Ab INITIO CALCULATIONS AND KINETIC MODELING OF HALON AND HALON REPLACEMENTS

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Introduction

The mode of action of the chemical-acting flame suppression agents such as the halons is generally, though not universally, accepted. The details of the several reactions involved in chemical suppression have been studied by many groups using experimental and computational techniques. In this paper we report on the calculation of formation enthalpies for a number of halocarbons used, or proposed for use, in flame suppression. Additional calculations have been completed on the radical species and transition states that are important in describing key reactions of flame suppressants. These data are being used to calculate kinetic rate constants that will be used to improve the detailed description of flame extinguishment. Comparisons of computational and experimental results are given.

Calculations and Results

Ab initio calculations were performed using the Gaussian 92 and 94 codes on Cray X-MP, Cray Y-MP, Cray C90, Convex C3820, SUN-Sparc, HP-PARisk, and SGI Power-Challenge computers. Table 1 lists the 69 reactions for which calculations have been completed or are in progress. Some results of these calculations are given below.

Enthalpies of formation for fluoromethanes and chlorofluoromethanes, using a variety of ab initio methods have been reported. Comparisons between results using the G2, G2(MP2) and CBS-Q methods reveal that all exhibit systematic errors dependent on the number of halogens in the molecule. Figure 1 shows the deviations from experiment for chloromethanes, fluoromethanes, and chlorofluoromethanes. The errors are easily corrected using isodesmic reactions to provide results that compare favorably with experiment. An equivalent process, first employed in the BAC-MP4 method, is the employment of bond additivity corrections (BACs), which also give results in good agreement with experiment. Figure 2 shows the results corrected using BACs, with the BAC-MP4 results shown for comparison. Calculations on fluoromethanes also reveal systematic errors as shown in Figure 3. The use of BACs has again been found to correct all results, generally to within experimental error. The corrected formation enthalpies for the three methods used in this study and the BAC-MP4 results are shown in Figure 4.
The ultimate reason for calculation of the formation enthalpies, and the energies of various transition states, is to provide reliable rate equations for reactions for which experimental data are not available. Reactions of species such as hydrogen and hydroxyl radicals with halocarbon molecules have been experimentally studied and they are being used to evaluate the accuracy of computationally derived rate constants. As an example, the reaction of the hydroxyl radical with the hydrochlorofluorocarbon, HCFC 124,

$$\text{CHFCI-CF}_3 + \text{HO}^* \longrightarrow \bullet \text{CFCI-CF}_3 + \text{H}_2\text{O}$$

has been thoroughly modeled. As shown in Figure 5, there is a small activation barrier (8.4 kJ/mol) at the G2(MP2) level of theory. Figure 6 shows the same activation barrier with the potential energy surface calculated as a function of the dihedral angles that define the positions of the CF$_3$ rotor and the O-H group.

Rate constants for the forward and reverse reactions are being calculated using canonical variational transition state theory with zero-curvature tunneling as implemented in POLYRATE. In addition to the energies, moments of inertia and vibrational frequencies for reactants, products, and transition states were obtained from the ab initio calculations. The results of these calculations are given in Figure 7. It is noted that such excellent agreement with experiment is not guaranteed. Thus, an active part of our research is defining the minimum size of the basis set and the level of electron correlation necessary for reliable results. It has been found that low energy vibrational frequencies are a significant source of error, so attention is being given to maximize the reliability of those calculations. Additional corrections necessary to provide the requisite level of fidelity to experiment are also being explored.

The reactions of other HCFCs with OH radicals have also been studied, as have various reactions of FCs, HFCs, and bromo- and iodo-methanes. Following are results of some of the studies.

The pyrolysis of CH$_2$X results in a dehydrohalogenation reaction to give methene and hydrogen halide in the cases where X = F and Cl. When X = I, an elimination reaction yields the methyl radical plus the iodine atom. When X = Br, the elimination reaction also appears to be favored. The reaction of iodomethane with the hydrogen atom was found to prefer the abstraction of HI, rather than the removal of H$_2$, in agreement with experiment. (See Figure 8) The reaction of oxygen atoms with CH$_4$I resulting in the formation of OI was found to occur without a barrier, other than the exothermicity of the reaction. This reaction, too, showed good agreement with experimental results.

The reaction of hydrogen atoms with fluoromethanes has been studied in some detail. Computational results have shown that the dominant reaction pathway is the abstraction of hydrogen, rather than the thermodynamically preferred abstraction of fluorine to form hydrogen fluoride. The reaction with CF$_3$ can proceed only via the slow abstraction of fluorine, so it is not expected to be an important species in flame suppression. That is, it is expected to contribute primarily as a physical flame suppressant. Details of this work will be published shortly.

Conclusion

Thermodynamic descriptors of a large number of reactions have been calculated using multiple ab initio protocols. Although some variation between the protocols is observed, it has been shown that the results are generally in excellent agreement with experiment. The rate constants
calculated from the ab initio results show an equally good agreement with experimental results, where available. Conclusions regarding preferred reaction pathways and products drawn from this work have suggested some differences from expected results and indicate the need for additional experimental confirmation.

References and Notes


2. 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.

3. The use of Department of Defense high performance computing facilities is acknowledged. (To be modified.)


Table 1: Reactions of halocarbons being investigated by computational methods.

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>CFC Reactants</th>
</tr>
</thead>
<tbody>
<tr>
<td>H abstraction by H</td>
<td>CH₄, CH₂F, CH₂F₂, CHF₃</td>
</tr>
<tr>
<td>(RH + H⁺ → R⁺ + H₂)</td>
<td>CH₃Cl, CH₂Cl₂, CHCl₃</td>
</tr>
<tr>
<td></td>
<td>CH₃I</td>
</tr>
<tr>
<td>Halogen abstraction by H</td>
<td>CH₂F, CH₂F₂, CHF₃, CF₄</td>
</tr>
<tr>
<td>(RX + H⁺ → R⁺ + HX)</td>
<td>CH₃Cl</td>
</tr>
<tr>
<td></td>
<td>CH₃I</td>
</tr>
<tr>
<td>H substitution</td>
<td>CH₃F, CH₃Cl₂, CHF₃, CF₄</td>
</tr>
<tr>
<td>(RX + H⁺ → RH + X⁻)</td>
<td>HCl</td>
</tr>
<tr>
<td>H abstraction by OH</td>
<td>CH₄, CH₂F, CH₂F₂, CHF₃, HF</td>
</tr>
<tr>
<td>(RH + OH⁻ → R⁺ + H₂O)</td>
<td>CH₃Cl, CH₂Cl₂, CHCl₃, HCl</td>
</tr>
<tr>
<td></td>
<td>CHF₂Cl, CHFCl₂</td>
</tr>
<tr>
<td></td>
<td>CH₃I</td>
</tr>
<tr>
<td></td>
<td>CH₃CH₂Cl (C₁ &amp; C₂), CH₂ClCH₂Cl</td>
</tr>
<tr>
<td></td>
<td>CH₃CF₂Cl, CH₃CFCl₂, CH₂ClCF₂Cl, CH₂ClCF₃, CHCl₃CF₃, CHFClCF₃</td>
</tr>
<tr>
<td>H abstraction by O</td>
<td>CH₄, CH₂F, CH₂F₂</td>
</tr>
<tr>
<td>(RH + O⁻ → R⁺ + OH⁻)</td>
<td>CH₃Cl, HCl</td>
</tr>
<tr>
<td></td>
<td>CH₃I</td>
</tr>
<tr>
<td>HX elimination</td>
<td>CH₂F, CH₂F₂, CHF₃</td>
</tr>
<tr>
<td>(RHX → R⁺ + HX)</td>
<td>CH₃Br, CH₃I</td>
</tr>
<tr>
<td></td>
<td>CH₃CH₂F, CH₃FO, CH₂ClO</td>
</tr>
<tr>
<td>H abstraction by a halogen</td>
<td>Cl: CH₄, CH₂F, CH₃Cl, H₂O₂</td>
</tr>
<tr>
<td>(RH + X⁻ → R⁺ + HX)</td>
<td>F: H₂O₂</td>
</tr>
<tr>
<td>I abstraction by OH</td>
<td>CH₃I, CF₃I</td>
</tr>
<tr>
<td>(RX + OH⁻ → R⁺ + HOX)</td>
<td></td>
</tr>
<tr>
<td>H abstraction by CH₃</td>
<td>CF₄, CH₃Cl</td>
</tr>
<tr>
<td>(RH + CH₃⁺ → R⁺ + CH₄)</td>
<td></td>
</tr>
<tr>
<td>Miscellaneous Abstraction Reactions</td>
<td>CH₃Cl + HO₂⁺ → CH₂Cl⁺ + H₂O₂</td>
</tr>
<tr>
<td></td>
<td>ClO⁺ + O → Cl⁺ + O₂</td>
</tr>
<tr>
<td></td>
<td>HCl + O⁻ → Cl⁻ + OH⁻</td>
</tr>
<tr>
<td></td>
<td>HCl + Cl⁺ → Cl₂ + H⁺</td>
</tr>
<tr>
<td>Miscellaneous Elimination Reactions</td>
<td>CH₂ClO⁺ → CH₂O + Cl⁻</td>
</tr>
<tr>
<td></td>
<td>CH₂ClO⁺ → CHClO + H⁺</td>
</tr>
</tbody>
</table>
Figure 1: Deviation from Experiment of Formation Enthalpies for Various Halomethanes.

G2(MP2)  
\[ \Delta H^0(\text{calc}) - \Delta H^0(\text{expt}) \text{ [kJ/mol]} \]

\[ \text{No. of C-F Bonds} \]

\[ \begin{array}{c}
\text{\#(C-Cl) = 0} \\
\text{\#(C-Cl) = 1} \\
\text{\#(C-Cl) = 2} \\
\text{\#(C-Cl) = 3} \\
\text{\#(C-Cl) = 4}
\end{array} \]

G2  
\[ \Delta H^0(\text{calc}) - \Delta H^0(\text{expt}) \text{ [kJ/mol]} \]

\[ \text{No. of C-F Bonds} \]

CBS-Q  
\[ \Delta H^0(\text{calc}) - \Delta H^0(\text{expt}) \text{ [kJ/mol]} \]

\[ \text{No. of C-F Bonds} \]
Figure 2: Deviation from Experiment of Corrected Formation Enthalpies for Various Halomethanes.
Figure 3: Deviation from Experiment of Formation Enthalpies for Fluoroethanes.

- **G2(MP2)**
  - Graph showing the deviation $\Delta H^0(\text{calc}) - \Delta H^0(\text{expt})$ in kJ/mol for various fluoroethanes.
  - Points represent different fluoroethanes.
  - No. of C-F Bonds on the x-axis.

- **G2**
  - Similar graph as G2(MP2) but for G2 calculations.

- **CBS-Q**
  - Another graph showing the deviation $\Delta H^0(\text{calc}) - \Delta H^0(\text{expt})$.
  - Points are labeled as less symmetrically substituted carbons.

- **Legend**:
  - Open circles represent less symmetrically substituted carbons.
  - Solid squares represent more symmetrically substituted carbons.

- **Axes**:
  - No. of C-F Bonds range from 0 to 6.
  - Deviation range from -50 to 10 kJ/mol.
Figure 4: Deviation from Experiment of Corrected Formation Enthalpies for Fluoroethanes.

- **G2(MP2) [BAC]**
  - $\Delta H^\circ_{f}(\text{calc}) - \Delta H^\circ_{f}(\text{expt})$ [kJ/mol] vs. No. of C-F Bonds
  - Data points indicate a trend that decreases with increasing number of C-F bonds.

- **G2 [BAC]**
  - $\Delta H^\circ_{f}(\text{calc}) - \Delta H^\circ_{f}(\text{expt})$ [kJ/mol] vs. No. of C-F Bonds
  - Similar trend as G2(MP2) [BAC], showing decreasing deviation with more C-F bonds.

- **CBS-Q [BAC]**
  - $\Delta H^\circ_{f}(\text{calc}) - \Delta H^\circ_{f}(\text{expt})$ [kJ/mol] vs. No. of C-F Bonds
  - A slight upward trend is observed, reflecting increased deviation.

- **BAC-MP4**
  - $\Delta H^\circ_{f}(\text{calc}) - \Delta H^\circ_{f}(\text{expt})$ [kJ/mol] vs. No. of C-F Bonds
  - The trend is similar to G2(MP2) [BAC] and G2 [BAC], indicating consistency in deviation pattern across different methods.
Figure 5: G2(MP2) reaction coordinate for CHFCl-CF$_3$ + OH → CFCI-CF$_3$ + H$_2$O
Figure 6: HF/6-31G(d) potential energy scan for the transition state of CHFCl-CF$_3$ + OH represented as 3-D and contour plot.
Figure 7: Comparison of the Calculated [G2(MP2)] vs. Experimental Arrhenius plot for the CHFCI-CF\textsubscript{3} + OH reaction.
Figure 8: Rate Constants as a Function of Temperature for Abstraction of I and Abstraction of H by Hydrogen Radical.