Journal of Fluorine Chemistry 131 (2010) 606–611

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Comparison of theoretical methods for assessing the heat of formation of C_1 and C_2 chlorofluorocarbons and hydrochlorofluorocarbons

Jiaheng Zhang, Wenfeng Zhou, Yubo Li, Haixiang Gao *, Zhiqiang Zhou **

Department of Applied Chemistry, China Agricultural University, Yuanmingyuan West Road 2#, Haidian District, Beijing 100194, China

ARTICLE INFO

Article history:
Received 27 November 2009
Received in revised form 25 January 2010
Accepted 28 January 2010
Available online 6 February 2010

Keywords:
Chlorofluorocarbons
Hydrochlorofluorocarbons
G3
Heat of formation
Atomization approach
Bond additive correction
Isodesmic reactions

ABSTRACT

The heat of formation of a number of key C_1 and C_2 chlorofluorocarbons and hydrochlorofluorocarbons have been calculated by G3, G3MP2, G3MP2B3 and G3B3 methods. Based on the results of the atomization approach, it was found that the errors are approximately dependent upon the number of C–F or C–Cl bonds. Moreover, the bond additive correction (BAC) procedure and isodesmic reactions approach improved the accuracy and decreased these system errors significantly. The extended comparison between the BAC procedure and isodesmic reaction approaches had been made; the latter yielded the best results and showed broader applicability.

1. Introduction

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are stable synthetic organic chemicals either fully or partially substituted with chlorine and fluorine atoms. From 1964 to 1996, CFCs were used worldwide as coolants for electrical appliances, as chemical intermediates, as solvents, as aerosol propellants, and in building insulation and food packing materials [1–3]. However, due to their volatility and high chemical stability, their release into the atmosphere posed a severe ozone depletion problem. Many countries signed the Montreal Protocol to ban the production of CFCs in 1996. As replacement products, a number of environmentally acceptable HCFCs containing neither chlorine nor bromine are now used, such as $C_2HCl_2F_3$ (HCFC-123), CF_3CHF_2 (HFC-125), and $CHCl_2F$ (HCFC-21) [4].

Beyond their immediate environmental and commercial advantages, our understanding of the exact thermodynamic properties of CFCs and HCFCs is incomplete, especially of their standard heat of formation ($\Delta_f H^0$). The pioneering research of Kirkbride and Davidson [5] in this direction was followed for half a century by studies that produced many important findings [6–9].

It is noteworthy that recent advances in computational quantum chemistry have made the calculation of the heat of formation a realistic endeavor. Furthermore, the theoretical prediction of heat of formation continues to arouse a considerable amount of interest [10,11]. Large systematic negative errors occur in computed enthalpies when using procedures such as density functional theory (DFT), complete basis set (CBS) and Gaussian-2 (G2) methods, combined with the atomization approach. Such procedures applied to CFCs and HCFs yield errors up to and greater than 50 kJ/mol [12].

In an effort to minimize the deviations of the computations, Naomi et al. used G2(MP2) methods via suitable isodesmic reactions, in conjunction with accepted values from the literature, to calculate all other species in the reactions. An isodesmic reaction is one in which the number of bonds of each type is conserved so that systematic errors tend to cancel each other out. Although this approach is generally more accurate than the atomization approach, its accuracy is limited by the availability of reliable data [13].

Based on it, Cloud and Schwartz obtained relatively accurate results by applying bond additive correction (BAC) method [14]. The essence of the BAC procedure is that it enables energies to be calculated accurately without the need to resort to expensive basis sets. It is a comparatively precise and reliable procedure whose goal is to generate a sufficiently complete set of consistent thermochemical data [15]. In the BAC procedure, the errors in certain theoretical levels of the electronic energy of a molecule are

---

* Corresponding author. Tel.: +86 10 62734876; fax: +86 10 62733830.
** Corresponding author. Tel.: +86 10 62733547; fax: +86 10 62733547.
E-mail addresses: hxgao@cau.edu.cn (H. Gao), zqzhou@cau.edu.cn (Z. Zhou).

0022-1139/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2010.01.010

treated as systematic additive corrections that depend on the bonding partner, distance, and nearest neighbors. The correction factor is obtained by comparing the calculated heat of formation with observed experimental values for reference compounds. On this basis, Cloud reported the mean absolute deviations (MADs) to be 4.6 kJ/mol (C_1 CFCs and HCFCs) and 11.7 kJ/mol (C_2 CFCs and HCFCs).

In subsequent work, Ma et al. proposed the Gaussian-3 theory, newly developed at that time, for correcting the zero-point energy in calculations of the heat of formation, ionization energy, proton affinity, and acidity of hydrochlorofluoromethanes (HCFMs) [16]. Compared with the BAC procedure, the Gaussian-3 theory together with the atomization approach gave the MAD as 3.9 kJ/mol (C_1 CFCs and HCFCs) using the Gaussian 94 and Gaussian 98 packages of programs.

Some evidence in recent years suggests that an accumulation of errors occurs when applying Gaussian-*n* theory to halide-containing molecules, particularly with respect to the calculation of the heat of formation of molecules containing chlorine [17]. However, the Gaussian-3 theory introduced towards the end of 1998 improved accuracy over the earlier Gaussian-2 and Gaussian-1 methods, and was computationally cheaper. Moreover, further modifications to G3 theory (G3X) in the form of B3LYP/6-31G(2df,p) geometry, B3LYP/6-31G(2df,p) zero-point energy and *g* polarization function in the G3Large basis set for third-row atoms at the Hartree–Fock (HF) level have improved accuracy even over G3 theory [18] Hence, in the present work, the above factors have prompted us to apply the Gaussian-3 and Gaussian-3X methods, in conjunction with the atomization approach, BAC procedure, and isodesmic reactions approach, to calculate the heat of formation of C_1 and C_2 CFCs and HCFCs. In addition, we plan to undertake a special study on methods to minimize the computational errors for these molecules and compare the accuracy of these combined procedures.

2. Computational methods

We have computed the heat of formation of 15 C_1 CFCs and HCFCs and 23 C_2 CFCs and HCFCs. Experimental values of $\Delta_f H^0$ for each of these molecules have been reported, providing a realistic basis for assessing the capability of the theoretical methods.

The geometric molecular structures were optimized iteratively. Electronic structure calculations were performed to determine the geometry, vibrational frequencies and electronic energy of the molecules. From the above-mentioned G3 suite of programs, the G3, G3MP2, G3MP2B3, and G3B3 methods were selected for the present study. In addition, single-point quadratic configuration interaction calculations using these methods were carried out for energy in the QCISD(T)/6-31G(d) set. The G3MP2B3 and G3B3 theories are further modifications of G3MP2 and G3; unlike them, they use geometries and zero-point vibrational energy (ZPVE) scaled by 0.96 from B3LYP/6-31G(d) calculations [19]. All calculations were performed with the Gaussian 03 package of programs [20].

3. Results and discussion

3.1. Atomization approach

The heat of formation of CFCs and HCFCs were calculated by the atomization approach using the G3, G3MP2, G3MP2B3, and G3B3 methods. These calculations involved determining the total atomization enthalpy via the atomization reaction, and the computed heat of formation was then obtained in combination with the calculated and experimental heat of formation of the atoms C, H, F, and Cl. The experimental data used were the JANAF values of C (169.73 kcal/mol), H (50.62 kcal/mol), F (17.42 kcal/mol), and Cl (27.49 kcal/mol) [21]. All calculation data are summarized in Table 1, together with the experimental values.

Table 1
Calculated heat of formation at 298.15 K for all compounds using the four computational methods in the atomization approach (in kJ/mol).

Species	G3	G3MP2	G3MP2B3	G3B3	Exp.
CH_4	−75.95	−74.66	−73.63	−74.84	−74.9[a]
CH_3F	−237.88	−236.20	−236.20	−236.94	−232.6[b]
CH_3Cl	−81.55	−82.12	−81.67	−79.97	−83.7[b]
CH_2F_2	−453.44	−451.46	−452.15	−452.37	−452.2[b]
CH_2FCl	−264.93	−264.60	−264.20	−262.48	−261.9[b]
CH_2Cl_2	−93.52	−95.58	−94.95	−90.67	−95.5[b]
CHF_3	−699.33	−696.77	−697.39	−697.37	−696.6[b]
CHF_2Cl	−485.30	−483.81	−483.34	−481.92	−481.6[b]
$CHFCl_2$	−286.72	−287.02	−286.03	−282.53	−283.3[b]
$CHCl_3$	−103.11	−106.02	−104.75	−98.47	−103.2[b]
CF_4	−936.88	−933.22	−933.25	−933.46	−933.2[a]
CF_3Cl	−714.27	−711.29	−710.55	−709.78	−707.9[b]
CF_2Cl_2	−500.25	−498.48	−497.21	−494.92	−491.6[b]
$CFCl_3$	−295.97	−296.00	−294.23	−289.80	−288.7[b]
CCl_4	−103.18	−105.75	−103.83	−96.72	−100.4[a]
C_2H_6	−85.29	−84.11	−83.06	−84.01	−84.7[a]
C_2H_5F	−274.78	−272.75	−272.38	−273.34	−263.2[b]
C_2H_5Cl	−111.89	−112.32	−111.40	−109.64	−112.3[c]
CH_3CHFCl	−314.08	−312.98	−311.90	−310.76	−313.4[d]
CH_2FCH_2F	−449.07	−446.24	−446.62	−447.52	−433.9[e]
CH_3CHF_2	−507.45	−504.53	−504.44	−505.43	−500.8[f]
CH_2ClCH_2Cl	−133.43	−135.36	−134.59	−130.22	−125.4[g]
CH_3CHCl_2	−136.22	−137.76	−136.45	−132.43	−127.6[g]
CH_3CF_3	−758.79	−754.53	−754.08	−755.56	−745.6[f]
CHF_2CH_2F	−668.06	−664.48	−665.68	−666.43	−664.8[h]
CH_3CCl_3	−151.06	−152.68	−150.69	−145.35	−144.6[g]
$CHCl_2CH_2Cl$	−145.75	−148.35	−146.96	−140.76	−148.2[i]
CH_2FCF_3	−916.38	−911.40	−912.07	−913.38	−895.8[f]
CHF_2CHF_2	−889.22	−884.60	−885.93	−886.89	−877.8[e]
$CHCl_2CHCl_2$	−162.86	−165.98	−164.00	−156.06	−155.6[g]
CH_2ClCCl_3	−161.37	−163.89	−161.66	−154.28	−135.6[j]
CHF_2CF_3	−1123.35	−1117.35	−1118.47	−1119.90	−1104.6[f]
C_2HCl_5	−170.08	−172.66	−169.79	−161.10	−145.0[k]
C_2F_6	−1356.12	−1348.70	−1349.43	−1351.38	−1342.7[f]
CF_2ClCF_3	−1147.35	−1140.42	−1140.18	−1141.31	−1118.8[d]
CF_2ClCF_2Cl	−939.33	−933.16	−931.84	−931.81	−937.0[d]
$CFCl_2CF_2Cl$	−741.66	−736.98	−735.02	−733.16	−706.3[d]
C_2Cl_6	−173.40	−174.57	−170.68	−162.05	−141.4[a]

[a] Ref. [22].
[b] Ref. [23].
[c] Ref. [24].
[d] Ref. [25].
[e] Ref. [26].
[f] Ref. [27].
[g] Ref. [28].
[h] Ref. [29].
[i] Ref. [30].
[j] Ref. [31].
[k] Ref. [32].

Figs. 1 and 2 show the errors in the heat of formation by the four methods from CH_4 to CCl_4 and from C_2H_6 to C_2Cl_6. We found that the errors for the C_1 CFCs and HCFCs (between −5 and 5 kJ/mol,

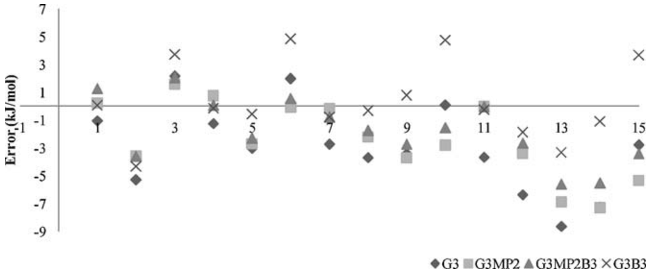

Fig. 1. Deviations of calculated heat of formation from experimental data for the C_1 CFCs and HCFCs from CH_4 to CCl_4.

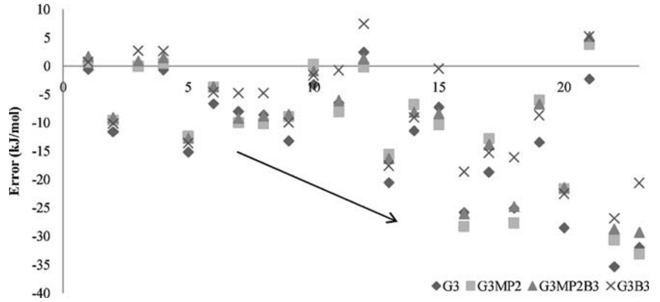

Fig. 2. Deviations of calculated heat of formation from experimental data for the C_2 CFCs and HCFCs from C_2H_6 to C_2Cl_6.

Table 2
Bond additive correction (BAC).

Method	Δ_{CF} (kJ/bond)	Δ_{CCl} (kJ/bond)
G3	−3.01	5.11
G3MP2	−1.94	5.16
G3MP2B3	−1.35	5.50
G3B3	−2.05	5.58

approximately) shown in Fig. 1 are much smaller than for the C_2 CFCs and HCFCs. The errors illustrated in Fig. 2 are several times greater. The values of the MAD for the C_1 CFCs and HCFCs were 3.6, 2.7, 2.3, and 2.0 kJ/mol for G3, G3MP2, G3MP2B3, and G3B3 methods, respectively. According to these MADs, we can draw conclusion that the ab initio method, especially the G3X methods, is suitable for heat of formation calculation of C_1 CFCs and HCFCs. Previously mentioned studies of C_1 CFCs and HCFCs gave a minimum deviation of 3.9 kJ/mol (G3/G94) and 2.4 kJ/mol (BAC), in agreement with our best estimation. In contrast, the MAD for C_2 was 12.9, 11.3, 11.0 and 9.8 kJ/mol for G3, G3MP2, G3MP2B3, and G3B3 methods. From Fig. 2 it can be seen that the errors increase in the negative direction with the increase in the number of C–F or C–Cl bonds. This trend is not observed in Fig. 1. In our study, the benchmark data come from experimental data, and it is necessary to take experimental errors into account especially the MADs that remains under ±5 kJ/mol. In our view, the errors should increase even in the C_1 compounds with the increase in the number of C–F and C–Cl. However, the experimental errors of benchmark data influenced this trend and make it unclear and the trend in C_2 compounds suffered from less effect from experimental errors of experiment values since the errors depend approximately on the number of C–F or C–Cl bonds. It was the aim of this study to minimize the deviations, especially for the C_2 CFCs and HCFCs, and to utilize the BAC procedure and isodesmic reaction approach for reducing errors.

3.2. *Bond additive correction (BAC)*

Implementation of the BAC procedure required calibration against molecules of known heat of formation in order to define the parameters. It was also assumed that the BAC corrected values are obtained through the linear function of the number of C–X bonds of each molecule (n_{CX}) and the parameters (Δ_{CX}), as indicated in the formula: $\Delta_f H^0$ (BAC) = $\Delta_f H^0$ (calc) − $n_{CX}\Delta_{CX}$ (X = F, Cl).

The parameters (Δ_{CX}) were analyzed according to the results of the atomization approach on linear fitting and are listed in Table 2. Values of the BAC corrected enthalpies of formation are contained in Table 3.

It can be readily appreciated from Table 2 that the systematic errors for the C–F bonds are much smaller than for C–Cl when using these four methods. By comparing these results with previous work from G2 and CBS calculations, it is evident that the G3, G3MP2, G3MP2B3, and G3B3 methods predict substantially lower systematic errors; comparison of the results shows that the G3 suite of methods performs better than the G2, the related G2(MP2), and the CBS series.

Table 3 shows the heat of formation obtained after bond additive correction. The values of the MAD for C_1 CFCs and HCFCs are 5.86, 6.59, 6.86, and 6.93 kJ/mol and for C_2 CFCs and HCFCs they are 7.64, 6.44, 6.31, and 6.74 kJ/mol. As mentioned above, the aim of bond additive correction is to minimize the deviations of calculations; the values of MAD for C_2 CFCs and HCFCs have been reduced as expected. Compared with the results of the atomization approach, the G3, G3MP2, G3MP2B3, and G3B3 methods resulted in better than 5.00 kJ/mol accuracy. In Cloud's paper, the same deviations using G2 and CBS series methods are significantly greater. On the other hand, we found that although the accuracy for C_2 CFCs and HCFCs is much improved, the results for C_1 CFCs and HCFCs resulted in larger errors than with atomization approach.

In an attempt to explain this discrepancy, we examined similar parameters (Δ_{CX}) for the results of C_1 CFCs and HCFCs using the G3

Table 3
Calculated heat of formation at 298.15 K for all compounds using the four computational methods after bond additive correction (in kJ/mol).

Species	G3	G3MP2	G3MP2B3	G3B3	Exp.
CH_4	−75.95	−74.66	−73.63	−74.84	−74.9[a]
CH_3F	−236.24	−234.98	−234.67	−235.33	−232.6[b]
CH_3Cl	−77.01	−76.84	−76.96	−76.91	−83.7[b]
CH_2F_2	−450.17	−449.04	−449.09	−449.13	−452.2[b]
CH_2FCl	−258.76	−258.12	−257.97	−257.80	−261.9[b]
CH_2Cl_2	−84.43	−85.03	−85.53	−84.56	−95.5[b]
CHF_3	−694.43	−693.13	−692.81	−692.51	−696.6[b]
CHF_2Cl	−477.49	−476.11	−475.57	−475.62	−481.6[b]
$CHFCl_2$	−276.00	−275.26	−275.08	−274.80	−283.3[b]
$CHCl_3$	−89.48	−90.20	−90.62	−89.30	−103.2[b]
CF_4	−930.34	−928.37	−927.14	−926.98	−933.2[a]
CF_3Cl	−704.82	−702.38	−701.25	−701.87	−707.9[b]
CF_2Cl_2	−487.90	−485.50	−484.73	−485.58	−491.6[b]
$CFCl_3$	−280.71	−278.96	−278.57	−279.01	−288.7[b]
CCl_4	−85.02	−84.64	−84.99	−84.49	−100.4[a]
C_2H_6	−85.29	−84.11	−83.06	−84.01	−84.7[a]
C_2H_5F	−273.14	−271.54	−270.85	−271.72	−263.2[b]
C_2H_5Cl	−107.35	−107.04	−106.69	−106.58	−112.3[c]
CH_3CHFCl	−307.91	−306.49	−305.67	−306.08	−313.4[d]
CH_2FCH_2F	−445.81	−443.82	−443.56	−444.29	−433.9[e]
CH_3CHF_2	−504.18	−502.10	−501.38	−502.20	−500.8[f]
CH_2ClCH_2Cl	−124.35	−121.81	−125.17	−124.11	−125.4[g]
CH_3CHCl_2	−127.14	−127.21	−127.02	−126.32	−127.6[g]
CH_3CF_3	−753.88	−750.89	−749.49	−750.71	−745.6[f]
CHF_2CH_2F	−663.16	−660.84	−661.10	−661.58	−664.8[h]
CH_3CCl_3	−137.43	−136.85	−136.56	−136.18	−144.6[g]
$CHCl_2CH_2Cl$	−132.13	−132.52	−132.82	−131.59	−148.2[i]
CH_2FCF_3	−909.84	−906.55	−905.96	−906.91	−895.8[f]
CHF_2CHF_2	−882.68	−879.75	−879.81	−880.42	−877.8[e]
$CHCl_2CHCl_2$	−144.70	−144.88	−145.16	−143.84	−155.6[g]
CH_2ClCCl_3	−143.21	−142.79	−142.82	−142.06	−135.6[j]
CHF_2CF_3	−1115.17	−1111.28	−1110.83	−1111.81	−1104.6[f]
C_2HCl_5	−147.37	−146.28	−146.23	−145.82	−145.0[k]
C_2F_6	−1346.31	−1341.42	−1340.26	−1341.67	−1342.7[f]
CF_2ClCF_3	−1134.64	−1129.08	−1127.82	−1130.16	−1118.8[d]
CF_2ClCF_2Cl	−923.71	−917.76	−916.30	−919.23	−937.0[d]
$CFCl_2CF_2Cl$	−723.13	−717.51	−716.30	−719.14	−706.3[d]
C_2Cl_6	−146.16	−142.91	−142.42	−142.71	−141.4[a]

[a] Ref. [22].
[b] Ref. [23].
[c] Ref. [24].
[d] Ref. [25].
[e] Ref. [26].
[f] Ref. [27].
[g] Ref. [28].
[h] Ref. [29].
[i] Ref. [30].
[j] Ref. [31].
[k] Ref. [32].

values of $\Delta_{CF} = -0.2329$ kJ/bond and $\Delta_{CCl} = 0.5623$ kJ/bond. The MAD for C_1 CFCs and HCFCs using these parameters is 3.76 kJ/mol, which is close to the atomization approach result.

It was also found that the deviations obtained from the experimental data for some C_2 CFCs were too large, implying that the parameters obtained for all molecules in general may not be suitable for these relatively precise C_1 CFCs and HCFCs. Another limitation of the BAC procedure is that it requires a series of calculated results and experimental data to obtain the parameters; this makes the BAC procedure unsuitable for enthalpy prediction unless series data are available.

Table 4

Calculated heat of formation at 298.15 K for all compounds using the four computational methods in isodesmic reactions approach (in kJ/mol).

Species	G3	G3MP2	G3MP2B3	G3B3	Exp.
CH_4	−75.95	−74.66	−73.63	−74.84	−74.9[a]
CH_3F	−236.15	−236.35	−237.12	−236.90	−232.6[b]
CH_3Cl	−80.06	−80.95	−81.75	−80.91	−83.7[b]
CH_2F_2	−451.06	−451.56	−452.75	−452.25	−452.2[b]
CH_2FCl	−262.79	−263.37	−263.96	−263.35	−261.9[b]
CH_2Cl_2	−91.60	−93.02	−93.86	−92.54	−95.5[b]
CHF_3	−696.30	−696.81	−697.67	−697.18	−696.6[b]
CHF_2Cl	−482.50	−482.52	−482.77	−482.72	−481.6[b]
$CHFCl_2$	−284.15	−284.41	−284.62	−284.32	−283.3[b]
$CHCl_3$	−100.76	−102.07	−102.49	−101.25	−103.2[b]
CF_4	−936.88	−933.22	−933.25	−933.56	−933.2[a]
CF_3Cl	−710.82	−709.95	−709.66	−710.51	−707.9[b]
CF_2Cl_2	−497.03	−495.80	−495.47	−496.63	−491.6[b]
$CFCl_3$	−292.97	−291.99	−291.65	−292.51	−288.7[b]
CCl_4	−103.18	−105.75	−103.83	−96.72	−100.4[a]
C_2H_6	−84.68	−84.68	−84.68	−84.68	−84.7[a]
C_2H_5F	−272.03	−272.23	−272.61	−272.45	−263.2[b]
C_2H_5Cl	−106.05	−107.27	−107.87	−106.76	−112.3[c]
CH_3CHFCl	−306.11	−306.84	−306.99	−306.32	−313.4[d]
CH_2FCH_2F	−444.20	−444.63	−445.45	−445.08	−433.9[e]
CH_3CHF_2	−502.57	−502.91	−503.27	−502.99	−500.8[f]
CH_2ClCH_2Cl	−122.36	−124.70	−125.92	−123.79	−125.4[g]
CH_3CHCl_2	−125.16	−127.09	−127.77	−126.00	−127.6[g]
CH_3CF_3	−751.77	−751.82	−751.52	−751.56	−745.6[f]
CHF_2CH_2F	−661.05	−661.77	−663.12	−662.43	−664.8[h]
CH_3CCl_3	−134.76	−136.39	−136.87	−135.37	−144.6[g]
$CHCl_2CH_2Cl$	−129.45	−132.07	−133.13	−130.77	−148.2[i]
CH_2FCF_3	−907.23	−907.60	−908.12	−907.82	−895.8[f]
CHF_2CHF_2	−880.07	−880.80	−881.98	−881.33	−877.8[e]
$CHCl_2CHCl_2$	−141.34	−144.07	−145.03	−142.53	−155.6[g]
CH_2ClCCl_3	−139.84	−141.98	−142.69	−140.75	−135.6[j]
CHF_2CF_3	−1112.06	−1112.45	−1113.13	−1112.77	−1104.6[f]
C_2HCl_5	−143.32	−145.13	−145.67	−144.02	−145.0[k]
C_2F_6	−1342.70	−1342.70	−1342.70	−1342.70	−1342.7[f]
CF_2ClCF_3	−1130.84	−1129.89	−1129.69	−1130.64	−1118.8[d]
CF_2ClCF_2Cl	−919.72	−918.12	−917.60	−919.15	−937.0[d]
$CFCl_2CF_2Cl$	−718.95	−717.40	−717.03	−718.50	−706.3[d]
C_2Cl_6	−141.42	−141.42	−141.42	−141.42	−141.4[a]

[a] Ref. [22].
[b] Ref. [23].
[c] Ref. [24].
[d] Ref. [25].
[e] Ref. [26].
[f] Ref. [27].
[g] Ref. [28].
[h] Ref. [29].
[i] Ref. [30].
[j] Ref. [31].
[k] Ref. [32].

3.3. *Isodesmic reactions*

The heat of formation was calculated using the isodesmic reactions approach. The simplest series of isodesmic reactions that can be applied to molecules in the present study are:

$$4CH_xCl_yF_z \rightarrow xCH_4 + yCCl_4 + zCF_4$$

and

$$6C_2H_xCl_yF_z \rightarrow xC_2H_6 + yC_2Cl_6 + zC_2F_6.$$

A well-balanced isodesmic reaction has a near-zero heat of reaction since similar bonds are broken and re-formed. For each side of the above equivalences, not only the number of atoms but also the number of bonds of each formal type is preserved and errors in correlation energy largely cancel out. The left-hand side is the target compound; the molecules on the right-hand side are the anchor compounds [33]. The more accurate the experimental heat of formation of the anchor compounds, the better are the results obtained. The heat of formation computed via isodesmic reactions are listed in Table 4.

It is evident from Table 4 that the isodesmic reactions approach is much better than the atomization approach. The average absolute deviations from experiment using isodesmic reactions for the C_1 CFCs and HCFCs were 2.52, 1.97, 1.84, and 2.11 kJ/mol compared with 3.6, 2.7, 2.3, and 2.0 kJ/mol by the atomization approach, and for the C_2 CFCs and HCFCs the isodesmic reaction values were 7.70, 6.52, 7.48, and 6.88 kJ/mol compared with 12.9, 11.3, 11.0, and 9.8 kJ/mol respectively. Compared with the BAC procedure, the values of the MAD for the C_2 CFCs and HCFCs were similar, and a larger improvement occurred for the C_1 CFCs and HCFCs.

As mentioned above, the data for the C_1 CFCs and HCFCs using the isodesmic reactions approach were more accurate than for the C_2 CFCs and HCFCs. In order to explain these discrepancies, we attempted to modify the anchor compounds for the C_2 CFCs and HCFCs isodesmic reactions. As we know, the accuracy of the isodesmic reaction is based on well-established experimental information for the anchor compounds. However, the deviations between the calculated heat of formation using the atomization approach and the experimental data are quite high (about 30 kJ/mol for C_2Cl_6 and 10 kJ/mol for C_2F_6); this limited our isodesmic reactions approach. We tested what would happen if C_2H_6, CCl_4, CF_4, and CH_4 were used as anchor compounds instead of C_2H_6, C_2Cl_6, and C_2F_6: the resulting isodesmic reactions and calculated heat of formation using the G3 method are shown in Table 5.

Table 5 reveals that the deviations for each of these isodesmic reactions were greater than those resulting from the BAC procedure (~4.0 kJ/mol) but generally smaller than those obtained from the atomization approach. More importantly, although more accurate anchor compounds were used, the accuracy of the isodesmic reactions was found to be lower than the former isodesmic reactions in which the target compounds and the anchor compounds shared greater similarity. Our calculation also support the notion that the precision of the isodesmic reactions requires that not only the number of types and bonds, but also groups and electronic environment, be preserved if possible. At this point, there was no alternative but to reconsider the isodesmic reactions used originally, that is, with C_2H_6, C_2Cl_6, and C_2F_6, as the anchor compounds.

3.4. *Analysis*

To find a general consensus on the comparison of these three approaches, we have made a corresponding statistical analysis which is illustrated in Table 6. As shown in this table, the statistical analysis support the notion that the isodesmic approach provided the best results, followed by the BAC procedure, and lastly the atomization calculations. From the mean deviations of the three approaches, it is shown that the calculations by the atomization approach and the isodesmic approach tend to underestimate heat of formation by 0.5–7.0 kJ/mol, while the BAC procedure tend to overestimate by approximately 2.0 kJ/mol. With the statistical regularity in mind, it is easy to shed light on predicting the heat of formation for chlorofluorocarbons and hydrochlorofluorocarbons

Table 5
Calculated heat of formation (in kJ/mol) usingC_2H_6, CCl_4, CF_4, and CH_4 as anchor compounds.

	Isodesmic reaction	G3	Exp.
C_2H_5F	$4C_2HF_5 + 5CH_4 \rightarrow 4C_2H_6 + 5CF_4$	−273.52	−263.2[a]
C_2H_5Cl	$4C_2HCl_5 + 5CH_4 \rightarrow 4C_2H_6 + 5CCl_4$	−110.86	−112.3[b]
CH_3CHFCl	$4CH_3CHFCl + 2CH_4 \rightarrow 4C_2H_6 + CF_4 + CCl_4$	−312.40	−313.4[c]
CH_2FCH_2F	$2CH_2FCH_2F + CH_4 \rightarrow 2C_2H_6 + CF_4$	−447.17	−433.9[d]
CH_3CHF_2	$2CH_3CHF_2 + CH_4 \rightarrow 2C_2H_6 + CF_4$	−505.53	−500.8[e]
CH_2ClCH_2Cl	$2CH_2ClCH_2Cl + CH_4 \rightarrow 2C_2H_6 + CCl_4$	−131.97	−125.4[f]
CH_3CHCl_2	$2CH_3CHCl_2 + CH_4 \rightarrow 2C_2H_6 + CCl_4$	−134.77	−127.6[f]
CH_3CF_3	$4C_2HF_3 + 3CH_4 \rightarrow 4C_2H_6 + 3CF_4$	−756.22	−745.6[e]
CHF_2CH_2F	$4CHF_2CH_2F + 3CH_4 \rightarrow 4C_2H_6 + 3CF_4$	−665.50	−664.8[g]
CH_3CCl_3	$4C_2HCl_3 + 3CH_4 \rightarrow 4C_2H_6 + 3CCl_4$	−149.18	−144.6[f]
$CHCl_2CH_2Cl$	$4CHCl_2CH_2F + 3CH_4 \rightarrow 4C_2H_6 + 3CCl_4$	−143.87	−148.2[h]
CH_2FCF_3	$CH_2FCF_3 + CH_4 \rightarrow C_2H_6 + CF_4$	−913.17	−895.8[e]
CHF_2CHF_2	$CHF_2CHF_2 + CH_4 \rightarrow C_2H_6 + CF_4$	−886.00	−877.8[d]
$CHCl_2CHCl_2$	$CHCl_2CHCl_2 + CH_4 \rightarrow C_2H_6 + CCl_4$	−160.56	−155.6[f]
CH_2ClCCl_3	$CH_2ClCCl_3 + CH_4 \rightarrow C_2H_6 + CCl_4$	−159.07	−135.6[i]
CHF_2CF_3	$4CHF_2CF_3 + 5CH_4 \rightarrow 4C_2H_6 + 5CF_4$	−1119.48	−1104.6[e]
C_2HCl_5	$4C_2HCl_5 + 5CH_4 \rightarrow 4C_2H_6 + 5CCl_4$	−167.35	−145.0[j]
CF_2ClCF_3	$4CF_2ClCF_3 + 6CH_4 \rightarrow 4C_2H_6 + 5CF_4 + CCl_4$	−1143.06	−1118.8[c]
CF_2ClCF_2Cl	$2CF_2ClCF_2Cl + 3CH_4 \rightarrow 2C_2H_6 + 2CF_4 + CCl_4$	−935.27	−937.0[c]
$CFCl_2CF_2Cl$	$4CFCl_2CF_2Cl + 6CH_4 \rightarrow 4C_2H_6 + 3CF_4 + 3CCl_4$	−737.82	−706.3[c]
Mean absolute deviation		10.67	

[a] Ref. [21].
[b] Ref. [22].
[c] Ref. [23].
[d] Ref. [24].
[e] Ref. [25].
[f] Ref. [26].
[g] Ref. [27].
[h] Ref. [28].
[i] Ref. [29].
[j] Ref. [30]

Table 6
Statistical analysis of these three approaches used in this study.

	Number of compounds	Maximum negative deviation	Maximum positive deviation	$\bar{\Delta}$	$\lvert\bar{\Delta}\rvert$	$\sqrt{(\Delta-\bar{\Delta})^2}$
Atomization approach	38	−35.36	7.44	−7.00	7.86	9.25
BAC procedure	38	−16.83	20.70	2.10	6.71	7.92
Isodesmic reactions approach	38	−12.65	19.40	−0.54	4.92	6.89

$\Delta = \Delta_f H^0_{calc(g)} - \Delta_f H^0_{exp(g)}$; $|\bar{\Delta}|$: mean absolute deviation.

in the future research so as to promote the research process in this field.

In the present work we have made a comparative study of the atomization approach, the BAC procedure and the isodesmic reactions approach, using the four G3X methods for applying the procedures: G3, G3MP2, G3MP2B3, and G3B3. As found in previous research, these methods performed much better than G2 and other DFT methods; of the four, the most time–economic method was G3B3 by comparing CPU cost in our study. The enthalpy values calculated by G3MP2 and G3MP2B3 were all relatively in agreement, with the G3MP2B3 method giving the slightly better results. Compared with these, the G3 method is more expensive and not sufficiently precise.

The analysis of the heat of formation obtained with each of the three approaches shows that the isodesmic approach yielded the best results, followed by the BAC procedure, and lastly the atomization calculations. This highlights the importance of cancellation of errors in the calculations; the isodesmic approach is better in this respect than the BAC procedure.

4. Conclusions

In this study, the heat of formation for 15 C_1 chlorofluorocarbons and hydrochlorofluorocarbons and 23 C_2 chlorofluorocarbons and hydrochlorofluorocarbons were calculated at the G3X level. Good agreement was found between our calculations and experimental values. Analyzing the results of the atomization approach, we have drawn the conclusion that the errors are approximately dependent upon the number of C–F or C–Cl bonds. Hence, we used the BAC procedure and isodesmic reactions approach in an attempt to improve the precision. Comparison with available experimental data for the atomization approach, BAC procedure, and isodesmic reactions approach for calculating enthalpy indicated that the latter two approaches can reduce system error and improve calculation precision. Furthermore, the isodesmic approach showed broader applicability than the BAC procedure.

Acknowledgements

The project sponsored by the Scientific Research Foundation for the returned overseas Chinese scholars, State Education Ministry.

References

[1] C. Scheutz, Y. Dote, A.M. Fredenslund, H. Mosbk, P. Kjeldsen, Environ. Sci. Technol. 41 (2007) 7714–7722.
[2] R. Tesser, M. Di Serio, R. Gargiulo, G. Basile, L. Bragante, E. Santacesaria, J. Fluorine Chem. 121 (2003) 15–22.
[3] S. Corr, J. Fluorine Chem. 118 (2002) 55–67.
[4] D.J. Wuebbles, K.O. Patten, Environ. Sci. Technol. 43 (2009) 3208–3213.

[5] F.W. Kirkbride, F.G. Davidson, Nature 174 (1954) 79–80.
[6] A.S. Rodgers, J. Phys. Chem. 71 (1967) 1996–2000.
[7] C.W. Baushlicher Jr., R. Alessandra, J. Phys. Chem. A 104 (2000) 9026–9028.
[8] N.L. Haworth, M.H. Smith, G.B. Bacskay, J.C. Mackie, J. Phys. Chem. A 104 (2000) 7600–7611.
[9] M. Namazian, M.L. Coote, J. Fluorine Chem. 130 (2009) 621–628.
[10] M. Oren, M.A. Iron, A. Burcat, J.M.L. Martin, J. Phys. Chem. A 108 (2004) 7752–7761.
[11] E.P.F. Lee, J.M. Dyke, W.K. Chow, F.T. Chau, D.K.W. Mok, J. Comput. Chem. 28 (2007) 1582–1592.
[12] R.J. Berry, D.R.F. Burgess Jr., M.R. Nyden, M.R. Zachariah, C.F. Melius, M. Schwartz, J. Phys. Chem. 99 (1996) 17145–17150.
[13] N.L. Haworth, M.H. Smith, G.B. Bacskay, J.C. Mackie, J. Phys. Chem. A 104 (2000) 7612–7616.
[14] C.F. Cloud III, M. Schwartz, J. Comput. Chem. 24 (2003) 640–646.
[15] M.R. Zachariah, C.F. Melius, J. Phys. Chem. A 101 (1997) 913–918.
[16] N.L. Ma, K.C. Lau, S.H. Chien, W.K. Li, Chem. Phys. Lett. 311 (1999) 275–280.
[17] A. Ricca, C.W. Bauschlicher Jr., J. Phys. Chem. 102 (1998) 876–880.
[18] L.A. Curtiss, K. Raghavachari, P.C. Redfern, J.A. Pople, J. Chem. Phys. 112 (2001) 7374–7383.
[19] A.G. Baboul, L.A. Curtis, P.C. Redfem, K. Raghavachar, J. Chem. Phys. 110 (1999) 7650–7657.
[20] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03 Revision C. 02, Gaussian, Inc., Wallingford, CT, 2004.
[21] L.A. Curtiss, K. Raghavacharin, P.C. Redfer, J.A. Pople, J. Chem. Phys. 106 (1997) 1063–1079.
[22] B. Ihsan, Thermochemical Data of Pure Substances. Two Volumes (Volume I: Ag–Kr and Volume II: La–Zr), third ed., 1995.
[23] M.W. Chase Jr., C.A. Davies, J.R. Downey Jr., D.J. Frurip, R.A. McDonald, A.N. Syverud, J. Phys. Chem. Data 14 (Suppl. 1) (1985).
[24] R.A. Fletcher, G. Pilcher, Trans. Faraday Soc. 67 (1971) 3191–3201.
[25] D.R. Lide (Ed.), CRC Handbook of Chemistry and Physics Internet Version, 87th ed., Taylor and Francis, 2007, http:/www.hbcpnetbase.com.
[26] D.R.F. Burgess Jr., M.R. Zachariah, W. Tsang, P.R. Westmoreland, Prog. Energy. Combust. Sci. 21 (1996) 453–529.
[27] S.S. Chen, A.S. Rodgers, J. Chao, R.C. Wilholt, B.J. Zwolinski, J. Phys. Chem. Ref. Data 4 (1975) 441–456.
[28] J.D. Cox, G. Pilcher, Thermochemistry of Organic and Organometallic Compounds;, Academic, New York, 1970.
[29] J.R. Lacher, H.A. Skinner, J. Chem. Soc. A (1968) 1034.
[30] T.S. Papina, V.P. Kolesov, Russ. J. Phys. Chem. (Engl. Transl.) 61 (1987) 1168–1170.
[31] S.V. Levanova, L.I. Bushneva, R.M. Rodova, A.M. Rozhnov, Y.A. Treger, Zh. Fiz. Khim. 50 (1976) 2701.
[32] F.W. Kirkbride, J. Appl. Chem. 6 (1956) 11–21.
[33] O.N. Ventura, M. Segovia, Chem. Phys. Lett. 403 (2005) 378–384.