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Heats of Formation for Cyclic C_4F_n, $n = 4-8$, and Their Cations

Charles W. Bauschlicher, Jr.*,[†] and Alessandra Ricca*,[‡]

Mail Stop 230-3, NASA Ames Research Center, Moffett Field, California 94035

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Heats of formation for cyclic C_4F_8 and $C_4F_8^+$ are determined at the G3MP2 level. The several decomposition pathways are investigated. The calculations confirm that $C_4F_8^+$ rearranges and its decomposition is responsible for both the $C_2F_4^+$ and $C_3F_5^+$ species observed in experiment. The heats of formation are presented for C_4F_n and $C_4F_n^+$, $n = 4-8$.

I. Introduction

Cyclic C_4F_8, denoted as c-C_4F_8, is used as a feedstock in the etching of silicon and silica.[1,2] This species is ionized and fragmented, and its fragments act as the etching agent as well as contributing to the formation of the protective polymer overlayer. Experiments[3,4] show that the ionization of C_4F_8 yields almost equal amounts of $C_2F_4^+$ and $C_3F_5^+$. CF_3^+ is also observed, but its concentration is about $^1/_4$ of that of $C_2F_4^+$ or $C_3F_5^+$. Neither $C_4F_7^+$ nor $C_4F_8^+$ is observed. The formation of $C_2F_4^+$ can be understood in terms of the ionized c-C_4F_8 dissociating to $C_2F_4^+$ and C_2F_4. The formation of $C_3F_5^+$ has been interpreted in terms of a rapid rearrangement of $C_4F_8^+$ followed by the loss of CF_3.

Previously, we have computed accurate thermochemical data for smaller fluorocarbons,[5,6] namely C_nF_m, where n is 3 or smaller, and CHF_n. We considered both the neutrals and the cations because both are involved in the etching process. These calculations were performed at the G3MP2 level of theory.[7] DFT methods, which are much less computationally intensive, are not consistently able to achieve an error of less than 2 kcal/mol and the G3 method,[8] which is more accurate than the G3MP2 approach, requires significantly greater computational resources. Since our previous calibration calculations[5,6] showed that the G3MP2 approach was accurate to ±2 kcal/mol for this class of compounds, the G3MP2 was an excellent compromise between computational cost and accuracy and was therefore the method of choice for these systems. In this work, we extend our calculations to C_4F_8 and its fragments and their corresponding cations.

II. Methods

The G3MP2 calculations were performed as presented by Pople and co-workers.[7] Calibration of this approach for the types of systems studied has been reported previously.[5,6] Since the G3MP2 approach can be quite expensive for species as large as c-C_4F_8, the rearrangement and dissociation of c-$C_4F_n^+$ were studied using the hybrid[9] B3LYP[10] approach in conjunction with the 6-31G(d) basis set.[11] This level of theory allowed us to follow the reaction path, using the internal reaction coordinate (IRC) approach,[12] to confirm that a transition state connected to the correct reactants and products. The G3MP2 approach was then applied to the more interesting parts of the potential. All calculations were performed using Gaussian 98.[13]

TABLE 1: G3MP2 Atomization Energies and Heats of Formation, in kcal/mol

	AE(0)	$\Delta H(0)$	$\Delta H(298)$
c-C_4F_8	1194.5	−366.8	−375.6
c-C_4F_7	1086.2	−277.0	−278.7
c-C_4F_6	1035.5	−244.7	−246.2
c-C_4F_5	919.1	−146.8	−147.4
c-C_4F_4	817.5	−63.7	−63.8
c-C_3F_6	865.3	−244.5	−246.1
C_3F_6($CF_2CF_2CF_2$, triplet)	826.3	−205.5	−206.6
c-$C_4F_8^+$	1191.1	−103.8	−104.2
c-$C_4F_7^+$	1108.3	−39.4	−39.6
c-$C_4F_6^+$	1032.5	17.9	18.1
c-$C_4F_5^+$	988.2	43.8	44.3
c-$C_4F_4^+$	880.7	132.8	133.8
$C_3F_6^+$($CF_2CF_2CF_2$)	883.7	−3.2	−2.8

III. Results and Discussion

In Table 1 we summarize the G3MP2 atomization energies at 0 K (AE(0)) and the heats of formation at 0 and 298 K, $\Delta H(0)$ and $\Delta H(298)$, respectively. To our knowledge, the only experimental value (−355.7 kcal/mol) for C_4F_8 is by Kolesov et al.[14] The difference between this value and our ΔH (298) value is far larger than the expected (±2 kcal/mol) errors in our results. Clearly, a new experimental determination would be desirable.

Our computed AE(0) results, along with our previously published[6] results, allow us to compute several interesting bond energies and reaction energies, and these are summarized in Table 2. We first consider the reaction energies, ignoring any barriers that might be present. For the neutral c-C_4F_8, the lowest energy process is to dissociate to two C_2F_4 molecules. Our computed value of 45.0 kcal/mol is in reasonable agreement with the experimental value of 49.9 ± 1.7 kcal/mol determined by Butler.[15] It actually requires less energy to pull a CF_2 out of C_4F_8 than to remove a F atom. For c-$C_4F_8^+$, dissociating to $C_2F_4^+$ and C_2F_4 is even more favorable than the analogous reaction for the neutral. However, the formation of $C_3F_5^+$ and CF_3 requires even less energy, but clearly requires some rearrangement of c-$C_4F_8^+$ before dissociation. As found for the neutral, the breaking of the C−F bond is the highest energy process of those studied for c-$C_4F_8^+$.

The results for c-C_4F_8 and c-$C_4F_8^+$ show that breaking C−C bonds is much more favorable than elimination of an F atom. Thus, the chemistry should be dominated by the smaller species that we have studied previously. However, there can be considerable energy in a chemical vapor deposition (CVD) reactor and thus some loss of F might occur; therefore we consider c-C_4F_n species with less than eight F atoms.

[†] Space Technology Division, NASA.

[‡] ELORET Corporation.

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TABLE 2: Selected Bond Energies for $C_4F_n^+$, in kcal/mol

reaction	bond energy	neutral analog
$c\text{-}C_4F_8^+ \rightarrow C_2F_4^+ + C_2F_4$	17.4	45.0
$c\text{-}C_4F_8^+ \rightarrow c\text{-}C_4F_7^+ + F$	82.8	108.3
$c\text{-}C_4F_8^+ \rightarrow C_3F_6^+ + CF_2$	53.4	75.1[a]
$c\text{-}C_4F_8^+ \rightarrow CF_2^+ + C_3F_6$	78.2	
$c\text{-}C_4F_8^+ \rightarrow C_3F_5^+ + CF_3$	2.6	81.9
$c\text{-}C_4F_8^+ \rightarrow CF_3^+ + C_3F_5$	30.8	
$c\text{-}C_4F_7^+ \rightarrow c\text{-}C_4F_6^+ + F$	75.8	50.7
$c\text{-}C_4F_7^+ \rightarrow C_2F_4^+ + C_2F_3$	60.5	62.7
$c\text{-}C_4F_7^+ \rightarrow C_2F_3^+ + C_2F_4$	60.2	
$c\text{-}C_4F_7^+ \rightarrow C_3F_5^+ + CF_2$	2.4	56.2
$c\text{-}C_4F_7^+ \rightarrow CF_2^+ + C_3F_5$	84.8	
$c\text{-}C_4F_6^+ \rightarrow c\text{-}C_4F_5^+ + F$	44.3	116.4
$c\text{-}C_4F_6^+ \rightarrow C_2F_4^+ + C_2F_2$	56.2	83.4
$c\text{-}C_4F_6^+ \rightarrow C_2F_2^+ + C_2F_4$	80.9	
$c\text{-}C_4F_6^+ \rightarrow C_2F_3^+ + C_2F_3$	110.3	137.9
$c\text{-}C_4F_6^+ \rightarrow C_3F_4^+ + CF_2$	43.3	65.6
$c\text{-}C_4F_6^+ \rightarrow C_3F_3^+ + CF_3$	28.0	101.0
$c\text{-}C_4F_6^+ \rightarrow C_3F_5^+ + CF$	48.9	127.8
$c\text{-}C_4F_5^+ \rightarrow c\text{-}C_4F_4^+ + F$	107.5	101.6
$c\text{-}C_4F_5^+ \rightarrow C_2F_3^+ + C_2F_2$	137.5	93.0
$c\text{-}C_4F_5^+ \rightarrow C_2F_2^+ + C_2F_3$	162.5	
$c\text{-}C_4F_5^+ \rightarrow C_3F_3^+ + CF_2$	66.3	67.3
$c\text{-}C_4F_5^+ \rightarrow CF^+ + C_3F_4$	93.3	71.5
$c\text{-}C_4F_4^+ \rightarrow C_2F_2^+ + C_2F_2$	126.5	62.8

[a] For the neutral, C_3F_6 is the cyclic form.

For $c\text{-}C_4F_7$ and $c\text{-}C_4F_7^+$ the loss of an F atom is much more competitive with dividing into two C_2 subunits than for C_4F_8 and its cation, but the rearrangement into $C_3F_5^+$ and CF_2 is very favorable for the cation. The C−F bonds are weaker for C_4F_7 and $C_4F_7^+$ than for C_4F_8 and $C_4F_8^+$ because the loss of the second F allows the formation of a C═C double bond.

An inspection of the remaining reactions suggests that, overall, there is always a path that breaks a C−C bond, to form two smaller species, that is more favorable than the loss of an F atom, provided that these processes, especially those that require a rearrangement, do not have high barriers. Therefore, we consider some of the dissociation mechanisms in more detail.

The first process that we consider in detail is the ionization and decomposition of $c\text{-}C_4F_8$. As noted above, we use the B3LYP/6-31G(d) level of theory since its lower computational cost than the G3MP2 approach allows us to explore more of the surface and we are able to follow the reaction path to determine the reactants and products associated with a given transition state. The C_4 ring structure in $c\text{-}C_4F_8$ is nonplanar, with one C about 0.4 Å out of the plane of the other three carbons. The vertical ionization potential is 11.24 eV. The equilibrium $C_4F_8^+$ structure is 11.0 kcal/mol lower in energy, as the C−C bonds increase from 1.54 Å in the neutral to 1.65 Å in the cation; see Figures 1 and 2. We note that we found two structures for $C_4F_8^+$, one where all four C−C bond lengths are equal, as in the neutral, and a second structure, where three of the C−C bonds are short (1.56−1.58 Å) and the fourth is long (2.08 Å). This second structure is about 1 kcal/mol above the more symmetric form of C_4F_8.

With a barrier of only 9 kcal/mol, the ring will open and convert to the trans $C_4F_8^+$ structure by way of transition state TS1. The trans open structure is 1.7 kcal/mol below the ring. The 1,3 F migration to form the 1-ene structure has a barrier (TS2) of 10.9 kcal/mol and is exothermic by 21.4 kcal/mol. The trans structure can also break the central C−C bond yielding $C_2F_4^+ + C_2F_4$. We have located the transition state (TS3) for this process and it is below the products. TS3 is the transition state between the trans and the electrostatically bound $C_2F_4^+\cdots C_2F_4$ complex; thus, there is no barrier in excess of the reaction endothermicity, as is typical for cations. The $C_2F_4^+ + C_2F_4$ asymptote is 19.6 kcal/mol above the ring; this is only 8.6 kcal/mol above the $C_4F_8^+$ produced by a vertical ionization process. Therefore, it is not surprising that the ionization of C_4F_8 yields $C_2F_4^+$ as one of its principal ion products.

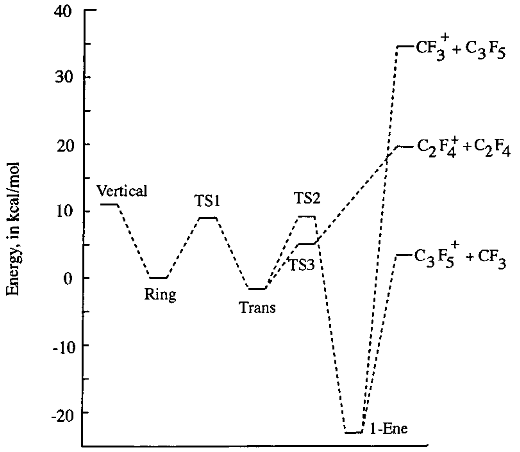

Figure 1. Relative energetics associated with the rearrangement and dissociation of $C_4F_8^+$.

TABLE 3: A Comparison of the Relative Energetics, in kcal/mol, for the Structures of $C_4F_8^+$ Using the G3MP2 and B3LYP/6-31G(d) Approaches (The Zero of Energy Is the Ring Structure)

species	G3MP2	B3LYP
TS1		9.0
trans	−4.6	−1.7
TS2[a]	9.8	9.2
1-ene	−25.7	−23.0
$C_2F_4^+ + C_2F_4$	17.4	19.6
$C_4F_7^+ + F$	82.8	91.7
$C_3F_6^+(CF_2CF_2CF_2^+) + CF_2$	53.4	
$C_3F_5^+ + CF_3$	2.6	3.4
$CF_3^+ + C_3F_5$	30.8	34.5

[a] There is no higher order correction included in either the transition state or the ring for this case.

The 1-ene is more stable than either the ring or the trans structures, and it requires only 29.4 kcal/mol to break the terminal C−C single bond, forming the $C_3F_5^+ + CF_3$, which is consistent with the observation of $C_3F_5^+$ in experiment. This asymptote is only 3.4 kcal/mol above the ring structure and is below the “vertical” $C_4F_8^+$. We have not tried to locate the transition state for the 1-ene to $C_3F_5^+ + CF_3$ fragmentation, because it is expected to be below the products as found for the $C_2F_4^+ + C_2F_4$ asymptote. The other possible product from fragmentation of the 1-ene is $CF_3^+ + C_3F_5$; this is more endothermic than either the $C_2F_4^+ + C_2F_4$ or $C_3F_5^+ + CF_3$ asymptotes (see Figure 1), and therefore it is not surprising that CF_3^+ has a much smaller concentration than $C_3F_5^+$ and $C_2F_4^+$. In fact, we cannot rule out the possibility that CF_3^+ comes from a secondary process that does not directly involve $C_4F_8^+$.

While the B3LYP/6-31G(d) level allows us to explore large parts of the surface in a cost-effective manner, it might not have the desired accuracy. Therefore, it is necessary to calibrate the energetics with higher levels of theory; we study the interesting parts of the surface at the G3MP2 level, and these results are compared with the B3LYP/6-31G(d) results in Table 3. Excluding the high energy loss of F, the agreement between the B3LYP and G3MP2 results is very good, suggesting that the B3LYP has identified the most interesting parts of the $C_4F_8^+$ rearrangement surface.

As for the cation, we were unable to find a direct path for the dissociation of the neutral $c\text{-}C_4F_8$ into two C_2F_4 molecules. As discussed by Yokoyama et al.,[17] a ring opening followed

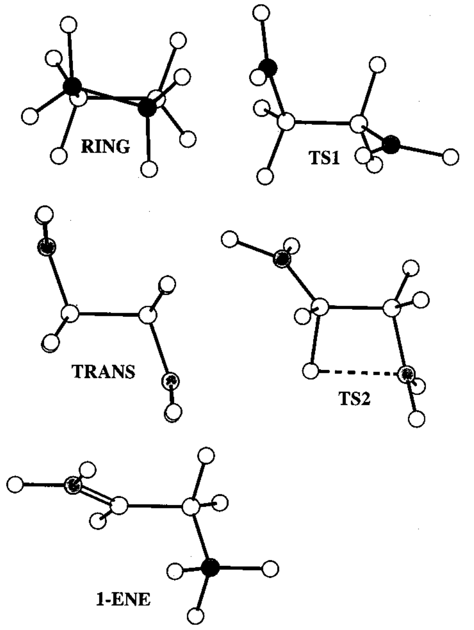

Figure 2. Structures associated with the rearrangement of $C_4F_8^+$. Two of the carbon atoms are shaded gray to help illustrate the rearrangement processes.

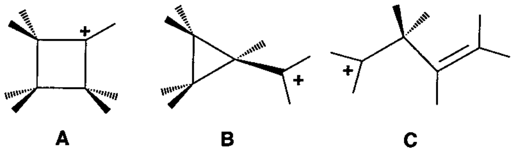

Figure 3. Known structures of $C_4H_7^+$: (A) the cyclobutyl cation, (B) the cyclopropylmethyl cation, and (C) the homoallylic cation.

by the breaking of the central C−C bond appears to be the C_4F_8 dissociation mechanism. At the B3LYP level, we computed barriers of 85.9 and 90.9 kcal/mol for the two steps. This is much higher than the activation energy of 74.3 ± 0.8 kcal/mol reported by Butler.[15] It is possible that we did not find the lowest transition state, or that our level of theory is not as accurate for the barrier heights as we assume, or that the experimental value is too low. The second barrier is computed to be 93.8 kcal/mol at the G3MP2 level, which appears to argue against a major problem with the level of theory. The most conservative conclusion is that our computed barriers could be too large. We should note that the transition state structure that we find for the breaking of the C−C bond looks more like the transition state for an F atom transfer to form the 1-ene, but the reaction path shows that it connects to the $C_2F_4 + C_2F_4$ product, and we are unable to find another transition state.

It is interesting to compare the chemistry of the fluorocyclobutyl cation, c-$C_4F_7^+$, with that of the cyclobutyl cation, c-$C_4H_7^+$. It is known experimentally that the cyclobutyl cation (A) rearranges to form a cyclopropylmethyl cation (B) which can open to form a homoallylic cation (C), as shown in Figure 3. Replacing the hydrogens by fluorines appears to affect the stability of the cations. At the B3LYP level of theory the fluoropropylmethyl cation is not stable and its geometry optimization converges to the geometry of the fluorohomoallylic cation. The repulsion between the fluorine atoms is much greater than for the hydrogen atoms and this leads to the opening of the three-membered ring. The fluorocyclobutyl cation is stable due to the larger size of the ring and its opening leads directly to the fluorohomoallylic cation. At the G3MP2 level, the ring opening of the fluorocyclobutyl cation is exothermic by 23.1 kcal/mol and has a barrier of 4.1 kcal/mol. The fluorohomoallylic cation can dissociate to form $C_3F_5^+ + CF_2$ or $C_3F_5 + CF_2^+$. The formation of $C_3F_5^+ + CF_2$ is endothermic by 25.5 kcal/mol while that of $C_3F_5 + CF_2^+$ is endothermic by 107.9 kcal/mol. Clearly, as soon as a fluorine is removed from c-$C_4F_8^+$, the ring opening to form $C_3F_5^+ + CF_2$ occurs very easily.

The heat capacity, entropy, and temperature dependence of the heat of formation are computed for the temperature range of 300−4000 K using a rigid rotor/harmonic oscillator approximation. The scaled HF frequencies are used in these calculations. These results are fit in two temperature ranges, 300−1000 and 1000−4000 K using the Chemkin[16] fitting program and following their constrained three-step procedure. The parameters obtained from the resulting fits can be found on the web.[18]

IV. Conclusions

We have computed the heats of formation of C_4F_n and $C_4F_n^+$, for $n = 4-8$, at the G3MP2 level of theory. The heat capacity, entropy, and temperature dependence of the heat of formation are fit to 14 parameters that can be found on the Web.[18] In addition, we have considered the mechanism by which some of the species fragment. The calculations show that the rearrangement of $C_4F_8^+$, $C_4F_7^+$, and $C_4F_6^+$ have low barriers, so that the most stable fragmentation products can be formed. This work suggests that fragmentation by breaking of C−C bonds is more favorable than the loss of a fluorine atoms.

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