Chapter 18

Ab Initio Calculations for Kinetic Modeling of Halocarbons

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The thermochemistry and reaction kinetics of halogenated hydrocarbons have been investigated by *ab initio* methods in order to improve our understanding of their flame chemistry and likely roles in flame suppression. Bond additivity corrections at the G2, G2(MP2), CBS-4 and CBS-Q levels of theory were developed for fluorinated and chlorinated C₁ and C₂ species, including saturated and unsaturated compounds. The resulting enthalpies of formation are in excellent agreement with experimental values. Transition states for the reactions of H atoms with hydrofluoromethanes were characterized at up to the G2 level of theory, and application of transition state theory yielded rate constants in good accord with experimental results. A similar analysis for H and OH reactions with CH₃I also agrees with the known thermochemistry and kinetics. These investigations provide insight into the major product channels and the temperature dependence of the rate constants. The implications for flame suppression by haloalkanes are discussed.

During the past two decades, it has become apparent that the release of volatile chlorofluorocarbons (CFCs) and halon fire suppressants (e.g. CF₃Br, CF₂ClBr, CF₂Br-CF₂Br) is a major cause of depletion of the stratosphere's ozone layer (1-3). Hence, there have been numerous restrictions placed upon the industrial use of CFCs and halons, which has led to concerted efforts to find new, "ozone-friendly" replacements (4). Potential replacement agents include hydrofluorocarbons and iodocarbons, which are degraded in the troposphere and, hence, pose no significant risk to the ozone layer. They also possess low global warming potentials.

The effectiveness of a proposed flame suppressant can be reliably predicted via kinetic modeling provided accurate thermochemical and kinetic data are available for the hundreds of reactions associated with the suppressant and its interactions with

flame species. Such data are often difficult to obtain from experiments, especially at combustion temperatures. Experimental determinations are further hampered by the transient nature of many of the intermediate species involved, which makes it difficult to isolate individual reactions and species for measurements. An *ab initio* computational alternative is desirable because it would enhance our understanding of these complex processes at a molecular level and provide a cost-effective way of screening/predicting suitable replacement agents for fire suppression.

Thermochemistry of Haloalkanes

Enthalpies of Formation from *ab Initio* Energies. *Ab initio* quantum mechanics has proven to be a most valuable tool for estimating thermochemical quantities (dissociation energies, enthalpies of formation, heat capacities, entropies, etc.) of gas phase molecules, radicals and ions in systems where experimental data are either unavailable or unreliable. Briefly outlined below is the procedure by which one may utilize quantum mechanical energies to furnish a direct estimate of the enthalpy of formation of a fluoroalkane.

The molecular atomization energy, ΣD_0 , is obtained from the calculated energies of the molecule and constituent atoms via the relation:

$$\Sigma D_0(C_xH_yF_z) = x E(\text{calc}, C) + y E(\text{calc}, H) + z E(\text{calc}, F) - E_0(\text{calc}, C_xH_yF_z) \quad (1)$$

E_0 for the molecule contains the zero-point energy (ZPE), obtained from calculated vibrational frequencies after adjustment by the appropriate scale factor (0.8929 for HF/6-31G(d) frequencies). The enthalpy of formation at 0 K can then be computed from the atomization energy and the experimental enthalpies of formation of the constituent atoms via:

$$\Delta_f H^0(C_xH_yF_z, 0 \text{ K}) = x \Delta_f H^0(C_{\text{gas}}, 0 \text{ K}) + y \Delta_f H^0(H_{\text{gas}}, 0 \text{ K}) + z \Delta_f H^0(F_{\text{gas}}, 0 \text{ K}) - \Sigma D_0(C_xH_yF_z) \quad (2)$$

Finally, the room temperature enthalpy is obtained from:

$$\Delta_f H^0(298.15 \text{ K}) = \Delta_f H^0(0 \text{ K}) + \delta H^0(C_xH_yF_z) - x \delta H^0(C) - 0.5y \delta H^0(H_2) - 0.5z \delta H^0(F_2) \quad (3)$$

$\delta H^0 = H^0(298.15 \text{ K}) - H^0(0 \text{ K})$ represents the thermal contribution to a species' enthalpy. It is obtained from experimental data for the elements. For the compound, one computes this quantity from the calculated rotational constants and scaled vibrational frequencies using standard statistical mechanical formulae.

Current state of the art *ab initio* methods such as Pople's G2 [Gaussian-2] (5, see chapter by Curtiss and Raghavachari) and simpler G2(MP2) (6) methods, and Petersson's CBS-4 and CBS-Q methods (7, see chapter by Petersson), have been proposed for the accurate determination of enthalpies of formation using the procedure

outlined above. The estimated accuracies of these methods, as ascertained by comparison with the "G2 test set" (5) of 55 molecules with accurately known atomization energies, are very good. For the test set, RMS deviations of the computed energies from experiment for the four protocols are 6.3, 6.7, 9.2, and 4.2 kJ mol⁻¹, respectively (7). The agreement is not surprising since the four methods were optimized to minimize disagreement with experimental data including the "G2 test set." However, these data include only one molecule with a carbon-halogen bond, CH₃Cl. Therefore, a systematic investigation of the ability of these methods to predict accurate enthalpies of formation of chlorofluorocarbons was conducted.

Chlorofluoromethanes. A previous study by Ignacio and Schlegel (8) utilized HF/6-31G(d) optimized geometries and vibrational frequencies, MP4/6-31G(d,p) energies and isodesmic reactions (using the experimental enthalpies of CH₄, CF₄ and CCl₄) to compute the enthalpies of formation of the remaining chlorofluoromethanes.

Based on the results they estimated the accuracy of this method to be ± 13 kJ mol⁻¹.

In order to test the capabilities of the currently utilized high level "compound methods" to calculate the enthalpies of halocarbons with improved accuracy, the G2 (5), G2(MP2) (6), CBS-Q and CBS-4 (7) methods were applied (9) to the chlorofluoromethanes which included the four fluoromethanes, the four chloromethanes and the six compounds containing both chlorine and fluorine. In I the calculated G2 and CBS-Q enthalpies are compared with experiment. Experimental enthalpies of the fluoromethanes were taken from Kolesov's compilation (10). For the remaining molecules the recommended JANAF (11) enthalpies were chosen for comparison. Deviations of the calculated enthalpies from experiment, [$\Delta_f H^0(\text{calc}) - \Delta_f H^0(\text{expt})$], are listed in parentheses. An alternative, although less complete, compilation of enthalpies of formation of the CFCs has been published by Pedley *et al.* (12). The literature values from this reference are within 2 kJ mol⁻¹ of those in the JANAF tables (11) for most species. However, for CF₂Cl₂ and CFCl₃, the enthalpies in the former reference are lower by 14 and 20 kJ mol⁻¹, respectively.

The computed enthalpies in I exhibit substantial deviations from experiment, with RMS errors of 15 and 19 kJ mol⁻¹ for G2 and CBS-Q, respectively. These deviations are systematic, with almost all calculated enthalpies lying lower than reported experimental values, as evidenced by the large negative mean deviations. These results are in sharp contrast to many earlier investigations of non-halogenated organic species; e.g. RMS deviations from experimental enthalpies for the "G2 test set" were typically 4-9 kJ mol⁻¹ for these methods (*vide supra*).

To explore the distribution of errors in these series in greater detail, it is instructive to plot the deviation from experiment, [$\Delta_f H^0(\text{calc}) - \Delta_f H^0(\text{expt})$], as a function of one type of carbon-halogen bond while holding the number of the other C-X bond types constant, e.g. a plot of error versus n_{CF} (number of CF bonds) in the series CH₃Cl, CH₂FCl, CHF₂Cl, CF₃Cl. This plot is displayed for the CBS-Q method in 1 (one finds similar trends using the other methods). One observes quite clearly that

the negative error increases monotonically with increasing number of either C-F or C-Cl bonds; the trend is "roughly" linear with C-X bond.

One approach to correct systematic errors in *ab initio* estimates of enthalpies of formation is to employ the concept of Bond Additivity Corrections (BACs), developed by Melius and coworkers (13,14, see chapter by Zachariah and Melius) for MP4/6-31G(d,p) enthalpies. In this method, 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 the following expression:

$$\begin{aligned}\Delta_f H^0(\text{BAC}) &= \Delta_f H^0(\text{calc}) - \sum n_i \Delta_i \\ &= \Delta_f H^0(\text{calc}) - [n_{\text{CH}} \Delta_{\text{CH}} + n_{\text{CF}} \Delta_{\text{CF}} + n_{\text{CCl}} \Delta_{\text{CCl}}]\end{aligned}\quad (4)$$

Table I. Calculated and Experimental Enthalpies of Formation in Chlorofluoromethanes^a

Species	Expt.	G2 ^b	CBS-Q ^b	G2 ^b	CBS-Q ^b
				[BAC]	[BAC]
CH ₄	-74.9±0.4	-77.7(-2.8)	-74.0(0.9)	-77.7(-2.8)	-74.0(0.9)
CH ₃ F	-232.6±8.4	-244.1(-11.5)	-238.7(-6.1)	-237.6(-5.0)	-235.2(-2.6)
CH ₂ F ₂	-452.2±1.8	-463.7(-11.5)	-457.6(-5.4)	-450.7(1.5)	-450.6(1.6)
CHF ₃	-697.6±2.7	-714.0(-16.4)	-706.7(-9.1)	-694.5(3.1)	-696.2(1.4)
CF ₄	-933.0±1.7	-956.5(-23.5)	-947.7(-14.7)	-930.5(2.5)	-933.7(-0.7)
CH ₃ Cl	-83.7±2.1	-85.5(-1.8)	-86.3(-2.6)	-82.7(1.0)	-77.8(5.9)
CH ₂ Cl ₂	-95.5±1.3	-98.1(-2.6)	-105.6(-10.1)	-92.4(3.1)	-88.6(6.9)
CHCl ₃	-103.2±1.3	-107.6(-4.4)	-125.3(-22.1)	-99.2(4.0)	-99.8(3.4)
CCl ₄	-96.0±2.1	-107.7(-11.7)	-137.3(-41.3)	-96.5(-0.5)	-103.3(-7.3)
CH ₂ FCI	-261.9±13.0	-273.3(-11.4)	-272.3(-10.4)	-264.0(-2.1)	-260.3(1.6)
CHF ₂ Cl	-481.6±13.0	-498.1(-16.5)	-495.9(-14.3)	-482.3(-0.7)	-480.4(1.2)
CF ₃ Cl	-707.9±3.3	-731.8(-23.9)	-728.2(-20.3)	-709.4(-1.5)	-709.2(-1.3)
CHFCI ₂	-283.3±13.0	-295.8(-12.5)	-301.4(-18.1)	-283.7(-0.4)	-280.9(2.4)
CF ₂ Cl ₂	-491.6±8.0	-513.9(-22.3)	-517.4(-25.8)	-495.3(-3.7)	-493.4(-1.8)
CFCl ₃	-288.7±6.3	-305.2(-16.5)	-318.8(-30.1)	-290.3(-1.6)	-289.8(-1.1)
RMS	±6.9	14.5	18.8	2.6	3.4
AVG	—	-12.6	-15.3	-0.2	0.7

^a $\Delta_f H^0$ at 298.15 K in kJ mol⁻¹ units

^b Values in parentheses represent deviations from experiment

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Linear regression was used to fit equation 4 to the experimental data on the series of 15 CFCs. This provided values for the BAC corrected enthalpies of formation in I and the three BAC parameters, Δ_{CH} , Δ_{CF} and Δ_{CCl} (II (A)) for all four *ab initio* methods. The values of Δ_{CH} were quite small, and were therefore set equal to zero. One sees from I that the BAC corrected enthalpies of formation are in extremely good agreement with experiment. The residual RMS deviations of 2.6 and 3.4 kJ mol⁻¹, are almost an order of magnitude lower than errors in the uncorrected enthalpies and, indeed, lie significantly below the RMS experimental uncertainty of 6.9 kJ mol⁻¹. The BACs have also removed the systematic underprediction of the enthalpies of

Table II. Fluoroalkane Bond Additivity Parameters and Resulting Errors^a

Method	Δ_{CF}	f_{C}	RMS1 ^b	AVE1 ^b	RMS2 ^c	AVE2 ^c
(A) Chlorofluoromethanes ($\Delta_{\text{CF}} + \Delta_{\text{CCl}}$) ^d						
G2	-6.51±0.41	0.0	14.5	-12.6	2.6	-0.2
G2(MP2)	-7.98±0.38	0.0	21.5	-19.3	2.4	0.0
CBS-4	-1.28±0.74	0.0	20.7	-15.3	4.7	0.6
CBS-Q	-3.51±0.55	0.0	18.8	-15.3	3.4	0.7
(B) Fluoroethanes (Δ_{CF})						
G2	-6.51±0.41	0.0	28.4	-25.8	7.6	-6.3
G2(MP2)	-7.98±0.38	0.0	33.4	-29.7	7.3	-5.8
CBS-4	-1.28±0.74	0.0	10.9	-10.0	8.6	-6.5
CBS-Q	-3.51±0.55	0.0	20.9	-18.4	9.7	-7.7
(C) Fluoroethanes ($\Delta_{\text{CF}} + f_{\text{C}}$)						
G2	-6.51±0.41	1.24±0.08	28.4	-25.8	5.3	-1.6
G2(MP2)	-7.98±0.38	1.20±0.06	33.4	-29.7	4.9	-1.0
CBS-4	-1.28±0.74	1.73±1.50	10.9	-10.0	7.2	-2.6
CBS-Q	-3.51±0.55	1.78±0.29	20.9	-18.4	5.3	-0.8
(D) Fluoroethylenes						
G2	-6.51±0.41	1.24±0.08	21.4	-18.2	4.7	-2.1
G2(MP2)	-7.98±0.38	1.20±0.06	25.2	-21.0	4.9	-1.9
CBS-4	-1.28±0.74	1.73±1.50	10.5	-8.7	5.8	-3.8
CBS-Q	-3.51±0.55	1.78±0.29	17.3	-13.7	5.2	-2.0

^a In units of kJ mol⁻¹^b Errors in *ab initio* enthalpies^c Errors in BAC corrected enthalpies^d Using a Δ_{CCl} of -2.80±0.41, -6.54±0.38, -10.62±0.74 and -8.50±0.55, respectively, for the G2, G2(MP2), CBS-4 and CBS-Q methods

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Figure 1. Deviations of CBS-Q enthalpies of formation of chlorofluoromethanes from experiment plotted as a function of the number of: (A) C-F bonds and (B) C-Cl bonds (Reproduced from reference 9. Copyright 1996 American Chemical Society.)

formation, as revealed by the extremely small average errors in the corrected results. Hence, BAC corrections for the G2 and CBS-Q methods were successfully employed to predict highly accurate enthalpies of formation in the chlorofluoromethanes. As shown by the statistical data presented in II (A), similar improvements were also obtained with the G2(MP2) and CBS-4 methods (9). The curvature exhibited in 1(B) and the increasingly negative slopes of the lines in 1(A) are manifestations of “heavy atom” interactions between the C-F and C-Cl bonds (9).

The application of spin-orbit coupling corrections to atomic energies can improve the agreement of G2 enthalpies of formation with experiment. These corrections (9) can remove some, but not all of the systematic errors in chloromethanes, and are far too small to account for the observed deviations in fluoromethanes and the mixed species. Therefore, spin-orbit corrections were not performed explicitly, but are absorbed by the empirical BAC parameters.

Fluoroethanes and Ethylenes. Next, the G2, G2(MP2), CBS-Q and CBS-4 quantum mechanical protocols were utilized to compute the enthalpies of formation of C_2 fluorocarbons. Contained in III (A) is a comparison of the computed G2 enthalpies for fluoroethanes with experiment (15-18). The deviations in the *ab initio* enthalpies are also presented in the Table and plotted (for the G2 and CBS-Q methods only) in 2 (closed squares and solid lines).

One observes from the RMS and average errors in the table that the G2 enthalpies exhibit large negative deviations from experiment. Furthermore, from 2, one sees that these negative errors are systematic with an approximately linear dependence upon the number of C-F bonds in the molecule.

Table III. C₂ Fluorocarbons: Calculated vs. Experimental Enthalpies^a

Species	Expt.	G2 ^b	G2[BAC] ^b
(A) Fluoroethanes			
CH ₃ -CH ₃	-84.1±0.4	-86.0 (-1.9)	-86.0 (-1.9)
CH ₃ -CH ₂ F	-263.2±1.6	-279.7 (-16.5)	-271.6 (-8.4)
CH ₂ F-CH ₂ F	-433.9±11.8	-459.8 (-25.9)	-443.7 (-9.8)
CH ₃ -CHF ₂	-500.8±6.3	-516.4 (-15.6)	-500.3 (0.5)
CH ₂ F-CHF ₂	-664.8±4.2	-687.0 (-22.2)	-662.8 (2.0)
CH ₃ -CF ₃	-745.6±1.6	-772.1 (-26.5)	-747.9 (-2.3)
CHF ₂ -CHF ₂	-877.8±17.6	-906.6 (-28.8)	-874.3 (3.5)
CH ₂ F-CF ₃	-895.8±4.2	-934.2 (-38.4)	-901.9 (-6.1)
CHF ₂ -CF ₃	-1104.6±4.6	-1145.9 (-41.3)	-1105.5 (-0.9)
CF ₃ -CF ₃	-1342.7±6.3	-1383.7 (-41.0)	-1335.3 (7.4)
RMS	±7.7	28.4	5.3
AVG	—	-25.8	-1.6
(B) Fluoroethylenes			
CH ₂ =CH ₂	52.4±0.8	53.3 (0.9)	53.3 (0.9)
CH ₂ =CHF	-140.1±2.5	-146.2 (-6.1)	-138.1 (2.0)
CHF=CHF[Z]	-297.1±10.0	-315.1 (-18.0)	-299.0 (-1.9)
CHF=CHF[E]	-292.9±10.0	-318.4 (-25.5)	-302.3 (-9.4)
CH ₂ =CF ₂	-336.4±4.0	-359.2 (-22.8)	-343.1 (-6.7)
CHF=CF ₂	-491.0±9.0	-512.5 (-21.5)	-488.3 (2.7)
CF ₂ =CF ₂	-658.5±2.9	-693.2 (-34.7)	-660.9 (-2.4)
RMS	±6.7	21.4	4.7
AVG	—	-18.2	-2.1

^a $\Delta_f H^0$ in units of kJ mol⁻¹

^b Values in parentheses represent deviations from experiment

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Figure 2. Deviations of the computed enthalpies of formation of fluoroethanes from experiment as a function of the number of C-F bonds. (A) G2 and (B) CBS-Q (Reproduced with permission from reference 19. Copyright 1997 Elsevier.)

Since the deviations are linearly dependent upon n_{CF} , one may, in principle, again apply the BAC correction to obtain corrected results. Furthermore, because of the close similarity of the fluoroethanes (C_2 s) to the fluoromethanes (C_1 s) in the earlier work, it would be reasonable to expect that the same C-F BAC parameter should also correct the systematic errors found in this study. The results of this procedure are displayed in category B of II. The second column contains the values of Δ_{CF} (9) with their estimated standard deviations. The last two pairs of columns represent the RMS and average errors without and with the application of the C-F BAC parameter. As noted above, the values of RMS2 and AVE2 in II (A) demonstrate that the application of C-F and C-Cl BACs removes virtually all systematic errors in the chlorofluoromethanes. From RMS2 in II (B), one sees, of course, that transferring the C-F BAC to fluoroethanes yields a substantial decrease in RMS deviations in the C_2 s. However, in contrast to the C_1 s, the comparatively large negative values of AVE2 reveal that not all of the negative systematic error has been removed by the bond additivity correction. While the problem could be remedied by refitting to minimize the RMS residuals in the fluoroethanes, this yields a larger value for Δ_{CF} , which would overcorrect enthalpies in the C_1 s. Further, it is physically unrealistic that the error due to a C-F bond should differ in the two series.

In order to explore the source of the remaining systematic errors in the fluoroethanes, results of the earlier investigation of the chlorofluoromethanes (9) were

re-examined. In that work, it was discussed at some length how trends and curvature in plots of $\Delta_f H^\circ(\text{calc}) - \Delta_f H^\circ(\text{expt})$ vs. $n_{\text{C-F}}$ (at fixed $n_{\text{C-Cl}}$) and vs. $n_{\text{C-Cl}}$ (at fixed $n_{\text{C-F}}$) provided definitive evidence of "heavy atom" interactions. In the earlier work, it was decided not to include heavy atom interactions since the RMS residuals using linearly independent BACs were already below the experimental uncertainties in the chlorofluoromethanes. In contrast, for the fluoroethanes, the comparatively large residual errors (RMS2 in II (B)) and negative average deviations (AVE2) indicate that the introduction of a heavy atom interaction parameter is necessary in this series to account for increased errors due to the presence of a second carbon atom attached to the carbon containing the C-C bond. Thus an interaction parameter, f_c (19), was incorporated into the BAC equation which, assuming no C-H bond error, becomes:

$$\Delta_f H^\circ(\text{BAC}) = \Delta_f H^\circ(\text{calc}) - n_{\text{CF}} \Delta_{\text{CF}} f_c \quad (5)$$

The value of the parameter is optimized (holding Δ_{CF} constant at the value determined for the CFCs) to minimize the RMS deviation from experiment in the fluoroethanes.

The resultant values of the interaction parameter with its error estimate are shown in the third column of II (C). RMS2 of category C shows that the residuals using a C-F BAC with an interaction parameter are reduced significantly (relative to category B) for all but the CBS-4 method. Further, the much smaller negative values of AVE2, relative to category B, indicate that almost all of the remaining systematic error has been removed from the BAC corrected enthalpies of formation. Values of RMS2 are well within the RMS experimental uncertainty (III (A)). The removal of systematic error is also demonstrated in 2, in which it is seen that errors in the BAC corrected enthalpies of formation (open circles and dashed line) are clustered about $\Delta_f H^\circ(\text{calc}) - \Delta_f H^\circ(\text{expt}) = 0$.

These studies have been extended to the fluoroethylenes ($\text{C}_2\text{H}_x\text{F}_{4-x}$, $x=0-4$) and fluoroacetylenes ($\text{C}_2\text{H}_x\text{F}_{2-x}$, $x=0-2$) using the G2, G2(MP2), CBS-Q and CBS-4 methods (20). It was decided to use the same parameter values for Δ_{CF} and f_c as were used for the fluoroethanes. As shown in III (B) for the G2 method, systematic errors in the calculated enthalpies (third column) are almost completely removed by application of the BAC and interaction parameter (fourth column). It is very satisfying to find that, for both methods, the RMS deviations in BAC corrected enthalpies of the fluoroethylenes are lower than RMS uncertainties in the experimental data (II(D)).

Extension of *ab Initio* Methods to Heavier Halogens. The G2 method was originally defined for the elements H through Cl. However, Radom and coworkers have recently developed basis sets for Br and I that permit G2 analysis of species containing these halogens (21). These authors described both effective core potential and all-electron basis sets that lead to G2[ECP] and G2[AE] energies, respectively. The G2[ECP] method is much faster computationally, as only the valence electrons are treated explicitly, and there is claimed to be little loss of accuracy as compared to G2[AE] results (21). These basis sets have been employed to analyze the

thermochemistry of bromine and iodine monoxides (22) and hydroxides (23,24) via G2 and related approaches. Hassanzadeh and Irikura have analyzed similar systems using CCSD(T) calculations with large basis sets (25), and Lee has investigated a series of triatomic bromine compounds at a similar level of theory (26). An early application of high-level methods to Br and I-containing compounds was by Kellö and Sadlej, who studied cyanogen halides (27). Typically, a variety of isodesmic or homodesmic reactions have been employed to relate the unknown heats of formation to experimental quantities.

A complication is that radicals with significant unpaired electron spin density close to Br or I nuclei exhibit significant spin-orbit coupling, a relativistic effect which is excluded from standard *ab initio* calculations, but which can lead to large energy corrections. This effect leads to splitting of electron levels. For example, standard calculations on ground-state halogen atoms yield the weighted mean energy of the two 2P_J levels ($J = 1/2$ and $3/2$), weighted by the $2J+1$ degeneracy. However, at 0 K only the lower energy $^2P_{3/2}$ level is populated. This correction is usually neglected for F and Cl atoms, because the 2P_J levels lie close together and the errors introduced are only 1.6 and 3.5 kJ mol $^{-1}$, respectively. These corrections are implicit in the C-F and C-Cl BACs discussed here, and have recently been shown to improve agreement with experimental energies of Cl-containing compounds (28). By contrast, for I atoms at 0 K the required correction is 30.3 kJ mol $^{-1}$ and must be included if chemical accuracy is to be achieved. The magnitude of the spin-orbit splitting between ground-state sub-levels for radicals may be computed (21) or, if available, empirical data can be employed. On the assumption that the spin-orbit states have similar geometries and vibrational frequencies, the influence of low-lying electronic states on thermodynamic functions such as C_p , S and $H_T - H_0$ is straightforward to evaluate (11), once the energy splittings and degeneracies are established.

Haloalkane Kinetics

Product Channels for H + Fluoromethanes. The decomposition of fluoromethanes in hydrocarbon flames has recently been investigated (29) using numerical simulations in conjunction with flame speed measurements. In stoichiometric methane/air flames at high (8%) inhibitor concentrations, the relative amounts of fluoromethane destroyed via reaction with H atoms, unimolecular decomposition and reaction with OH radicals were found to be 4:3:3 and 6:3:1, respectively, for CH_2F_2 and CHF_3 .

Destruction by H attack, which is the leading fluoromethane consumption pathway, has been the subject of several experimental and theoretical investigations.

There are three possible reaction channels; abstraction of F, abstraction of H, and substitution. For CH_3F all three channels are thermochemically reasonable (11):

Thus, the net decomposition rate, $k_6 = k_{6a} + k_{6b} + k_{6c}$. In their review Baulch *et al.* (30) suggested F-abstraction is the dominant channel. Their rate constant recommendation is largely based on the work of Westenberg and deHaas (31) who monitored the disappearance of CH_3F in the presence of a large excess of H, so that knowledge of the products was not necessary for the determination of the total rate constant. Similarly, Parsamyan and Nalbandyan (32) assumed F-abstraction to be the main pathway while analyzing their $\text{H} + \text{CH}_2\text{F}_2$ data. On the other hand BAC-MP4 calculations of Westmoreland *et al.* (33) predict H-abstraction to be the most important pathway for both reactions 6 and 7.

Recently, high level *ab initio* methods such as G2(MP2) and G2(ZPE=MP2) have been employed to compute the reaction barriers for these pathways; full details may be found elsewhere (34). H-abstraction is computed to have the lowest energy barrier, $E_0^\ddagger$, for reactions 6-8. For reaction 9 the barrier to F-substitution is very high which leaves F-abstraction as the only accessible channel.

Controversy also exists over the value of the rate constants. For example, measurements of k_6 differ by over two orders of magnitude at 600 K, where different measurement techniques overlap (31,35). To resolve these discrepancies the G2(MP2) results (34) were used in transition state theory (TST) calculations to predict the reaction rate constants, k_{TST} , as a function of temperature. The resulting Arrhenius plots of the rate constant are compared with experiment in 3.

$$k_{\text{TST}} = \Gamma \frac{k_{\text{B}} T}{h} \frac{Q_{\text{TS}^\ddagger}}{Q_{\text{H}} Q_{\text{CH}_{4-x}\text{F}_x}} \exp \left(-\frac{E_0^\ddagger}{RT} \right) \quad (10)$$

where Γ is the quantum mechanical tunneling correction derived at the zero-curvature level (36) and the partition functions, Q , include rotational symmetry numbers. This is the simplest form of TST. Q was derived on the usual basis of the rigid rotor - harmonic oscillator approximation. Any anharmonicity would lead to slightly higher values of Q , with a likely larger effect on the TS because of its looser modes. Thus, k_{TST} may be underestimated. However, an opposing factor is that neglect of variational effects implies k_{TST} will tend to be too high. The zero-curvature tunneling model neglects two opposing effects. One is that this one-dimensional model does not allow for multi-dimensional corner-cutting tunneling paths, which would increase Γ . On the other hand, the MP2 imaginary frequencies employed here are probably too high, which will lead to overestimated Γ values. A new method for improved calculations of

the energy barrier is outlined in Petersson's chapter in this book. The effects of these neglected factors appear either to be small or to cancel because, as shown below, the canonical TST model generally agrees well with experiment.

For $\text{H} + \text{CH}_3\text{F}$, the minor F-abstraction and substitution channels are predicted to have small rate constants, hence the total rate constant k_6 is essentially equal to k_{6b} . This agrees with the recommended rate constant in the 600-1000 K range within the factor of 5 experimental error limits (30). If the entire difference between theory and experiment is assigned to errors in the *ab initio* $E_0^\ddagger$ for this reaction, then this corresponds to a computational error of only 4 kJ mol^{-1} (at 800 K). Employing the critical evaluation by Baulch *et al.* (30), some of the earlier measurements are seen to be in error (37,38).

The computed rate constant for reaction 7 was within a factor of 2 of the value reported by Parsamyan and Nalbandyan (32). For reaction 8 the computed rate constant compares well with the reported experimental determinations (39-41). For reaction 9 ($\text{H} + \text{CF}_4$), the calculated rate constant is of the same order of magnitude as the measurements by Kochubei and Moin (42). However, the measurements imply that the computed G2(MP2) barrier has been overestimated by about 22 kJ mol^{-1} .

Thus the *ab initio* potential energy surfaces suggest that, contrary to some earlier assumptions, H atoms react predominantly with the C-H bonds in fluoromethanes and that the dominant product is H_2 . F atom abstraction is unfavorable

Figure 3. H + fluoromethanes: G2(MP2) Arrhenius plots (solid lines) vs. experiment (Reproduced with permission from reference 34. Copyright 1997 Elsevier.)

kinetically, even though HF formation is the most exothermic pathway. G2(MP2) based TST results are in good accord with experimentally determined rate constants for H attack on CH_3F , CH_2F_2 and CHF_3 . CF_4 is several orders of magnitude less reactive than the other fluoromethanes towards atomic hydrogen, because it does not contain labile C-H bonds. The high C-F bond strength also makes unimolecular dissociation unfavorable under combustion conditions. Slow F-atom abstraction is the only plausible pathway for H-atom attack on CF_4 . Thus CF_4 is essentially inert in a flame and the flame suppressant activity of CF_4 is largely physical, i.e. through cooling and dilution. By contrast, the other fluoromethanes react quickly with H atoms to yield F-containing radicals that undergo further chemistry. This allows for the possibility of chemical flame suppression radical scavenging by CH_3F , CH_2F_2 and CHF_3 .

The Reactions of H Atoms and OH Radicals with Iodomethane. As a demonstration of the application of G2 analysis to iodine chemistry, results obtained via the G2[AE] method of Radom and coworkers (21) are presented for the reactions of H and OH with CH_3I . These data were used to assess the combustion chemistry of CH_3I , an important intermediate in the chemistry of iodine-mediated flame suppression by agents such as CF_3I (43). First the thermochemistry was examined, as a check of the accuracy of the G2 method, and then the reaction kinetics were analyzed and compared with experiment. One aim was to distinguish between various possible sets of products, which for some systems has been a difficult experimental problem. The present work describes an *ab initio* analysis of the kinetics of the reactions

The results are employed to derive high-temperature rate constants via TST and to assess branching ratios for H vs I abstraction. Contributions from the I-displacement channels were assumed to be negligible based on the G2(AE) results reported for $\text{CH}_3\text{I} + \text{H} \rightarrow \text{CH}_4 + \text{I}$ (44).

The transition state for reaction 11a was first investigated by Schiesser *et al.* using moderately sized ECP basis sets (45), while details of the G2 analysis of channels 11a-12b may be found elsewhere (46). As a check on the accuracy of the G2 methodology, $\Delta_f H^\circ_{298}$ was computed for the C-H and C-I bond breaking reactions 11a and 11b. The results are -9.0 and $-61.7 \text{ kJ mol}^{-1}$, in excellent accord with the experimental values of -5.3 ± 6.7 and $-62.2 \pm 0.9 \text{ kJ mol}^{-1}$ (47), and thus the thermochemistry of the C-H and C-I bonds is seen to be well-described at the G2 level.

As in the H + fluoromethane example discussed above, the rate constants k were computed via canonical TST (see equation 10). The scaled HF/6-31G(d) and MP2=full/6-31G(d) frequencies of the TSs are similar, except for the low frequency C-I-H bending mode. This apparently reflects the neglect or overestimation of the influence of electron correlation on this mode, which has a significant influence on the TST rate constant. As a compromise, the geometric mean of TST calculations based on both sets of frequencies was derived. The rate constants are plotted in 4. The results for H + CH₃I are consistent with the known bond strengths D_{298} (47), where the weaker C-I bond ($D_{298} = 239 \text{ kJ mol}^{-1}$) is much more reactive than the C-H bond ($D_{298} = 431 \text{ kJ mol}^{-1}$). This is in accord with previous experimental studies which concluded or assumed that HI was the dominant product (48-51), and yields a k_{11} which agrees well with the room temperature experimental data.

TS structures for attack by the OH radical at the H and I atoms of CH₃I were also investigated. In the latter case no barrier beyond the endothermicity was discernible on the HF/6-31G(d) potential energy surface. Consideration of the QCISD(T)/6-311G(d,p) energies calculated at selected points along the MP2/6-31G(d) intrinsic reaction coordinate showed that the energy is below that of HOI + CH₃ at all points. A distinct TS therefore cannot be localized and canonical TST cannot be applied to this channel. k_{12b} was roughly estimated via the relation $k = A \exp(-E_a/RT)$

Figure 4. Computed TST results (solid lines) vs. experiment for: (A) H + CH₃I. (B) OH + CH₃I. The dashed line for the CH₃ + HOI channel shows an empirical estimate. (Reproduced with permission from reference 46. Copyright 1997 Elsevier.)

by assuming a pre-exponential factor $A = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, equal to that measured for $\text{CF}_3\text{I} + \text{OH}$ (52), and an activation energy $E_a = 23 \text{ kJ mol}^{-1}$. This is equal to the endothermicity at 298 K based on $D_{298}(\text{HO-I}) = 216 \text{ kJ mol}^{-1}$ (52).

4(B) shows that, by contrast to H atom attack, the bond that is more reactive towards OH is the stronger C-H bond and that $\text{CH}_2\text{I} + \text{H}_2\text{O}$ formation, the more exothermic channel, is expected to dominate at all temperatures. A check on the reliability of the kinetic calculations is comparison with the measurements of the total removal rate constant $k_{12} = k_{12a} + k_{12b}$ made by Brown *et al.* (53). They are seen to be in excellent agreement, as is the room temperature k_{12} value obtained by Gilles *et al.* (51). Again, the geometric mean of the HF and MP2-based TST results gives good accord with experiment and provides a TST extrapolation of these measurements to combustion conditions. The k_{12} value from the extrapolation to 2000 K is about 25 times greater than the value obtained from a simple linear Arrhenius extrapolation of the data of Brown *et al.* (53), which reflects the significant curvature of the theoretical Arrhenius plot. This predicted curvature is similar to that measured for the analogous reaction of OH with CH_4 (54). The TST analysis also indicates that HOI formation by OH attack on CH_3I is of only minor importance in both flames and the atmosphere.

The TST rate constants for reactions 11 and 12 and experimental data (51,55) for

were employed in a numerical simulation of an adiabatic premixed stoichiometric CH_4/air flame at atmospheric pressure, modeled with CHEMKIN (56) using the GRI-Mech mechanism (57). The results apply to trace quantities of CH_3I (i.e. the C/H/O chemistry was assumed to be unaffected). As may be seen from 5, the dominant removal pathway is via H-atom attack. The next most important removal pathway, about an order of magnitude less effective than reaction 11, is attack by OH. Thus CH_2I will be a minor product of CH_3I decay, with HI as the dominant product.

Summary

Ab initio methods have been applied to investigate the thermochemistry of halogenated alkanes and the kinetics of major pathways for their reactions in flames. Where the computed thermochemistry and rate expressions can be compared with experimental values, the results are in good accord and provide a means to extrapolate limited temperature information over wider temperature ranges. The *ab initio* calculations of enthalpies of formation and rate constants are sufficiently accurate to survey a wide range of possible steps in combustion mechanisms, in order to help limit the number of processes to be included in combustion models and to aid in the identification of key reactions that merit more detailed laboratory study.

Figure 5. Reciprocal lifetimes for traces of CH_3I in an adiabatic premixed stoichiometric CH_4/air flame at atmospheric pressure with respect to unimolecular decomposition and attack by H, O and OH (solid lines, left axis), and the temperature profile (dashed line, right axis).

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