr>
<tr>
<td>CH3F</td>
<td>-232.6(8.4)</td>
<td>-244.1(-11.5)</td>
<td>-245.0(-12.4)</td>
<td>-236.9(-4.3)</td>
<td>-238.7(-6.1)</td>
<td></td>
</tr>
<tr>
<td>CH3F2</td>
<td>-452.2(1.8)</td>
<td>-463.7(-11.5)</td>
<td>-466.9(-14.7)</td>
<td>-451.1(-1.1)</td>
<td>-457.6(-5.4)</td>
<td></td>
</tr>
<tr>
<td>CH2F3</td>
<td>-697.6(2.7)</td>
<td>-714.0(-16.4)</td>
<td>-718.9(-21.3)</td>
<td>-696.0(0.7)</td>
<td>-706.7(-9.1)</td>
<td></td>
</tr>
<tr>
<td>CF4</td>
<td>-933.0(1.7)</td>
<td>-956.5(-23.5)</td>
<td>-962.6(-29.6)</td>
<td>-936.6(-3.3)</td>
<td>-947.7(-14.7)</td>
<td></td>
</tr>
<tr>
<td>CH2Cl2</td>
<td>-83.7(2.1)</td>
<td>-85.5(-1.8)</td>
<td>-88.1(-4.4)</td>
<td>-88.9(-5.2)</td>
<td>-86.3(-2.6)</td>
<td></td>
</tr>
<tr>
<td>CHCl3</td>
<td>-103.2(1.3)</td>
<td>-107.6(-4.4)</td>
<td>-119.2(-16.0)</td>
<td>-126.5(-23.3)</td>
<td>-125.3(-22.1)</td>
<td></td>
</tr>
<tr>
<td>CCl4</td>
<td>-96.0(2.1)</td>
<td>-107.7(-11.7)</td>
<td>-123.7(-22.7)</td>
<td>-143.8(-47.8)</td>
<td>-137.3(-41.3)</td>
<td></td>
</tr>
<tr>
<td>CH2FCl</td>
<td>-261.9(13.0)</td>
<td>-273.3(-11.4)</td>
<td>-278.3(-16.4)</td>
<td>-272.5(-10.6)</td>
<td>-272.3(-10.4)</td>
<td></td>
</tr>
<tr>
<td>CH2FCI</td>
<td>-481.6(13.0)</td>
<td>-498.1(-16.5)</td>
<td>-504.7(-23.1)</td>
<td>-494.4(-12.8)</td>
<td>-495.9(-14.3)</td>
<td></td>
</tr>
<tr>
<td>CClF3</td>
<td>-707.9(3.3)</td>
<td>-731.8(-23.9)</td>
<td>-739.6(-31.7)</td>
<td>-725.9(-18.0)</td>
<td>-728.2(-20.3)</td>
<td></td>
</tr>
<tr>
<td>CClF2</td>
<td>-283.3(13.0)</td>
<td>-295.8(-12.5)</td>
<td>-304.7(-21.4)</td>
<td>-304.8(-21.5)</td>
<td>-301.4(-18.1)</td>
<td></td>
</tr>
<tr>
<td>CFFCl2</td>
<td>-491.6(8.9)</td>
<td>-513.9(-22.3)</td>
<td>-524.0(-30.5)</td>
<td>-522.1(-30.5)</td>
<td>-517.4(-25.8)</td>
<td></td>
</tr>
<tr>
<td>CFCl3</td>
<td>-288.7(6.3)</td>
<td>-305.2(-16.5)</td>
<td>-317.8(-29.1)</td>
<td>-326.0(-37.3)</td>
<td>-318.8(-30.1)</td>
<td></td>
</tr>
<tr>
<td>rms</td>
<td>6.9</td>
<td>14.5</td>
<td>21.5</td>
<td>20.7</td>
<td>18.8</td>
<td></td>
</tr>
</tbody>
</table>
| avg     | -12.6 | -19.3 | -15.3 | -15.3 | }

a In hartrees. b Required for the BAC-MP4 calculations.

c AB Initio Enthalpies

d Enthalpies Calculated with Bond Additivity Corrections

Results and Discussion

Displayed in Table 3 are the experimental and various calculated enthalpies of formation at 298.15 K for methane, the fluoromethanes, the chloromethanes, and the chlorofluoromethanes. The experimental enthalpies of all chlorinated species, with their reported error estimates in parentheses, were taken from the JANAF compilation, as was the value for CH4. The experimental enthalpies of the fluoromethanes are from the compilation by Kolesov. The tabulated values are the calculated enthalpies represent the deviations from experimental values, with rms errors ranging from 15 to 22 kJ/mol (Table 3A). These deviations are systematic, with almost all calculated enthalpies lying lower than the reported experimental values, as evidenced by the large negative mean deviations that range from -13 to -19 kJ/mol. Furthermore, the negative deviations tend to rise with increasing halogen substitution. In our earlier investigation of the fluoromethanes, it was found that the enthalpies determined with the computa-
The deviations as a function of the number of C–Cl bonds: (■) zero C–Cl bond; (●) one C–Cl bond; (▲) two C–Cl bonds.

(B) Deviations of $\Delta H^\circ[G2(MP2)]$ from experimental values as a function of the number of C–Cl bonds: (■) zero C–F bonds (●) one C–F bond; (▲) two C–F bonds; (•) three C–F bonds.

In Figures 1B and 2B are plotted enthalpy differences $\Delta H^\circ$ as a function of $n_{CF}$ and $n_{CCl}$ for fixed $n_{CF}$ and $n_{CCl}$, respectively.

In Figures 1A and 2A, it was found that the negative error in the CFC’s increase linearly with the number of C–F bonds, and that the negative curvature in Figures 1A and 2A will be discussed in the next section.

**Bond Additivity Corrections.** One approach to correct systematic errors in $ab$ initio estimates of enthalpies of formation is to employ the concept of bond additivity corrections (BAC’s), developed by Melius and co-workers. 15, 16 for MP4/6-31G(d,p) enthalpies. In this method, which is an extension of the use of isodesmic reactions, 22, 23 it is assumed that the deviation of calculated enthalpies from experiment is a linear function of the number of each type of bond in the molecule, as indicated in eq 1:

$$\Delta H^\circ(BAC) = \Delta H^\circ(calc) - \sum n_i \Delta_i = \Delta H^\circ(calc) - [n_{CF} \Delta_{CF} + n_{CCl} \Delta_{CCl}]$$  (1)

In the BAC-MP4 procedure, 15, 16 the BAC parameters ($\Delta_i$) are taken to be dependent upon bond length and nearest neighbors. The BAC-MP4 method has been used to calculate geometries and energies of about 100 stable and radical, C1 and C2 fluorinated hydrocarbons, including partially oxidized species. However, there is insufficient variation in the bond lengths in the CFC’s (Table 1) to permit establishment of a bond length dependence from results on this series. 24 Consequently, in order to avoid overparametrization, we have chosen to utilize BAC’s that are linearly independent, as represented by eq 1.

The standard errors in the parameters obtained from the regression analysis reveal that for each value of $n_{CCl}$ the negative errors in the CFC’s increase linearly with the number of C–F bonds, 21 the same behavior was observed in the earlier investigation of the fluoromethanes 5 [square

**Table 4: Bond Additivity Corrections**

<table>
<thead>
<tr>
<th>method</th>
<th>$\Delta_{CF}$</th>
<th>$\Delta_{CCl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G2</td>
<td>-6.51(0.41)</td>
<td>-2.80(0.41)</td>
</tr>
<tr>
<td>G2(MP2)</td>
<td>-7.98(0.38)</td>
<td>-6.54(0.38)</td>
</tr>
<tr>
<td>CBS-4</td>
<td>-1.28(0.74)</td>
<td>-10.62(0.74)</td>
</tr>
<tr>
<td>CBS-Q</td>
<td>-3.51(0.55)</td>
<td>-8.50(0.55)</td>
</tr>
</tbody>
</table>

* In units of kJ/bond.

In Figures 1A and 2A, it was found that the slopes of the straight lines becomes more negative with increasing $n_{CCl}$. In Figures 1B and 2B are plotted enthalpy deviations vs $n_{CCl}$ for fixed $n_{CF}$. Here, it was found that the negative error increases with degree of chlorination. However, in these graphs, particularly for $n_{CF} = 0, 1$ (G2(MP2) and G2) and $n_{CF} = 1, 2$ (CBS-Q and CBS-4), the curves exhibited negative curvature, as seen in the figures (and verified by standard deviations in the second-order regression coefficients).

From these results, one may conclude that the calculated errors are, indeed, systematic and dependent upon the number of C–F and C–Cl bonds in the molecule. The significance of the increasingly negative slopes in Figures 1A and 2A and of the negative curvature in Figures 1B and 2B will be discussed in the next section.

In the BAC-MP4 procedure, 15, 16 the BAC parameters ($\Delta_i$) are taken to be dependent upon bond length and nearest neighbors. The BAC-MP4 method has been used to calculate geometries and energies of about 100 stable and radical, C1 and C2 fluorinated hydrocarbons, including partially oxidized species. However, there is insufficient variation in the bond lengths in the CFC’s (Table 1) to permit establishment of a bond length dependence from results on this series. 24 Consequently, in order to avoid overparametrization, we have chosen to utilize BAC’s that are linearly independent, as represented by eq 1. This latter assumption is addressed further below.

We have utilized linear regression to fit eq 1 to the experimental data for the chlorine- and fluorine-substituted methanes (given in Table 3A) to obtain values for the linear BAC parameters $\Delta_{CF}$ and $\Delta_{CCl}$ (see Table 4) for all four $ab$ initio methods. Corrected enthalpies of formation are given in Table 3B. The quantities in parentheses in Table 4 represent the standard errors in the parameters obtained from the regression analysis. 25 We employed the constraint $\Delta_{CH} = 0$, since regression analysis with unconstrained $\Delta_{CH}$ had little impact on the standard errors (i.e., $\Delta_{CH} \approx \sigma$).

As seen in Table 3B, it is clear that the corrected enthalpies of formation are in extremely good agreement with experimental values. The residual rms deviations, which range from 2.4 to 4.7 kJ/mol, are almost an order of magnitude lower than errors in the uncorrected enthalpies (Table 3A), and, indeed, lie significantly below the rms experimental uncertainty of 6.9 kJ/mol. 26 The BAC’s have also removed the systematic under-
prediction of the enthalpies of formation, as revealed by the small average errors in the corrected results. The last column in Table 3B contains the calculated BAC-MP4 enthalpies with their associated errors. The accuracy of these results is comparable to that obtained by applying BAC’s to the other methods, with rms and average deviations of 3.8 and 1.0 kJ/mol, respectively. It is of further interest to note that the parameters utilized in the BAC-MP4 method were developed to yield accurate enthalpies in a wide range of compounds and were not optimized to match experimental values in this particular series of molecules.

The numerical values of the BAC parameters in Table 4 represent the magnitude of the systematic error due to each of the three types of bonds in the CFC’s. As indicated above, the standard errors were essentially unaffected by whether or not \( \Delta_{\text{CH}} \) was constrained to zero. This is not surprising, since earlier computational studies using the G2 and G2(MP2) methods have shown no inherent systematic errors in calculated atomization energies or enthalpies of formation in hydrocarbons or other C–H bond-containing compounds. The present work indicates that the same result is true for the CBS-4 and CBS-Q methods. Regression analysis using subsets of the C1 CFC’s also had little impact on the parameters, that is, the changes in \( \Delta_{\text{CF}} \) and \( \Delta_{\text{CCl}} \) are comparable in magnitude to \( \sigma(\Delta_{\text{CF}}) \) and \( \sigma(\Delta_{\text{CCl}}) \), respectively, using only the fluoromethanes, the chloromethanes, or the three reference compounds (CH\(_4\), CF\(_4\), CCl\(_4\)).

From Table 4, one observes that the systematic error (as represented by the magnitude of the BAC) for C–Cl bonds using the G2 method is substantially lower than for C–F bonds (|\( \Delta_{\text{CCI}} \)| < \( 1/2 |\Delta_{\text{CF}}| \)). By use of G2(MP2), the systematic error for C–Cl bonds is also somewhat smaller than for C–F bonds. In contrast, both CBS procedures exhibit far greater errors for C–Cl than for C–F bonds (|\( \Delta_{\text{CCI}} \)| \( \gg |\Delta_{\text{CF}}| \)).

As noted previously, the bond additivity correction may represent in part the spin–orbit coupling error in the atomic halogen energies used to compute the atomization energy. If this were true, such errors would be expected to propagate in the atomization energies of chlorine-containing species in the “G2/CBS test set” such as HCl, CH\(_3\)Cl, and Cl\(_2\). Indeed, the CBS-Q method leads to atomization energy deviations \( |\Delta_{\text{CF}}| - |\Delta_{\text{CCl}}| \) of 5.3, 6.4, and 4.2 kJ/mol for the fluoromethanes and the various C1 and C2 radical species, the efficacy of the introduction of interaction parameters to the BAC equation will be further explored.

Summary and Conclusions

The application of \textit{ab initio} MO methods to the determination of thermochemical properties in halocarbons have been extended to G2, G2(MP2), CBS-4, CBS-Q, and BAC-MP4 calculations of enthalpies of formation of the chlorofluoromethanes. Calculated values of \( \Delta_{\text{H}}(\text{calc}) \) for the use of the four \textit{ab initio} methods exhibit comparatively large systematic negative errors from the experimental values, up to \(-50\) kJ/mol, which are directly dependent upon the number of C–F and C–Cl bonds in the molecule.

The application of bond additivity corrections (BAC’s) to remove the systematic errors yields corrected enthalpies that are in extremely close agreement with experimental values, with rms deviations that range from 2.4 kJ/mol [G2(MP2)] to 4.7 kJ/mol [CBS-4], which is well below the rms experimental uncertainty of 6.9 kJ/mol. The BAC-MP4 method (which has already been parametrized to remove systematic bond errors) yields comparably good agreement with experimental enthalpies. On the basis of these results, it is concluded that any of these five calculational procedures, together with bond additivity corrections to remove systematic error, may profitably be used to obtain very accurate enthalpies of formation in chlorofluorocarbon species.

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References and Notes


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(9) Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are necessarily the best available for the purpose.


(19) An alternative, although less complete, compilation of enthalpies of formation of the CFC's has been published in Pedley, J. B.; Naylor, R. D.; Kirby, S. P. Thermochemical Data of Organic Compounds; Chapman & Hall: London, UK, 1986. The literature values from this reference are within 2 kJ/mol of those in the JANAF tables (ref 18) for most species. However, for CFCl3 and CFCl2, the enthalpies in the former reference are lower by 14 and 20 kJ, respectively.


(21) Fits of $\Delta H^\text{calc} - \Delta H^\text{expt}$ vs $n_{CF}$ to second-order polynomials yielded statistically insignificant quadratic terms for all four $ab initio$ methods. The one exception to this trend is that, as discussed in the text, the plot of the CBS-4 enthalpy deviations vs $n_{CF}$ in the nonchlorinated FC's does not show any systematic error.


(25) The equality of the standard errors for the three parameters results from the multicollinearity of the independent variables, i.e., $n_{CF} + n_{CF} + n_{CCI} = 4$. Wesolowski, G. O. Multiple Regression and Analysis of Variance; John Wiley and Sons: New York, 1976; Chapter 3.

(26) It should be noted that if the experimental enthalpies of the CFC's are chosen from the Kolesov compilation (ref 20) rather than the JANAF tables (ref 18), the rms errors in the calculated enthalpies increase significantly (e.g., from 2.6 to 4.5 kJ/mol for the G2 method). This results entirely from very different choices in reference values for CFCl3 and CFCl2 (all other experimental enthalpies agree to within 0−2 kJ/mol), for which there are broad ranges of reported experimental enthalpies of formation (ref 20).


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