

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/5306228>

Gaussian-3 Study of the Thermochemistry of the Germane and its Fluoro Chloro Derivatives

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · AUGUST 2008

Impact Factor: 2.69 · DOI: 10.1021/jp8012267 · Source: PubMed

CITATIONS

2

READS

19

2 AUTHORS, INCLUDING:



Carlos J. Cobos

National Scientific and Technical Research...

126 PUBLICATIONS 3,032 CITATIONS

SEE PROFILE

Gaussian-3 Study of the Thermochemistry of the Germane and its Fluoro Chloro Derivatives

Pablo R. Duchowicz* and Carlos J. Cobos

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CONICET, CICPBA, Casilla de Correo 16, Sucursal 4, (1900) La Plata, Argentina

Received: February 11, 2008; Revised Manuscript Received: April 6, 2008

The thermochemistry of all fluoro and chloro substituted germane molecules have been theoretically studied. Computed G3//B3LYP standard enthalpies of formation at 298 K obtained from isodesmic reaction schemes were compared with values derived via total atomization energies. Bond dissociation energies and energy barriers for the lowest dissociation pathways were estimated at 0 K. From these data, the most probable dissociation products at 0 K were predicted for the thermal decomposition reactions of the gaseous species. Calculated results are compared with experimental determinations as well as other theoretical data when available. The following isodesmic enthalpies of formation in $\text{kcal}\cdot\text{mol}^{-1}$ were calculated for 10 new germane species simultaneously substituted with fluoro and chloro atoms, for which no previously available computations were found in the literature: GeHFCl_2 , -125.8 ; GeCl_2F , -104.3 ; GeHFCl , -67.5 ; GeF_2Cl_2 , -186.3 ; GeF_3Cl , -242.9 ; GeH_2FCl , -89.7 ; GeCl_3F , -159.6 ; GeHClF_2 , -168.0 ; GeF_2Cl , -144.3 ; GeFCl , -81.1 .

1. Introduction

During the past two decades, physical chemistry has been faced with the search of reliable structural and thermochemical parameters of molecular species with lacking or uncertain data, especially by complementing available experimental information with high-accuracy quantum mechanics predictions. There exists a permanent practical interest on focusing in first-principles descriptive models, in order to rule out some compounds on the basis of their calculated relevant properties, avoiding therefore the cost and waste associated with the design of new materials.

For the particular case of the chemistry of germane (GeH_4) related compounds, several thermochemical and kinetic aspects of interest remain still largely unknown. The availability of such parameters has applications in a variety of modern technologies such as in information-recording media, optical-tracking devices, and photoreceptors.^{1–3} In the industry, these are utilized during the design and understanding of chemical vapor deposition processes, constituting a crucial step for creating thin germanium films in semiconductor devices such as transistor elements.^{4,5} Although mostly GeH_4 is employed for such depositions, other Ge-containing molecules could also be utilized.

Among the current thermochemical properties most usually employed in chemical research, the standard enthalpy of formation (ΔH_f°) represents the standard enthalpy of reaction for the formation of a compound in gas phase from its elements in their reference standard state at 298 K and 1 atm. In practical applications, it is a measure of molecular stability, whereas to the theoreticians, ΔH_f° results are important for the investigation of bond dissociation energies (BDE), resonance energies, and the nature of chemical bonds. It is also possible to assert the most probable dissociation products of a thermal decomposition reaction by means of the knowledge of ΔH_f° for each species involved during the transformation. For instance, thermody-

namical measurements show that only few halogenated germane derivatives have accurately determined enthalpies of formation at 298 K, such as $\Delta H_f^\circ(\text{GeH}_4, g) = 21.6 \pm 0.5 \text{ kcal}\cdot\text{mol}^{-1}$,⁶ $\Delta H_f^\circ(\text{GeF}_4, g) = -284.4 \pm 0.1 \text{ kcal}\cdot\text{mol}^{-1}$,⁷ $\Delta H_f^\circ(\text{GeCl}_4, g) = -118.4 \pm 0.6 \text{ kcal}\cdot\text{mol}^{-1}$,⁸ or $\Delta H_f^\circ(\text{GeCl}_2, g) = -38.9 \pm 1.0 \text{ kcal}\cdot\text{mol}^{-1}$,⁹ whereas other radicals containing Ge atoms give rise to higher uncertainties, that is, $\Delta H_f^\circ(\text{GeH}_3, g) = 47.9 \pm 2.4 \text{ kcal}\cdot\text{mol}^{-1}$.¹⁰

In recent years, a series of Gaussian-n (Gn) theories were proposed among the most popular theoretical methods for the calculation of the molecular energy for systems containing first-, second-, and third-row nontransition atoms.^{11–14} Gn theory represents a hybrid procedure based on ab initio molecular orbital theory, where the total energy is obtained by assuming the additivity of a series of calculations at lower levels of theories and empirical corrections. The goal of these methods was an accuracy of $\pm 2 \text{ kcal}\cdot\text{mol}^{-1}$ for the atomization energies, ionization potentials, electron affinities, and proton affinities. Therefore, the G2/97 test set developed for assessing the predictability of this technique consists on 299 experimental energies and leads, for the case of G3 theory, to an average absolute deviation of only $1.01 \text{ kcal}\cdot\text{mol}^{-1}$.¹⁵ A comparison between the G2 and G3 techniques reveals that the later have the following additional features: (a) single-point correlation energies calculated with different basis sets, the largest being the G3Large basis, (2) a spin–orbit correction for first- and second-row elements added to the total energy, (3) a modified higher-level correction with four parameters instead of two, and (4) a core-correlation term added at the second order Moller–Plesset level. This causes the G3 theory to correct many of the deficiencies of G2, with a large improvement for non-hydrogen systems such as SiF_4 and CF_4 , substituted hydrocarbons, and unsaturated rings.¹³

A recent study reported by Wang et al.¹⁶ examines the geometries and vibrational frequencies of germane, chlorinated and fluorinated germanes, and their radical fragments, at the B3LYP/6-31G(2df,p) model chemistry. In addition, the enthal-

* Corresponding author. Fax: (+54) 221 425 4642. E-mail: pduchowicz@gmail.com and duchow@inifta.unlp.edu.ar.

pies of formation and BDE for different possible dissociation channels are calculated by resorting to the G3//B3LYP theory. The authors achieve good agreements in the reported vibrational frequencies when compared to the observed IR and Raman spectra, whereas the estimated values of ΔH_f° are within two times the experimental uncertainties.

In present study, the same level of theory of G3//B3LYP as employed by Wang et al. in their previous work¹⁶ is applied, with the aim of calculating standard enthalpies of formation at 298 K and BDE and energy barriers for the lowest dissociation pathways at 0 K. From these estimated data, the most probable dissociation products at 0 K are expected to be obtained for the thermal decomposition reactions of 10 additional molecules not studied by Wang et al. and characterized for including all possible chlorine and fluorine substitutions in the structure of germane. The simultaneous presence of chlorine and fluorine atoms leads to the complete unavailability of both experimental geometrical and thermochemical parameters. From our knowledge, no theoretical studies have been reported up to now for such kind of molecular system. In contrast to the previously reported study that employs the atomization energy approach, enthalpies of formation are calculated through an alternative approach such as the isodesmic reaction scheme. Section 2 deals with the computational methods employed, and Section 3 presents the results and discussion achieved in present study. Finally, we outline the main conclusions of this research.

2. Computational Details

All electronic structure calculations have been performed with the Gaussian 03 program package.¹⁷ The geometries of germanes and their radicals are optimized at the B3LYP level with the 6-31G(2df,p) basis set, whereas a scale factor of 0.9854 is employed for zero-point vibrational energy corrections (ZPE) at the same level.¹⁸ The performed harmonic vibrational analysis characterized the optimized geometries of the 10 substituted germanes as minima on the potential energy surface without any negative mode. All the molecules were calculated with singlet-state multiplicity.

The newly developed 6-31G(d) basis set with the 3d shell included as the valence shell for germanium is employed here.¹⁹ All the molecular geometries are subjected to G3 single-point calculations with high-level correction parameters (HLC, in mhartrees) of $A = 6.688$, $B = 3.007$, $C = 6.763$, and $D = 1.107$. The resulting G3//B3LYP energy is provided by the following equation

$$E_0(\text{G3//B3LYP}) = \text{MP4/d} + [\text{QCISD(T)/d} - \text{MP4/d}] + \\ [\text{MP4/plus} - \text{MP4/d}] + [\text{MP4/2df,p} - \text{MP4/d}] + \\ [\text{MP2(FU)/G3L} - \text{MP2/2df,p} - \text{MP2/plus} + \text{MP2/d}] + \\ \text{E(SO)} + \text{E(HLC)} + \text{E(ZPE)} \quad (1)$$

where d = 6-31G(d), plus = 6-31+G(d), 2df,p = 6-31G(2df,p), G3L = G3large basis set, and E(SO) = spin-orbit correction for atoms given in ref 14. Thus, eq 1 assumes approximating via shorter calculations a quadratic configuration interaction QCISD(T, full) energy obtained with the G3large basis set.

The isodesmic scheme constitutes a very useful treatment for predicting accurate values of ΔH_f° ,²⁰ and it is based on considering the same total number of each type of bond in the reactants and products with the main purpose of compensating for errors due to the inherent limitation of the model chemistry employed for explaining the correlation energy. In addition, the transformation must be isogyric, that is, involving an equal number of reactants and product species having the same spin

multiplicity. In this procedure, the heat of formation for the molecule of interest is calculated by combining the theoretically computed enthalpy change of the selected reaction with well-established heats of formation for other reaction components. In present analysis, we employ the experimental ΔH_f° data from germane species that have reported the lowest experimental error: GeH_4 , GeF_4 , GeCl_4 , GeCl_2 , and GeH_3 (see above).

The energy barrier height (ΔE^\ddagger) corresponding to each molecular elimination reaction is achieved by optimizing the transition state (TS) structure based on the STQN procedure,²¹ also implemented in Gaussian. In brief, this method uses a linear or quadratic synchronous transit approach to get closer to the quadratic region of the TS, generating an initial guess for the TS that is located midway between the equilibrium reactants and products, and then a quasi-Newton or eigenvalue-following algorithm to complete the optimization. Both the QST2 and QST3 variants from the STQN method were employed for carrying out all the calculations. It has to be mentioned that the location of the TS is not an easy task, involving the search of a first-order saddle point in the multidimensional potential energy hypersurface. All the TS structures under analysis revealed to be first-order saddle points presenting a single imaginary frequency.

3. Results and Discussion

Tables 1–5 record the bond lengths and angles, vibrational frequencies, rotational constants, total energies, enthalpies of formation at 298 K, and BDE and energy barrier heights at 0 K, for the gaseous molecular set under consideration: GeHFCI_2 , GeCl_2F , GeHFCI , GeF_2Cl_2 , GeF_3Cl , GeH_2FCI , GeCl_3F , GeHClF_2 , GeF_2Cl , and GeFCl . Because no experimental data are available at all for the 10 germanes simultaneously substituted with chlorine and fluorine atoms, Table 1 includes for reference purposes the observed geometrical parameters obtained from spectroscopic studies for GeH , GeF , GeH_4 , GeF_4 , GeCl_4 , GeCl_2 , GeClH_3 , and GeFH_3 species. It can be appreciated that in substituted trigonal and tetrahedral structures, the chemical bond lengths, as calculated by resorting to the B3LYP/6-31G(2df,p) model chemistry, are of similar magnitude as those for the cited reference compounds. For instance, the calculated Ge–H bond length is of 1.567 Å for GeHFCI , lying between the reported bonds for Ge–H (1.588 Å) and GeFH_3 or GeClH_3 (1.522 and 1.537 Å, respectively). The Ge–Cl bonds of GeCl_2F (2.173 Å), GeHFCI (2.173 Å), and GeF_2Cl (2.170 Å) are midway the lengths of GeClH_3 (2.150 Å) and GeCl_2 (2.183 Å). The respective Ge–F bonds for GeCl_2F (1.732 Å), GeHFCI (1.737 Å), and GeF_2Cl (1.726 Å) can be compared to the observed values for GeF_4 , GeFH_3 , and GeF (1.67, 1.732, and 1.745 Å, respectively). Regarding the tetrahedral species, similar trends can be further established. The Ge–H bond lengths are GeHFCI_2 (1.525 Å), GeH_2FCI (1.529 Å), and GeHClF_2 (1.523 Å), whereas the experimental value of 1.5251 Å stands for GeH_4 , 1.537 Å for GeClH_3 , and 1.522 Å for GeFH_3 . The Ge–Cl bonds are GeHFCI_2 (2.137 Å), GeF_2Cl_2 (2.116 Å), GeF_3Cl (2.105 Å), GeH_2FCI (2.153 Å), GeCl_3F (2.126 Å), and GeHClF_2 (2.129 Å), compared to the values of 2.113 Å for GeCl_4 and 2.150 Å for GeClH_3 . Finally, the Ge–F bonds are GeHFCI_2 (1.720 Å), GeF_2Cl_2 (1.707 Å), GeF_3Cl (1.702 Å), GeH_2FCI (1.728 Å), GeCl_3F (1.715 Å), and GeHClF_2 (1.713 Å) and can refer to the observed values of 1.67 Å for GeF_4 and 1.732 Å for GeFH_3 .

The theoretical (scaled) vibrational frequencies and rotational constants at the B3LYP/6-31G(2df,p) level are listed in Tables 2 and 3. Apparently, neither IR nor Raman spectroscopies have yet resolved the vibrational spectra for the 10 species under

TABLE 1: Geometrical Parameters (Bond Lengths in Angstroms and Bond Angles in Degrees) Calculated at the B3LYP/6-31G(2df,p) Level and Available Experimental Values

| species | symmetry | molecular parameter |
|----------------------------------|-----------------------|---|
| GeH | | 1.588 ^a |
| GeF | | 1.745 ^a |
| GeH ₄ | <i>T_d</i> | GeH: 1.525 ^b |
| GeF ₄ | <i>T_d</i> | GeF: 1.67 ^b |
| GeCl ₄ | <i>T_d</i> | GeCl: 2.113 ^b |
| GeCl ₂ | <i>C_{2v}</i> | GeCl: 2.183, ^b ClGeCl: 100.3 ^b |
| GeClH ₃ | <i>C_{3v}</i> | GeH: 1.537, ^b GeCl: 2.150, ^b HGeH: 111.0 ^b |
| GeFH ₃ | <i>C_{3v}</i> | GeH: 1.522, ^b GeF: 1.732, ^b HGeH: 113.0 ^b |
| GeHFC1 ₂ | <i>C_s</i> | GeH: 1.525, GeCl: 2.137, GeF: 1.720, ClGeF: 106.8, ClGeH: 111.9, ClGeCl: 110.0 |
| GeCl ₂ F | <i>C_s</i> | GeCl: 2.173, GeF: 1.732, ClGeF: 106.1, ClGeCl: 111.0 |
| GeHFC1 | <i>C₁</i> | GeH: 1.567, GeCl: 2.173, GeF: 1.737, ClGeF: 106.3, ClGeH: 107.9 |
| GeF ₂ Cl ₂ | <i>C_{2v}</i> | GeCl: 2.116, GeF: 1.707, ClGeF: 109.3, ClGeCl: 113.3, FGeF: 106.2 |
| GeF ₃ Cl | <i>C_{3v}</i> | GeCl: 2.105, GeF: 1.702, ClGeF: 111.0, FGeF: 107.7 |
| GeH ₂ FC1 | <i>C_s</i> | GeH: 1.529, GeCl: 2.153, GeF: 1.728, ClGeF: 106.8, ClGeH: 108.8 |
| GeCl ₃ F | <i>C_{3v}</i> | GeCl: 2.126, GeF: 1.715, ClGeF: 107.6, ClGeCl: 111.3 |
| GeHClF ₂ | <i>C_s</i> | GeH: 1.523, GeCl: 2.129, GeF: 1.713, ClGeF: 108.2, ClGeH: 108.2, FGeF: 105.3 |
| GeF ₂ Cl | <i>C_s</i> | GeCl: 2.170, GeF: 1.726, ClGeF: 108.5, FGeF: 104.1 |
| GeFC1 | <i>C_s</i> | GeF: 1.745, GeCl: 2.208, FGeCl: 98.7 ^c |

^a Reference 16. ^b Reference 25. ^c Reference 26.**TABLE 2: Scaled Vibrational Frequencies (in cm⁻¹) Calculated at the B3LYP/6-31G(2df,p) Level (Scale Factor 0.9854)**

| species | requencies |
|----------------------------------|---|
| GeHFC1 ₂ | 142, 193, 214, 420, 443, 686, 693, 745, 2197 |
| GeCl ₂ F | 123, 177, 197, 374, 407, 712 |
| GeHFC1 | 188, 401, 587, 650, 715, 1959 |
| GeF ₂ Cl ₂ | 137, 164, 195, 236, 245, 424, 471, 751, 775 |
| GeF ₃ Cl | 170, 171, 240, 242, 264, 457, 747, 791, 795 |
| GeH ₂ FC1 | 196, 424, 549, 645, 730, 793, 854, 2181, 2201 |
| GeCl ₃ F | 133, 133, 168, 223, 223, 398, 456, 457, 755 |
| GeHClF ₂ | 179, 216, 253, 441, 690, 703, 753, 772, 2218 |
| GeF ₂ Cl | 158, 197, 240, 392, 714, 733 |
| GeFC1 | 215, 386, 708 |

discussion. Therefore, we decided to include the calculated transitions for supporting future experimental assignments.

Table 4 displays both predicted and experimental enthalpies of formation at 298 K comprising all possible halogen substitutions in the structure of germane, including those molecules analyzed in the previous study through the atomization energy procedure¹⁶ and the new set of germanes studied here with the isodesmic approach. To this end, the following reaction schemes were employed, where the symbols with X, Y, Z, and W stand either for H, F or Cl:

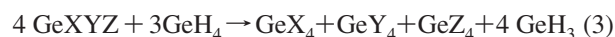
TABLE 3: Rotational Constants (in GHz) Calculated at the B3LYP/6-31G(2df,p) Level

| species | rotational constant |
|----------------------------------|----------------------|
| GeHFC1 ₂ | 3.869, 2.140, 1.564 |
| GeCl ₂ F | 3.958, 2.075, 1.519 |
| GeHFC1 | 13.374, 3.429, 2.784 |
| GeF ₂ Cl ₂ | 2.585, 1.747, 1.473 |
| GeF ₃ Cl | 3.523, 2.114, 2.113 |
| GeH ₂ FC1 | 12.652, 3.420, 2.795 |
| GeCl ₃ F | 1.639, 1.639, 1.173 |
| GeHClF ₂ | 5.673, 2.882, 2.225 |
| GeF ₂ Cl | 5.848, 2.829, 2.168 |
| GeFC1 | 12.626, 3.631, 2.820 |

Tetra-substituted derivatives: GeH₂F₂, GeH₂Cl₂, GeHF₃, GeHCl₃, GeHFC1₂, GeHClF₂, GeH₂FC1, GeH₃F, GeH₃Cl, GeF₃Cl, GeCl₃F, GeF₂Cl₂



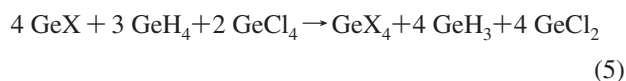
Tri-substituted derivatives: GeF₃, GeCl₃, GeF₂Cl, GeCl₂F, GeHF₂, GeHCl₂, GeH₂F, GeH₂Cl, GeHFC1



Di-substituted derivatives: GeH₂, GeF₂, GeHF, GeHCl, GeFC1



Mono-substituted derivatives: GeH, GeF, GeCl



As can be easily appreciated from Table 4, the atomization based ΔH_f° values differ up to 7.0 kcal·mol⁻¹ (GeCl₃F) from those encountered here by resorting to isodesmic reaction schemes, not considering the atomic and molecular species having experimentally observed values. This also corresponds to the magnitude for the upper limit by which the calculated atomization ΔH_f° differs with respect to the experimentally assigned values for GeH₄ (−3.3 kcal·mol⁻¹), GeF₄ (−5.9 kcal·mol⁻¹), GeCl₄ (−7.2 kcal·mol⁻¹), GeCl₂ (−5.2 kcal·mol⁻¹), and GeH₃ (−0.1 kcal·mol⁻¹). It is known that the isodesmic approach is considered a better strategy, enabling to obtain very accurate reaction parameters that avoid systematic errors due to the neglect of electron correlation at the G3//B3LYP level. Furthermore, the predicted isodesmic ΔH_f° would be no more accurate than the least accurate of the experimental values used to compute it; the free radical GeH₃ has the least accurate ΔH_f° value (2 kcal·mol⁻¹) among the observed data.

Discarding the species with measured heats of formation, there exist an overall tendency for atomization and isodesmic ΔH_f° values to increasingly differ with the presence of an increasing number of electronegative fluorine and chlorine atoms in tetra-substituted germanes. For instance, both approaches deviate following the sequence GeH₃F (4.0), GeH₃Cl (4.2), GeH₂F₂ (4.8), GeH₂FC1 (5.0), GeH₂Cl₂ (5.2), GeHF₃ (5.6), GeHClF₂ (5.8), GeHFC1₂ (6.0), GeHCl₃ (6.2), GeF₃Cl (6.5), GeF₂Cl₂ (6.8), GeCl₃F (7.0). The same argument applies to di-substituted species: GeH₂ (3.3), GeHF (4.1), GeHCl (4.3), GeF₂ (4.8), GeFC1 (5.0). On the contrary, this tendency results in the opposite for the mono- and tri-substituted germanes; such differences increase with decreasing number of electronegative atoms. For the first case, we have GeCl (−5.7), GeF (−5.9), and GeH (−6.7), whereas the tri-substituted species follow the sequence GeCl₃ (−3.8), GeCl₂F (−4.0), GeF₂Cl (−4.2), GeF₃

(−4.4), GeHCl₂ (−4.7), GeHFCI (−4.9), GeHF₂ (−5.2), GeH₂Cl (−5.7), GeH₂F (−5.9).

One possible way to verify that the predicted isodesmic heats of formation via the G3/B3LYP procedure have a correct trend is to plot ΔH_f° as a function of the degree of halogen substitutions and to contrast these predictions with the experimental data when available. It was pointed out in the study of Wang et al.¹⁶ that in the tetrahedral series GeH_nF_(4−n) and GeH_nCl_(4−n) ($n = 1, \dots, 4$) this thermochemical property decreases approximately linearly with the successive substitution of Ge–H bonds with Ge–F or Ge–Cl bonds. However, it is also feasible to represent the two series in a single plot that describes the overall effect of chlorine and fluorine atoms on ΔH_f° together with their joint influence. This description is provided by Figure 1. In order to systematize the monotonic variation of ΔH_f° values for all the 15 tetrahedral species, it is necessary to consider the relative effect of the halogen substitutions in the structure of germane molecule. From the analysis of the present molecular set, it is possible to establish a ranking for the number of chlorine and fluorine atoms present in the structure of GeH₄ that causes a decrement in its heat of formation:

$$H < Cl < 2Cl < F < 3Cl \quad (6)$$

Inequality 6 is deduced from the fact that there exist a tendency to incorporate more chlorine atoms in GeH₄ instead of fluorine, so that the value of ΔH_f° decreases and holds within the previously mentioned accuracy of 2 kcal·mol^{−1}. For instance, the substitution of GeH₄ ($\Delta H_f^\circ = 21.6$ kcal·mol^{−1}) by using a single Cl atom ($H < Cl$) leads to a smaller isodesmic ΔH_f° for GeH₃Cl of −13.0 kcal·mol^{−1}. According to the ranking of inequality 6, two Cl atoms can be present in the structure ($\Delta H_f^\circ(\text{GeH}_2\text{Cl}_2) = -48.7$ kcal·mol^{−1}) before substituting GeH₄ with one F ($\Delta H_f^\circ(\text{GeH}_3\text{F}) = -52.7$ kcal·mol^{−1}) so that ΔH_f° decreases monotonically ($2Cl < F$). Next, because $F < 3Cl$, F can be substituted with three Cl to achieve a lower value for the property, $\Delta H_f^\circ(\text{GeHCl}_3) = -84.3$ kcal·mol^{−1}. By applying again inequality 6, the next molecule in this decreasing series would be GeH₂FCI because $2Cl < F$, leading to $\Delta H_f^\circ = -89.7$ kcal·mol^{−1}. Because $F < 3Cl$, it follows GeCl₄ with $\Delta H_f^\circ = -118.4$ kcal·mol^{−1}. In order to continue ranking the fluorinated germanes, inequality 6 is further applied, leading to the following sequence: $\Delta H_f^\circ(\text{GeHFCl}_2) = -125.8$ kcal·mol^{−1} ($2Cl$

TABLE 4: Scaled Zero-Point Vibrational Energies and Total Energies at 0 K (in Hartrees) with Predicted and Experimental Enthalpies of Formation at 298 K (kcal·mol^{−1}) for Gaseous Species

| species | ZPE | $E_0(\text{G3//B3LYP})$ | isodesmic ΔH_f° | atomization ΔH_f° | Dif. ^a | Experimental ^b ΔH_f° |
|----------------------------------|---------|-------------------------|------------------------------|--------------------------------|-------------------|--|
| Ge | 0.00000 | −2076.37975 | | | | 88.7 |
| H | 0.00000 | −0.50092 | | | | 52.1 |
| F | 0.00000 | −99.68576 | | | | 19.0 |
| Cl | 0.00000 | −459.99251 | | | | 29.0 |
| F ₂ | 0.00241 | −199.87715 | | | | 0 |
| H ₂ | 0.01003 | −1.16712 | | | | 0 |
| HF | 0.00924 | −100.40284 | | | | −65.3 |
| HCl | 0.00662 | −460.65704 | | | | −22.1 |
| Cl ₂ | 0.00123 | −920.07605 | | | | 0 |
| GeCl | 0.00087 | −2536.52343 | 17.8 | 23.4 | −5.7 | |
| GeCl ₂ | 0.00206 | −2996.66899 | | −44.2 | | −39.0 |
| GeCl ₃ | 0.00353 | −3456.73415 | −65.0 | −61.2 | −3.8 | |
| GeCl ₄ | 0.00548 | −3916.87463 | | −125.6 | | −118.4 |
| GeF | 0.00159 | −2176.26153 | −20.7 | −14.9 | −5.9 | |
| GeF ₂ | 0.00370 | −2276.15946 | −125.0 | −129.8 | 4.8 | |
| GeF ₃ | 0.00639 | −2375.95445 | −184.5 | −180.1 | −4.4 | |
| GeF ₄ | 0.00973 | −2475.84532 | | −290.7 | | −284.8 |
| GeH | 0.00421 | −2076.98607 | 68.4 | 75.1 | −6.7 | |
| GeH ₂ | 0.01067 | −2077.59678 | 60.4 | 57.1 | 3.3 | |
| GeH ₂ Cl | 0.01484 | −2537.70133 | 9.0 | 14.7 | −5.7 | |
| GeH ₂ Cl ₂ | 0.01824 | −2997.84821 | −48.7 | −53.9 | 5.2 | |
| GeH ₂ F | 0.01564 | −2177.43880 | −29.1 | −23.2 | −5.9 | |
| GeH ₂ F ₂ | 0.02017 | −2277.33374 | −131.7 | −136.5 | 4.8 | |
| GeH ₃ | 0.01876 | −2078.18249 | | 54.6 | | 54.7 |
| GeH ₃ Cl | 0.02399 | −2538.33395 | −13.0 | −17.2 | 4.2 | |
| GeH ₃ F | 0.02490 | −2178.07390 | −52.7 | −56.7 | 4.0 | |
| GeH ₄ | 0.02910 | −2078.82207 | | 18.3 | | 21.6 |
| GeHCl | 0.00671 | −2537.12982 | 12.5 | 8.2 | 4.3 | |
| GeHCl ₂ | 0.00928 | −2997.21793 | −28.2 | −23.5 | −4.7 | |
| GeHCl ₃ | 0.01195 | −3457.36252 | −84.3 | −90.5 | 6.2 | |
| GeHF | 0.00742 | −2176.86943 | −26.9 | −31.0 | 4.1 | |
| GeHF ₂ | 0.01090 | −2276.69835 | −108.0 | −102.8 | −5.2 | |
| GeHF ₃ | 0.01498 | −2376.59401 | −210.9 | −216.5 | 5.6 | |
| GeHFCl ₂ | 0.01288 | −3097.10524 | −125.8 | −131.8 | 6.0 | |
| GeCl ₂ F | 0.00442 | −3096.47348 | −104.3 | −100.3 | −4.0 | |
| GeHFCI | 0.01010 | −2636.95720 | −67.5 | −62.6 | −4.9 | |
| GeF ₂ Cl ₂ | 0.00763 | −3196.33575 | −186.3 | −193.0 | 6.8 | |
| GeF ₃ Cl | 0.00870 | −2836.10255 | −242.9 | −249.4 | 6.5 | |
| GeH ₂ FCI | 0.01925 | −2637.59006 | −89.7 | −94.7 | 5.0 | |
| GeCl ₃ F | 0.00661 | −3556.61673 | −159.6 | −166.6 | 7.0 | |
| GeHClF ₂ | 0.01398 | −2736.84909 | −168.0 | −173.8 | 5.8 | |
| GeF ₂ Cl | 0.00547 | −2736.21372 | −144.3 | −140.1 | −4.2 | |
| GeFCI | 0.00294 | −2636.41279 | −81.1 | −86.1 | 5.0 | |

^a Diff.: isodesmic − atomization. ^b Reference 27.

< F), (GeH₂F₂) = −131.7 kcal·mol^{−1} (2Cl < F), (GeCl₃F) = −159.6 kcal·mol^{−1} (F < 3Cl), (GeHClF₂) = −168.0 kcal·mol^{−1} (2Cl < F), (GeF₂Cl₂) = −186.3 kcal·mol^{−1} (Cl < 2Cl), (GeHF₃) = −210.9 kcal·mol^{−1} (2Cl < F), (GeF₃Cl) = −242.9 kcal·mol^{−1} (H < Cl), (GeF₄) = −284.8 kcal·mol^{−1} (Cl < F). The same inequality as eq 6 applies to tri-substituted germane radicals (refer to Figure 1), whereas for the case of di-substituted and mono-substituted germanes, we have

$$H < Cl < F < 2Cl \quad (7)$$

It has to be noticed that although not reflected in the scales adopted by these graphs, the slope of the plot tends to be higher for the series with lower coordination numbers.

The calculation of BDE at 0 K together with the energy barrier heights for each TS structure is carried out by employing the total energies obtained through the G3//B3LYP level, and

TABLE 5: BDE and Energy Barrier Heights (kcal·mol^{−1}) for Most Probable Dissociation Channels at 0 K Calculated with G3//B3LYP Level^a

| dissociation channel | BDE | ΔE^\ddagger | geometry of TS |
|---|-------|---------------------|---|
| GeH → Ge + H | 66.1 | | |
| GeF → Ge + F | 123.0 | | |
| GeH ₂ → Ge + H ₂ | 31.3 | | |
| GeHF → Ge + HF | 54.5 | | |
| GeF ₂ → GeF + F | 133.1 | | |
| GeH ₃ → GeH + H ₂ | 18.4 | 36.5 | GeH ¹ :1.579, GeH ² :1.708, GeH ³ :1.615, H ² H ³ :1.425, H ² GeH ³ :50.7, H ¹ GeH ² :75.8, H ¹ GeH ³ :102.0 |
| GeH ₂ F → GeF + H ₂ | 6.4 | 40.2 | GeH ¹ :1.684, GeH ² :1.694, GeF:1.758, H ¹ H ² :1.699, H ¹ GeH ² :60.4, H ¹ GeF:104.8, H ² GeF:92.5 |
| GeHF ₂ → GeF ₂ + H | 23.8 | | |
| GeF ₃ → GeF ₂ + F | 68.5 | | |
| GeH ₄ → GeH ₂ + H ₂ | 36.5 | 49.7 | GeH ¹ :1.718, GeH ² :1.568, GeH ³ :1.540, GeH ⁴ :1.540, H ¹ H ² :1.250, H ¹ GeH ² :44.4, H ¹ GeH ³ :82.7, H ¹ GeH ⁴ :82.7, H ³ GeH ⁴ :109.8 |
| GeH ₃ F → GeHF + H ₂ | 23.4 | 56.6 | GeH ¹ :1.537, GeH ² :1.761, GeH ³ :1.550, GeF:1.746, H ² H ³ :1.384, H ¹ GeH ² :75.8, H ¹ GeH ³ :114.9, H ¹ GeF:108.0, H ² GeF:97.4, H ³ GeF:110.3, H ² GeH ³ :48.9 |
| GeH ₂ F ₂ → GeHF + HF | 38.6 | 62.2 | GeF ¹ :1.980, GeF ² :1.734, GeH ¹ :1.635, GeH ² :1.558, F ¹ H ¹ :1.285, F ¹ GeF ² :102.5, F ¹ GeH ¹ :40.2, F ¹ GeH ² :104.4, F ² GeH ¹ :117.3, F ² GeH ² :100.8, H ¹ GeH ² :130.7 |
| GeHF ₃ → GeF ₂ + HF | 19.9 | 58.8 | GeH:1.619, GeF ¹ :1.922, GeF ² :1.718, GeF ³ :1.718, HF ¹ :1.348, HGeF ¹ :43.7, HGeF ² :125.5, HGeF ³ :125.5, F ¹ GeF ² :104.3, F ¹ GeF ³ :104.3, F ² GeF ³ :101.7 |
| GeF ₄ → GeF ₃ + F | 128.7 | | |
| GeCl → Ge + Cl | 94.9 | | |
| GeHCl → Ge + HCl | 58.4 | | |
| GeCl ₂ → GeCl + Cl | 96.0 | | |
| GeH ₂ Cl → GeCl + H ₂ | 6.8 | 39.2 | GeH ¹ :1.662, GeH ² :1.681, GeCl:2.222, H ¹ H ² :1.668, H ¹ GeH ² :59.8, H ¹ GeCl:104.0, H ² GeCl:89.2 |
| GeHCl ₂ → GeCl ₂ + H | 30.1 | | |
| GeCl ₃ → GeCl ₂ + Cl | 45.6 | | |
| GeH ₃ Cl → GeHCl + H ₂ | 23.2 | 54.1 | GeH ¹ :1.536, GeH ² :1.742, GeH ³ :1.552, GeCl:2.188, H ² H ³ :1.354, H ¹ GeH ² :77.0, H ¹ GeH ³ :112.9, H ¹ GeCl:109.1, H ² GeCl:95.5, H ³ GeCl:111.0, H ² GeH ³ :48.1 |
| GeH ₂ Cl ₂ → GeHCl + HCl | 38.5 | 52.3 | GeCl ¹ :2.566, GeCl ² :2.170, GeH ¹ :1.645, GeH ² :1.551, Cl ¹ H ¹ :1.662, Cl ¹ GeCl ² :105.4, Cl ¹ GeH ¹ :39.3, Cl ¹ GeH ² :97.0, Cl ² GeH ¹ :119.3, Cl ² GeH ² :103.4, H ¹ GeH ² :123.3 |
| GeHCl ₃ → GeCl ₂ + HCl | 22.9 | 50.3 | GeH:1.619, GeCl ¹ :2.507, GeCl ² :2.156, GeCl ³ :2.156, HCl ¹ :1.749, HGeCl ¹ :43.9, HGeCl ² :123.6, HGeCl ³ :123.6, Cl ¹ GeCl ² :104.3, Cl ¹ GeCl ³ :104.3, Cl ² GeCl ³ :107.0 |
| GeCl ₄ → GeCl ₃ + Cl | 92.8 | | |
| GeHFCl ₂ → GeFCl + HCl | 22.2 | 52.2 | GeCl ¹ :2.488, GeH:1.617, GeF:1.723, GeCl ² :2.150, ClH:1.754, Cl ¹ GeH:44.6, FGeCl ¹ :102.3, FGeCl ² :104.7, Cl ² GeH:128.0, Cl ¹ GeCl ² :106.1 |
| GeF ₂ Cl ₂ → GeF ₂ + Cl ₂ | 62.9 | 77.7 | GeCl ¹ :3.341, GeCl ² :2.099, GeF ¹ :1.708, GeF ² :1.708, Cl ¹ Cl ² :2.834, Cl ¹ GeCl ² :57.5, Cl ¹ GeF ¹ :88.0, Cl ¹ GeF ² :88.0, Cl ² GeF ¹ :117.6, Cl ² GeF ² :117.6, F ¹ GeF ² :110.0 |
| GeF ₃ Cl → GeF ₃ + Cl | 97.6 | | |
| GeH ₂ FCl → GeHCl + HCl | 39.9 | 54.2 | GeH ¹ :1.645, GeCl:2.566, GeF:1.734, GeH ² :1.555, ClH:1.662, H ¹ GeCl: 39.3, FGeH ¹ :116.4, FGeH ² :102.2, H ² GeCl:98.4, H ¹ GeH ² :126.1 |
| GeCl ₃ F → GeCl ₂ F + Cl | 94.6 | | |
| GeHClF ₂ → GeF ₂ + HCl | 20.5 | 54.0 | GeCl:2.465, GeH:1.612, GeF ¹ :1.719, GeF ² :1.719, ClH:1.763, ClGeH:45.5, ClGeF ¹ :103.9, ClGeF ² :103.9, HGeF ¹ :125.3, HGeF ² :125.3, F ¹ GeF ² :102.9 |
| GeFCl → GeF + Cl | 99.6 | | |
| GeF ₂ Cl → GeF ₂ + Cl | 38.4 | | |
| GeFCl ₂ → GeFCl + Cl | 41.0 | | |
| GeHFCl → GeF + HCl | 25.6 | 29.3 | GeH:1.817, GeCl:2.581, GeF:1.748, HCl:1.591, HGeCl:37.6, HGeF:98.5, ClGeF:96.1 |

^a The geometries for the transitions states are at B3LYP/6-31G(2df,p).

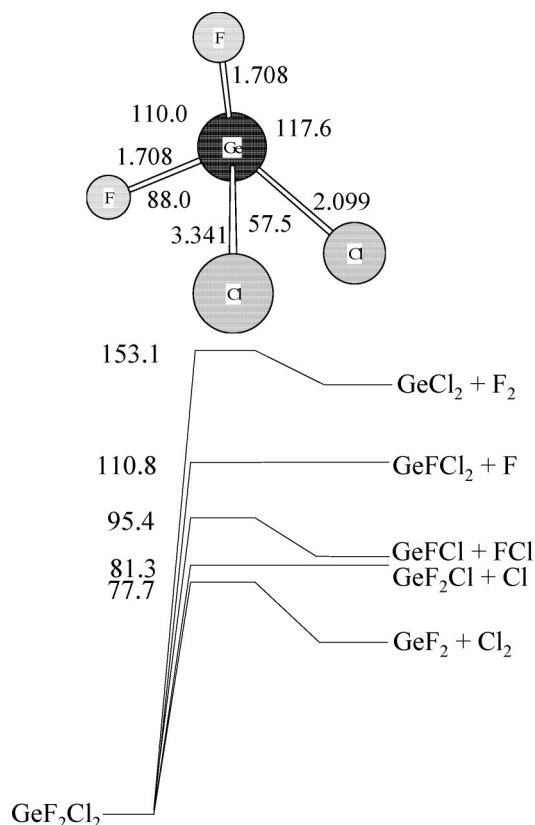


Figure 1. Dissociation channels for GeF_2Cl_2 .

these results enable to predict the most probable dissociation products for the thermal decomposition reactions of halogermanes. As it is the case for their silicon analogues, the molecular eliminations tend to be the most energetically favored dissociation channel over bond breakage for most of the germane species, although involving energy barriers. For instance, from the inspection of Table 5, it is expected that the free radical GeHF_2 with $\text{BDE} = 23.8 \text{ kcal}\cdot\text{mol}^{-1}$ produces a hydrogen atom upon heating instead of forming the molecule HF , having an associated $\Delta E^\ddagger = 38.3 \text{ kcal}\cdot\text{mol}^{-1}$ (not included in this table). Similarly, the thermal dissociation of GeF_3 ($\text{BDE} = 68.5 \text{ kcal}\cdot\text{mol}^{-1}$) and GeF_4 ($\text{BDE} = 128.7 \text{ kcal}\cdot\text{mol}^{-1}$) would generate a fluorine atom. Figures 2 and 3 include two examples of dissociation channels corresponding to GeH_4 and GeF_2Cl_2 , respectively, indicating the energy barriers that lead to the formation of the reaction products at 0 K and the molecular geometry of the most probable dissociation path. The dissociations of GeH_n species have been theoretically studied previously,²² and the value of $\Delta E^\ddagger = 49.7 \text{ kcal}\cdot\text{mol}^{-1}$ achieved here for the dissociation of GeH_4 generating the hydrogen molecule is in line with previous experimental findings ($\Delta E^\ddagger = 50\text{--}54 \text{ kcal}\cdot\text{mol}^{-1}$).^{23,24}

The analysis of these results suggests that for most tri- and tetra-substituted germanes, it seems easier to generate a halogen hydride as thermal dissociation product, that is, GeH_2F_2 , GeHF_3 , GeH_2Cl_2 , and GeHCl_3 , including the least electronegative atom in the gaseous hydride, when the structure is simultaneously substituted by different halogens, that is, GeHFC_2 , GeH_2FC_2 , GeHClF_2 , and GeHFC_2 . This is not valid when few halogen atoms compose the germane derivative, that is, GeH_4 , GeH_3F , GeH_3Cl , GeH_3 , GeH_2F , and GeH_2Cl , where the most probable dissociation channel produces the hydrogen molecule. For the case of many halogens involved in the structure, the atomic elimination of the least electronegative species appear to be the

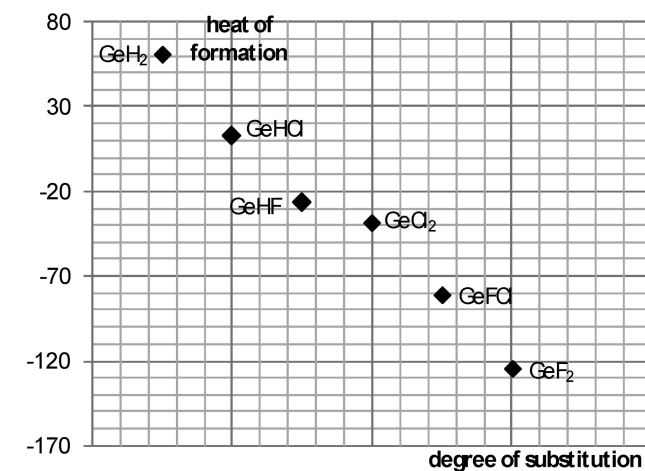
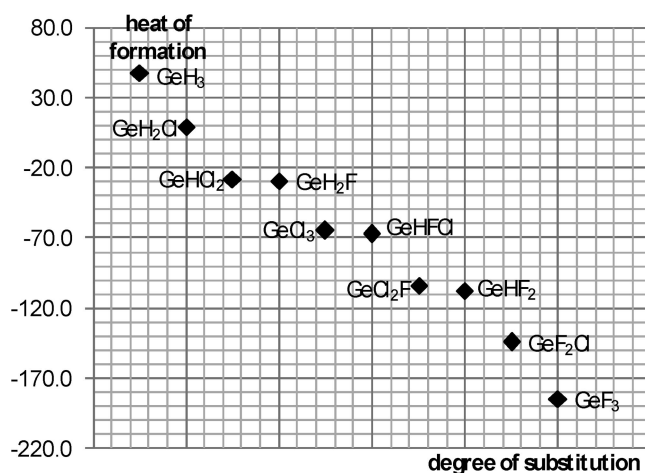
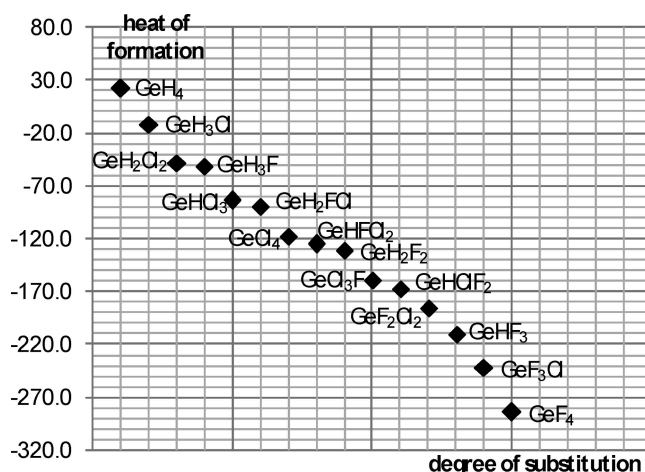


Figure 2. Isodesmic enthalpies of formation at the G3//B3LYP level for tetra-, tri- and di-substituted germanes.

most probable dissociation, that is, GeF_4 , GeCl_4 , GeF_3Cl , GeCl_3F , GeHF_2 , GeHCl_2 , GeF_3 , GeCl_3 , GeF_2Cl , and GeFCl_2 , with the exception of GeF_2Cl_2 that leads to the formation of chlorine molecule.

4. Conclusions

Presented systematic theoretical study characterized further the thermochemistry of halogen-substituted germanes of the type $\text{GeH}_x\text{F}_y\text{Cl}_z$, a molecular system for which few experimental data are available in the current literature. The analysis based on the G3//B3LYP method enabled to obtain the transition struc-

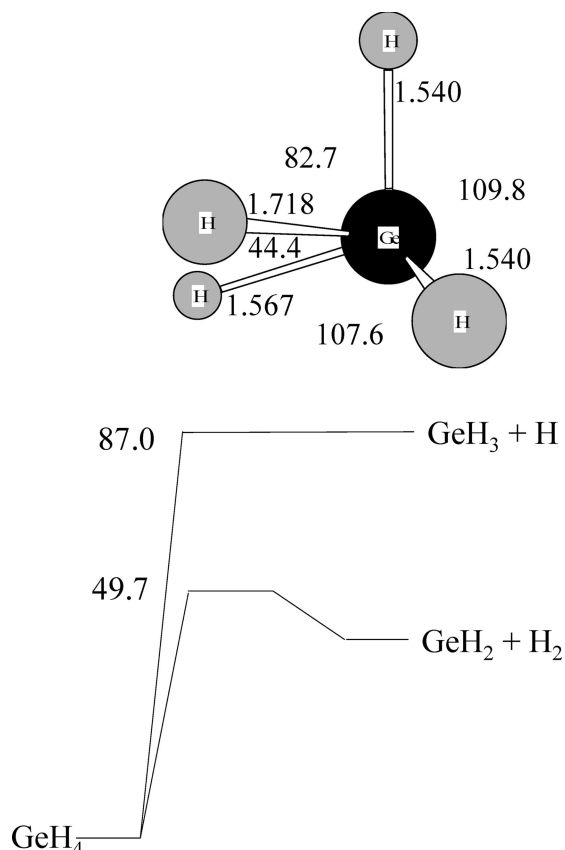


Figure 3. Dissociation channels for GeH_4 .

tures of germane derivatives and thus allowed the prediction of the most probable dissociation products at 0 K for their thermal decomposition reactions. On the other hand, the application of isodesmic reaction schemes lead to enthalpies of formation for all the gaseous molecular and fragment species, which were after that contrasted with previously reported results obtained by resorting to the atomization procedure.

Acknowledgment. This research project was supported by the Universidad Nacional de La Plata, the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CICPBA). C.J.C. also thanks the Agencia Nacional de Promoción Científica y Tecnológica (PICT 38444) and the Max Planck Institute for Biophysical Chemistry Göttingen (Karl Friedrich Bonhoeffer Institute) through the Partner Group for Chlorofluorocarbons in the Atmosphere.

References and Notes

(1) Gibson, S. T.; Greene, J. P.; Berkowitz, J. J. *Chem. Phys.* **1986**, 85, 4815.

- (2) McGrath, M. P.; Rowland, F. S. *J. Phys. Chem.* **1994**, 98, 4773.
- (3) O'Hare, P. A. G.; Curtiss, L. A. *J. Chem. Thermodynamics* **1995**, 27, 643.
- (4) Fajgar, R.; Jakoubková, M.; Bastl, Z.; Pola, J. *Appl. Surf. Sci.* **1995**, 86, 530.
- (5) Zhang, J. J.; Shimizu, K.; Hanna, J. *J. Non-Cryst. Solids* **2002**, 163, 299.
- (6) Gunn, S. R.; Green, L. G. *J. Phys. Chem.* **1961**, 65, 779.
- (7) Adams, G. P.; Charlu, T. V.; Margrave, J. L. *J. Chem. Eng. Data* **1970**, 15, 42.
- (8) Rau, H. *J. Chem. Thermodyn.* **1984**, 16, 287.
- (9) Uy, O. M.; Muenow, D. W.; Margrave, J. L. *J. Chem. Soc., Faraday Trans.* **1969**, 65, 1296.
- (10) Noble, P. N.; Walsh, R. *Int. J. Chem. Kinetics* **1983**, 15, 547.
- (11) Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **1999**, 110, 7650.
- (12) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, 94, 7221.
- (13) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, 109, 7764.
- (14) Curtiss, L. A.; Redfern, P. C.; Rassolov, V.; Kedziora, G.; Pople, J. A. *J. Chem. Phys.* **2001**, 114, 9287.
- (15) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, 106, 1063.
- (16) Wang, L.; Zhang, J. *J. Phys. Chem. A* **2004**, 108, 10346.
- (17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.05; Gaussian, Inc.: Wallingford, CT, 2003.
- (18) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **2001**, 114, 108.
- (19) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. *J. Comput. Chem.* **2001**, 22, 976.
- (20) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*; 2nd ed.; Gaussian Inc.: Pittsburgh, PA, 1996.
- (21) Jensen, F. *Introduction to Computational Chemistry*; John Wiley & Sons: Chichester, England, 1999, p 316.
- (22) Chambreau, S. D.; Zhang, J. *Chem. Phys. Lett.* **2002**, 351, 171.
- (23) Newman, C. G.; Dzarnoski, J.; Ring, M. A.; O'Neal, H. E. *Int. J. Chem. Kin.* **1980**, 12, 661.
- (24) Botintsev, V. N.; Zaslanko, I. S.; Mikhayev, V. S.; Smirnov, V. N. *Kinet. Catal.* **1985**, 26, 1297.
- (25) Bond Lengths and Angles in Gas-Phase Molecules. *Handbook of Chemistry and Physics*, 79th ed.; CRC: Boca Raton, FL, 1998; Vol. 9, p 18.
- (26) Caunt, A. D.; Mackle, H.; Sutton, L. E. *Trans. Faraday Soc.* **1951**, 47, 943.
- (27) NIST. <http://webbook.nist.gov/chemistry>, 2007.

JP8012267