

Ab Initio Calculations and Kinetic Modeling of Halon and Halon Replacements

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Introduction

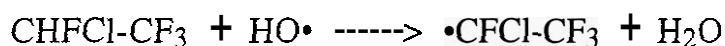
The mode of action of the chemical-acting flame suppression agents such as the halons is generally, though not universally, accepted. The details of the several reactions involved in chemical suppression have been studied by many groups using experimental and computational techniques'. In **this** paper 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^{2,3}. Table 1 lists the 72 reactions for which calculations have been completed or are in progress. Some results of these calculations are given below.

Enthalpies of formation for fluoromethanes⁴ and chlorofluoromethanes⁵, 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-MP4⁶ results shown for comparison. Calculations on fluoroethanes 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,



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 CF₃ 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 POLYRATE⁸. 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 abstraction reaction of iodomethane with hydrogen atoms was found to lead preferentially to HI, rather than H₂, in agreement with experiment. (See Figure 8)

The reaction of the hydroxyl radical with CH₃I results in the formation of H₂O. Thus, in this case the stronger C-H bond is more reactive than the weaker C-I bond, in agreement with experiment. A transition state theory-based extrapolation to combustion conditions indicates that HOI formation by OH attack on CH₃I can be of only minor importance in both flames and the atmosphere'.

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 CF₄ can proceed only via the slow abstraction of fluorine, so it is not expected to be an important species in chemical flame suppression. That is, CF₄ 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

1. For recent review, see Burgess, D. R. F., Jr.; Zachariah, M. R.; Tsang, W.; Westmoreland, P. R.; *Thermochemical and Chemical Kinetic Data for Fluorinated Hydrocarbons*, NIST Technical Note 1412, U. S. Government Printing Office, Washington, 1995.
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 at the Corps of Engineers Waterways Experimental Station is acknowledged.
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Table 1: Reactions of halocarbons being investigated by computational methods.

Reaction Type	ZFC Reactants
H abstraction by H (RH + H• ⇒ R• + H ₂)	CH ₄ , CH ₃ F, CH ₂ F ₂ , CHF ₃ CH ₃ Cl, CH ₂ Cl ₂ , CHCl ₃ CH ₃ I
Halogen abstraction by H (RX + H• ⇒ R• + HX)	CH ₃ F, CH ₂ F ₂ , CHF ₃ , CF ₄ CH ₃ Cl CH ₃ I
H substitution (RX + H• ⇒ RH + X•)	CH ₃ F, CH ₂ F ₂ , CHF ₃ , CF ₄ HCl
H abstraction by OH (RH + OH• ⇒ R• + H ₂ O)	CH ₄ , CH ₃ F, CH ₂ F ₂ , CHF ₃ , HF CH ₃ Cl, CH ₂ Cl ₂ , CHCl ₃ , HCl CH ₂ FCl, CHF ₂ Cl, CHFCl ₂ CH ₃ I CH ₃ CH ₂ Cl (C ₁ & C ₂), CH ₂ ClCH ₂ Cl CH ₃ CF ₂ Cl, CH ₃ CFCl ₂ , CH ₂ ClCF ₂ Cl, CH ₂ ClCF ₃ , CHCl ₂ CF ₃ , CHFClCF ₃
H abstraction by O (RH + O• ⇒ R• + OH.)	CH ₄ , CH ₃ F, CH ₂ F ₂ CH ₃ Cl, HCl CH ₃ I
HX elimination (RHX ⇒ R• + HX)	CH ₃ F, CH ₂ F ₂ , CHF ₃ CH ₃ Br, CH ₃ I CH ₃ CH ₂ F, CH ₂ FO, CH ₂ ClO
H abstraction by a halogen (RH + X• ⇒ R• + HX)	Cl: CH ₄ , CHF ₃ , CH ₃ Cl, H ₂ O ₂ F: H ₂ O ₂
I abstraction by OH (RX + OH• ⇒ R• + HOX)	CH ₃ I, CF ₃ I
Abstraction by CH ₃	CH ₃ Cl + •CH ₃ ⇒ CH ₄ + •CH ₂ Cl CF ₄ + •CH ₃ ⇒ CH ₃ F + •CF ₃ CF ₃ Cl + •CH ₃ ⇒ CH ₃ Cl + •CF ₃
Miscellaneous Abstraction Reactions	CH ₃ Cl + HO ₂ • ⇒ •CH ₂ Cl + H ₂ O ₂ •ClO + O: ⇒ •Cl + O ₂ HCl + O: ⇒ •Cl + OH• HCl + Cl• ⇒ Cl ₂ + H•
Miscellaneous Elimination Reactions	•CH ₂ ClO ⇒ CH ₂ O + Cl• •CH ₂ ClO ⇒ CHClO + H• •CH ₂ ClO ⇒ HCl + •CHO

Figure 1: Deviation from Experiment of Formation Enthalpies for Various Halomethanes.

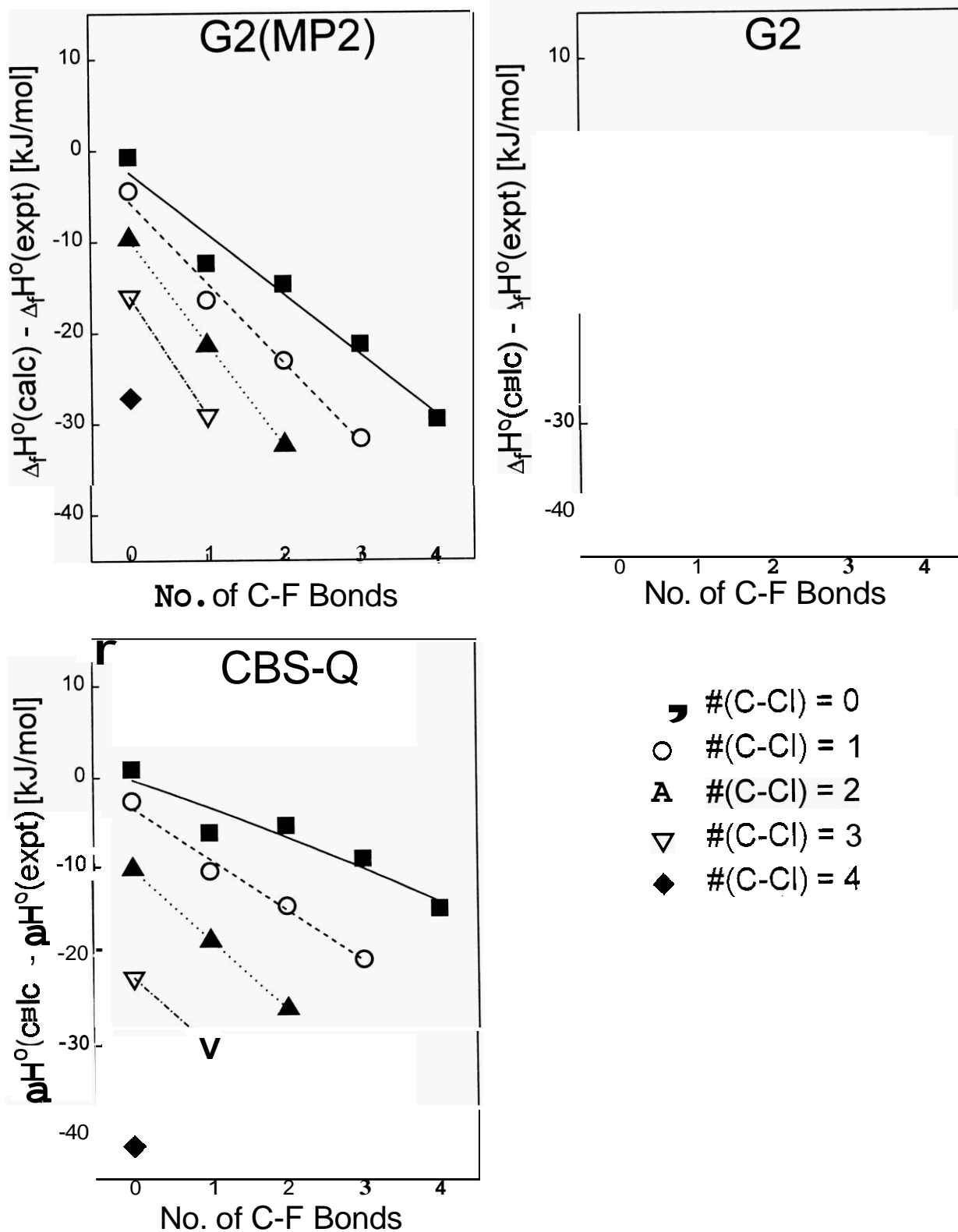


Figure 2: Deviation from Experiment of Corrected Formation Enthalpies for Various Halomethanes.

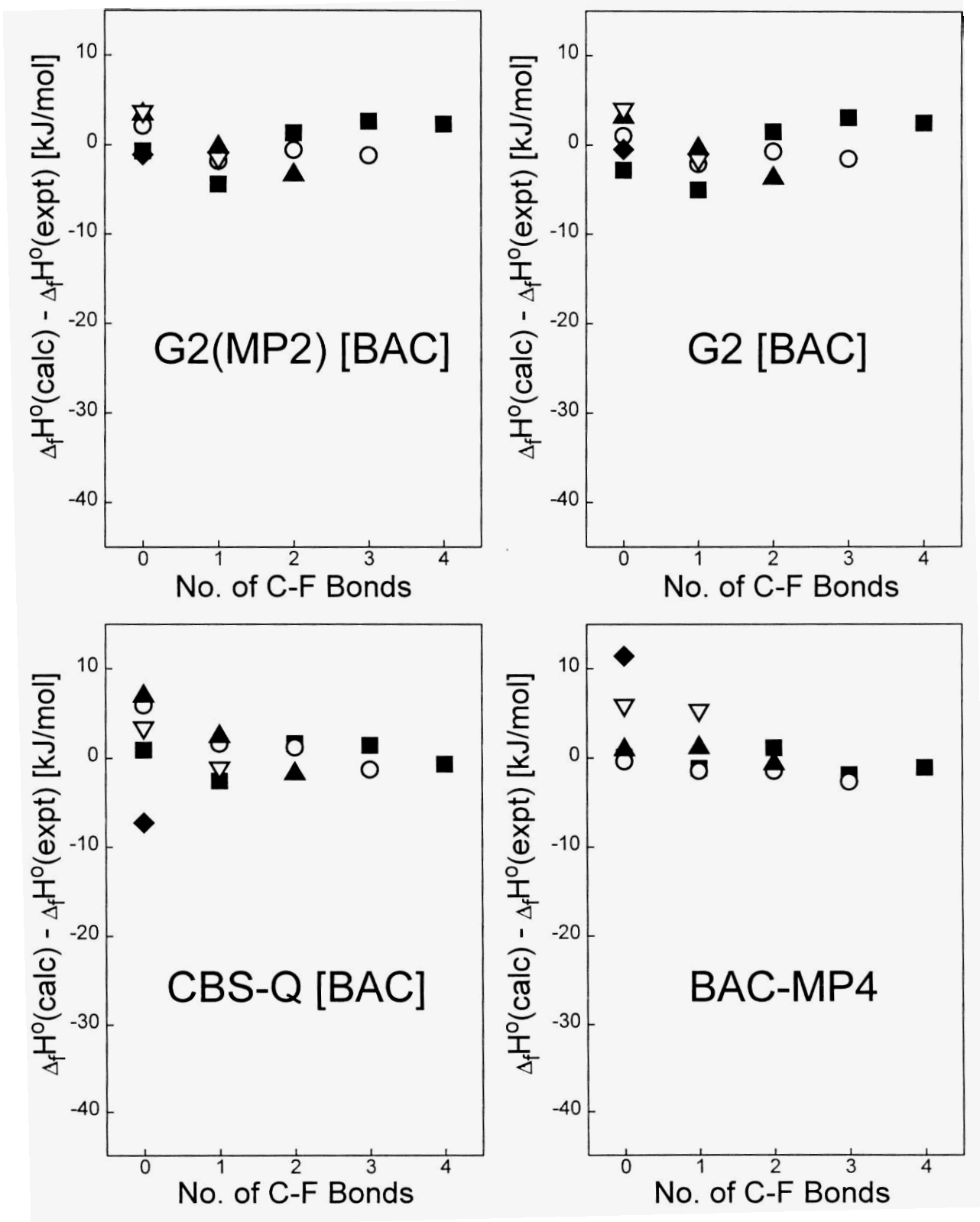
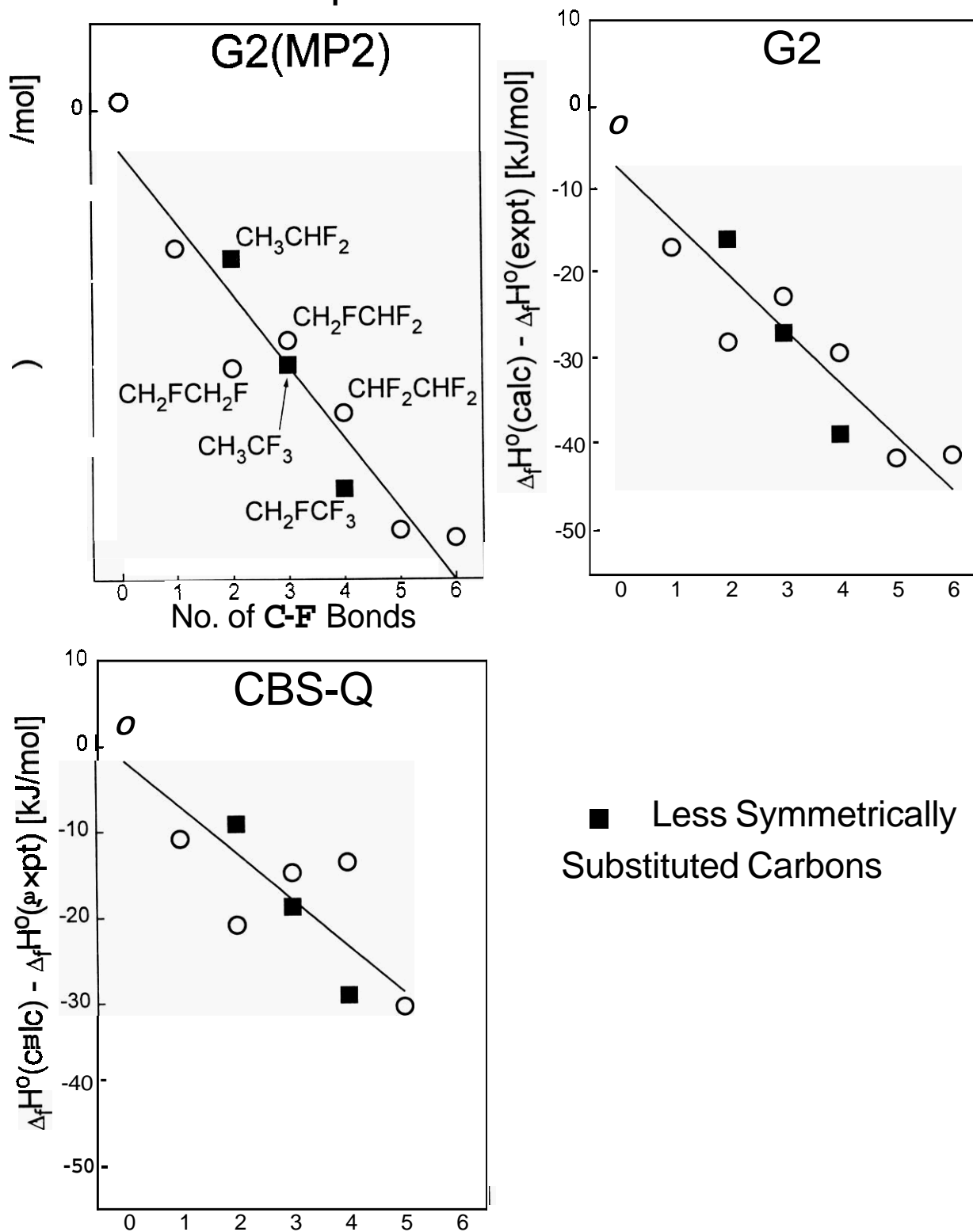


Figure 3: Deviation from Experiment of Formation Enthalpies for Fluoroethanes.



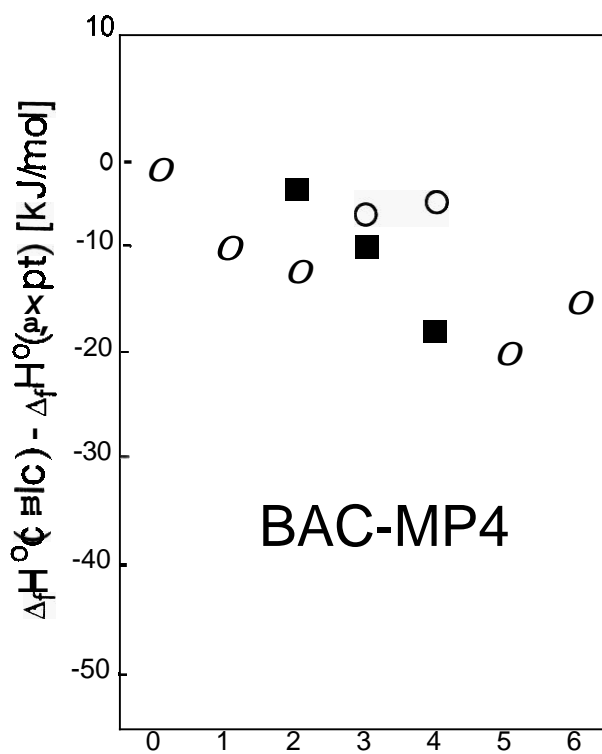
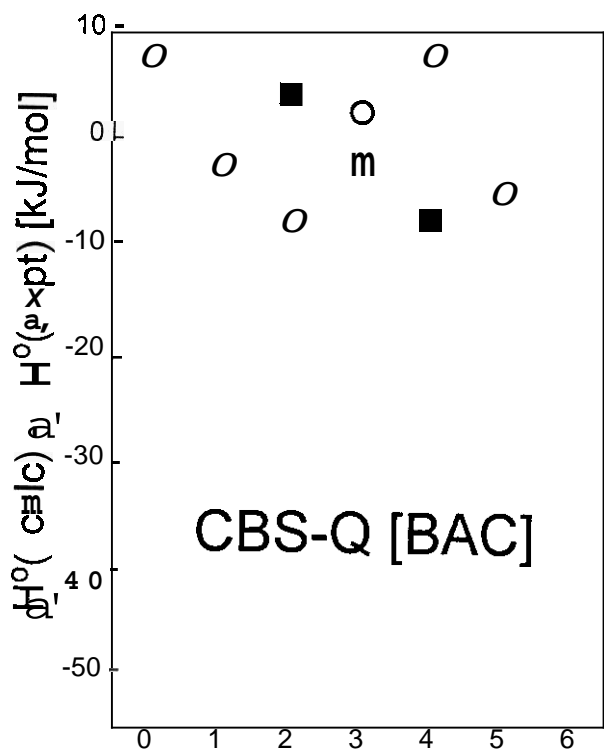
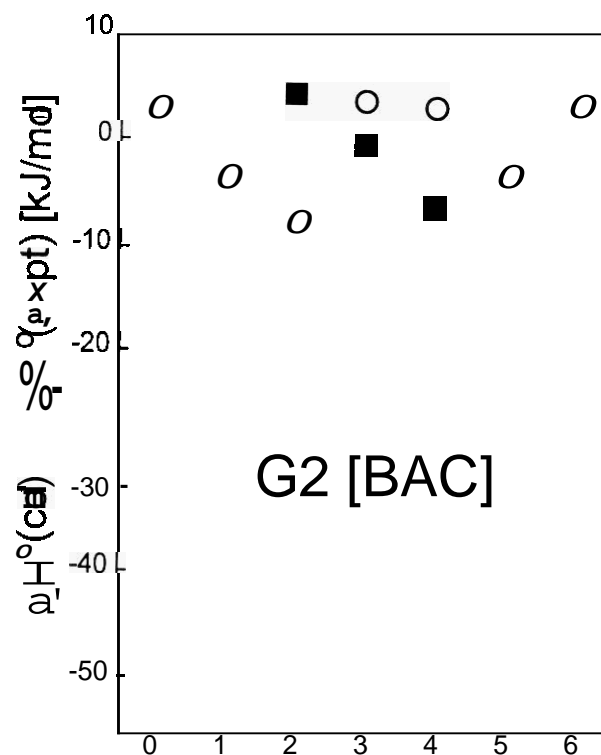
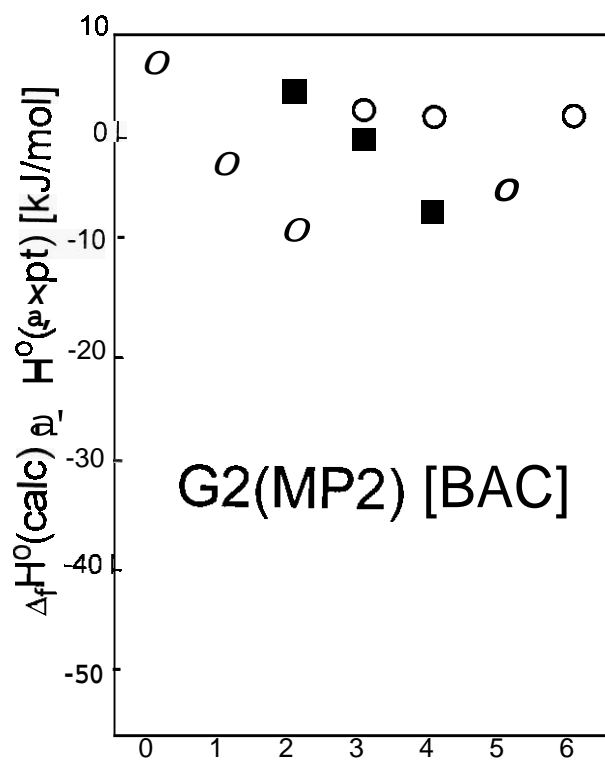


Figure 5: G2(MP2) reaction coordinate for
 $\text{CHFCl-CF}_3 + \text{OH} \rightarrow \text{CFCl-CF}_3 + \text{H}_2\text{O}$

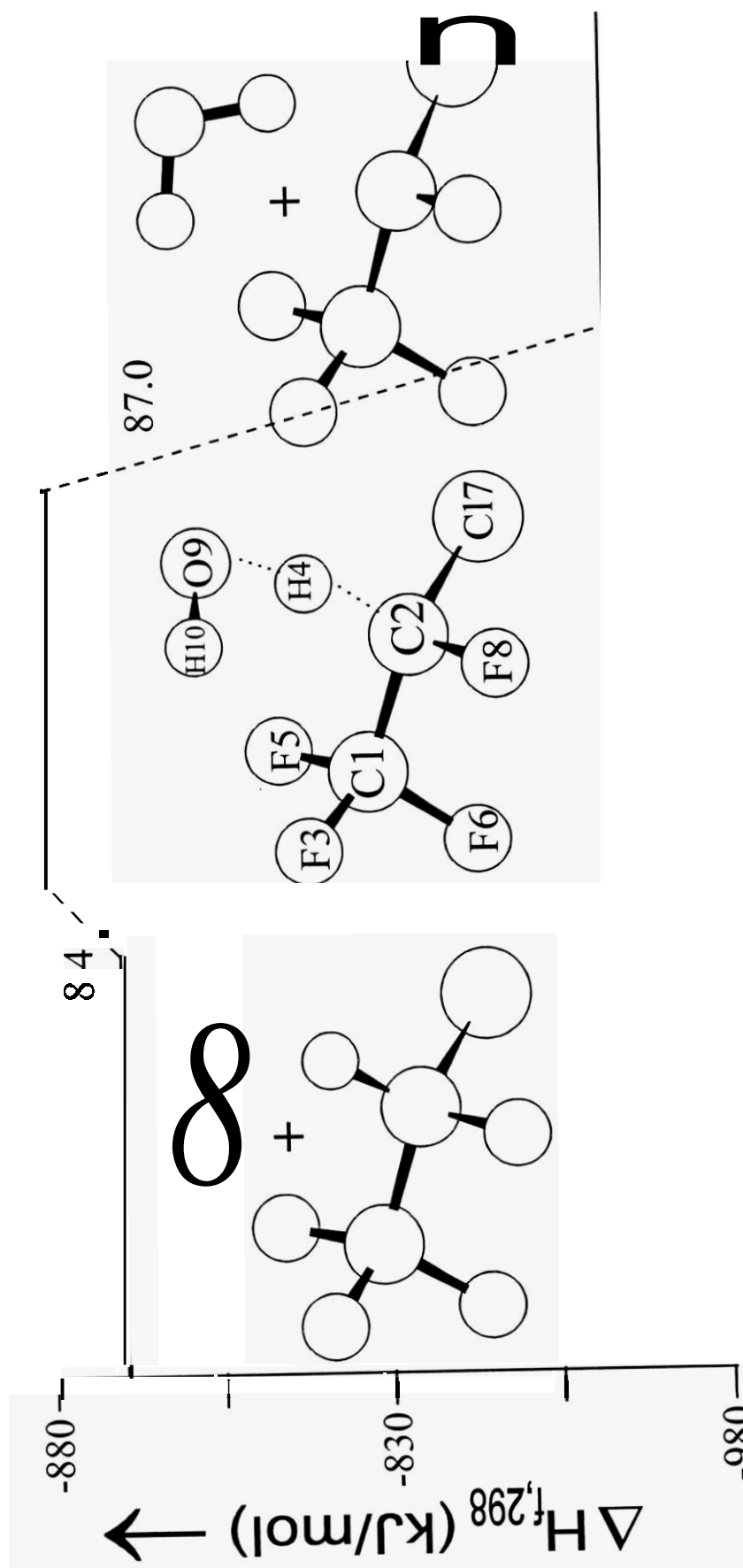


Figure 6: HF/6-31G(d) potential energy scan for the transition state of $\text{CHFC1-CF}_3 + \text{OH}$ represented as 3-D and contour plot.

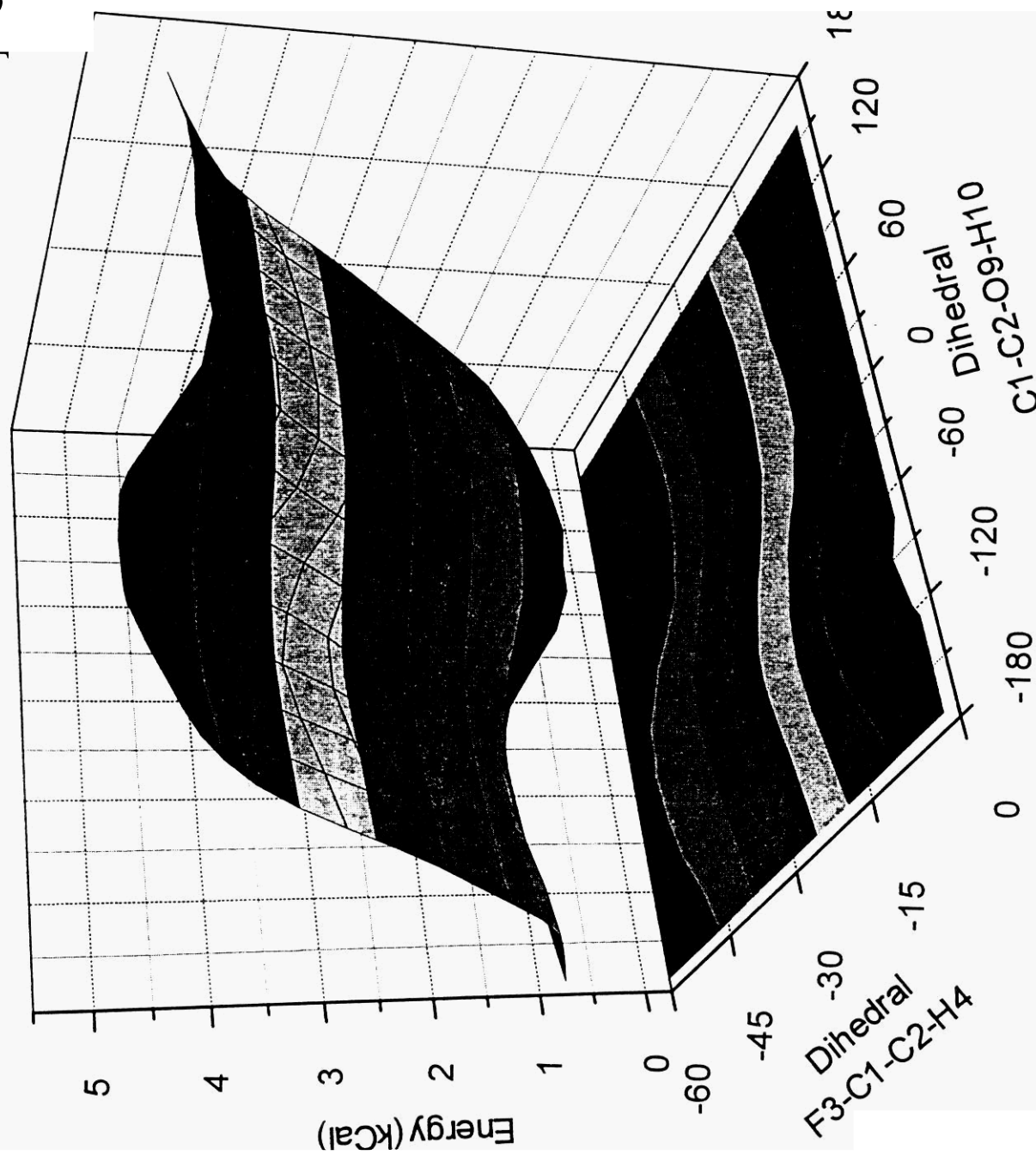


Figure 7: Comparison of the Calculated [G2(MP2)] vs. Experimental Arrhenius plot for the $\text{CHFCI-CF}_3 + \text{OH}$ reaction.

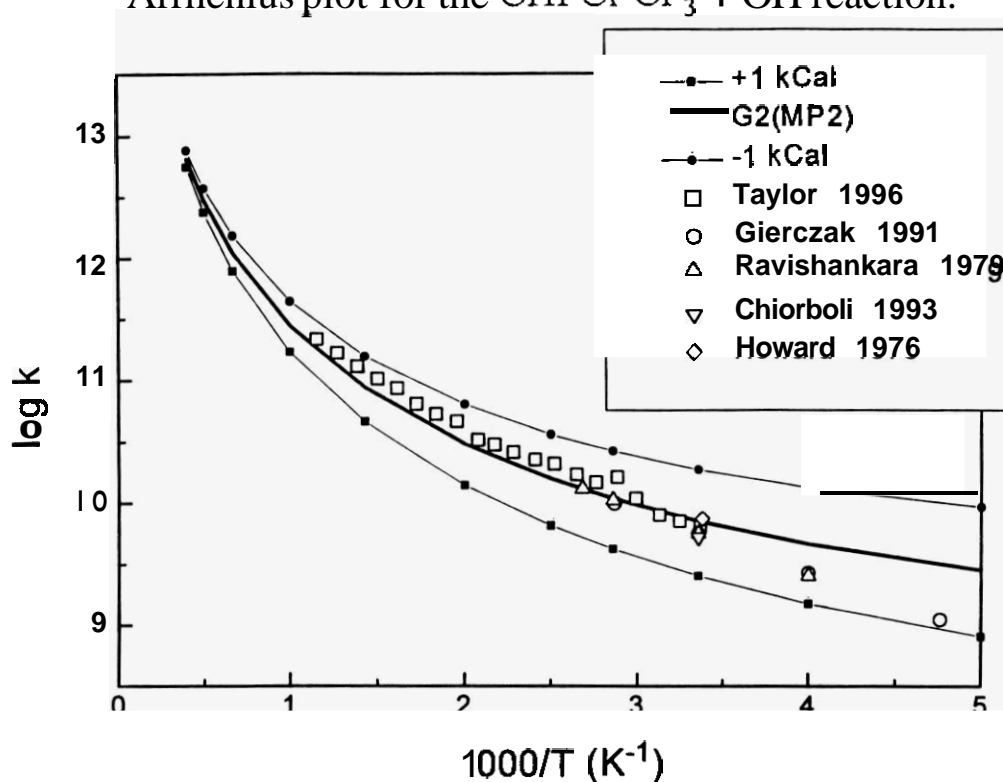


Figure 8: Rate Constants as a Function of Temperature for Abstraction of I and Abstraction of H by Hydrogen Radical.

