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Direct C−C Bond Breaking in the Reaction of O(^{3}P) with Flouropolymers in Low Earth Orbit

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Spacecraft flying in low Earth orbit (LEO) are exposed to a harsh environment which includes frequent bombardment by fast atomic oxygen (AO) and ultraviolet (UV) radiation. As a result, many spacecraft surface materials are severely eroded. In the case of fluoropolymers, a controversy exists whether AO or UV or AO/UV synergy is responsible for the degradation. In this study, with the use of ab initio calculations, we address the question whether the most abundant species in LEO, viz., atomic oxygen in its ground state, O(^{3}P), alone can cause the degradation in fluoropolymer materials. The smallest fluorocarbons C_NF_{2N+2} (N = 2, 3, 5) serve as models of fluoropolymers. Since electronegativity of fluorine seems to preclude F-abstraction by O(^{3}P), we concentrate on direct O(^{3}P) attacks on carbon−carbon bonds. For the case of fluoroethane (N = 2), we explore the triplet potential energy surface of the following reaction: $O(^3P) + CF_3{-}CF_3 \rightarrow {}^{\bullet}O{-}CF_3 + {}^{\bullet}CF_3$. Analogous reactions, where O(^{3}P) attacks a central carbon atom, are studied for the higher fluorocarbons. Results obtained using the Hartree−Fock method and density functional theory are reported. We conclude that O(^{3}P) species in LEO possesses enough translational energy to degrade fluorocarbon materials.

Introduction

The international space station (ISS), the space shuttle, and many other satellites circumnavigate the Earth at altitudes of 180−650 km above its surface, in low Earth orbit (LEO). At these altitudes the largest component of the atmosphere[1] is atomic oxygen (AO). This highly reactive species is formed when oxygen molecules are split by short wavelength solar ultraviolet radiation in an environment where the mean free path is sufficiently large that the probability of recombination is negligible. The O-atom number density at space shuttle altitudes is typically on the order of 10^8 cm^{-3}. A body orbiting relative to this density in LEO, traveling at 7.2 km/s, experiences a flux of 10^{14} O atoms/(cm^2 s). Oxygen atoms hit a spacecraft surface with mean impact energies of approximately 4.5 eV (103.8 kcal/mol) with the energy spread (full width at half-maximum) of about 50 kcal/mol.[2] Significant changes in the condition of spacecraft surface materials can occur due to exposure to the LEO environment. In particular, organic polymers in LEO can lose weight and, depending on thickness, may even be eroded away completely.[3−10]

"Concern over the degradation of materials by atomic oxygen sparked a huge effort, involving both space- and ground-based studies, that has been aimed at the identification, understanding, and mitigation of problems caused by atomic oxygen in LEO," according to T. K. Minton and D. J. Garton[11] (see also refs 2−10 and 12−27). Nevertheless, to date there is no clear understanding of elementary reaction mechanisms for the interaction of AO with surface materials. In particular, this remark holds true for flouropolymers, the subject of this paper.

Spacecraft flying in LEO require thermal control blankets which provide protection from solar heating.[8] One of the materials used extensively for spacecraft thermal control is FEP (fluorinated ethylene propylene) Teflon, which has its second (unexposed) surface metalized with silver or aluminum. The spacecraft thermal control is achieved by means of high reflection of incident solar energy (which has an intensity peak near 0.55 μm) and high thermal emittance of FEP Teflon at spacecraft temperatures (which radiate near 10 μm). FEP Teflon, however, is susceptible to erosion, cracking, and subsequent mechanical failure in LEO.[21] The recession of the polymer surface due to LEO exposure causes a reduction in thermal emittance.

One of the difficulties in determining whether FEP Teflon will survive during a mission is the wide disparity of erosion rates observed for this material in space and in ground-based facilities.[21] (The erosion rates observed in ground-based facilities generally greatly exceed those observed in space.) Each environment contains different concentrations of oxygen atoms and ions, and different levels of vacuum ultraviolet (UV) radiation in addition to parameters such as the energy of arriving species and temperature. These variations make it difficult to determine what is causing the observed differences in erosion rates.

Differently from LEO environment where the oxygen atoms are neutral, O$^+$ ions are often present in significant portions during ground-based experimental simulations. It is then not clear how much each species is contributing to the erosion.

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Another important question that is unanswered to date is how the fluoropolymer erosion rates depend on AO incident energy. It has often been concluded by experimentalists (see ref 18, for instance) that exposure to AO alone does not cause erosion in fluoropolymers, but in all of those cases, however, the incident AO energy was significantly lower than that observed in LEO.

Some investigators have suggested that high erosion rates of the FEP Teflon observed in low-energy AO ground-based laboratory facilities may be due to significant UV exposure (at higher levels than occur in space).[22] Indeed, there is evidence that exposure to UV could produce chain scission radicals in FEP Teflon (while the C−F bond scission products are not observed).[23,24] These radicals could react with atomic oxygen forming volatile products, which would result in material mass loss. Tests conducted at fast AO beam facilities with simultaneous exposure to UV where incident AO energy was ∼5[19] and ∼30 eV[26] showed erosion rates higher than those observed in space by one and 3 orders of magnitude, respectively. At a facility[18] where it was possible to expose materials to a relatively fast (∼2.2 eV) energy AO beam without UV presence, the erosion rate was very low and close to that observed in some space flights (the erosion rates of FEP Teflon measured in space experiments can also differ significantly[7]) but greatly increased when UV was added. In addition, ground-simulation test results showed that FEP Teflon, exposed to UV radiation only, suffered no thickness loss and possessed a hard embrittled surface layer (attributed to cross-linking) that was absent in the samples exposed to UV and AO simultaneously.[22,25]

On the other hand, we have used plasmas, and a variety of Faraday cages that can shield or allow UV radiation exposure of fluoropolymers, to explore possible UV synergistic effects with atomic oxygen.[21] This was accomplished by using either conductive boxes with tortuous path openings to the plasma or conductive boxes with screen openings in the lid. We have found that atomic oxygen alone can cause erosion of fluoropolymers and observed no UV synergistic effect at LEO UV levels.[21] (At much higher intensity levels than those characteristic of LEO, a UV contribution to broken bonds and degradation might well be enhanced.)

Despite all the experimental work, to date there is no clear understanding of fluoropolymer erosion mechanisms in LEO, and the use of ground-based simulation facilities for some space materials qualification could lead to erroneous conclusions. Many factors are at play during experimental simulations, and it is often difficult if not impossible to investigate their separate contributions to the erosion yield of fluoropolymers. On the other hand, use of computational tools offers an advantage of dealing with one particular chemical species at a time and investigating one particular reaction at a time without having to worry about the background UV presence. Therefore, in this work we address the problem computationally seeking to answer the seemingly obvious question, whether the most abundant chemical species in LEO, viz., atomic oxygen in its ground state, $O(^3P)$, with incident energies of approximately 4.5 eV and with neither UV nor O^+ presence could cause the degradation in fluoropolymer materials. An answer to this isolated question will tend to clarify our understanding of the problem of fluoropolymers degradation in LEO.

Poly(tetrafluoroethylene) (PTFE) as well as fragments of the FEP Teflon polymer chain has a structure similar to that of polyethylene, differing only by substitution of fluorine atoms for hydrogen atoms. The electronegativity of fluorine would seem to preclude an abstraction mechanism similar to that which occurs in the case of hydrogen. On the other hand, the results of our previous work on polyethylene suggest the possibility that chain breaking by $O(^3P)$ could be a contributing cause of degradation.[27] We use the phrase "chain breaking" as in our previous paper[27] to mean a single attack of $O(^3P)$ directly on a polymer backbone, resulting in a broken carbon−carbon bond, and thus, a broken polymer chain. Such chain breaking, if it should occur, would represent a new and efficient mechanism to explain polymer degradation.

Computational Details

Quantum mechanical calculations were carried out with the MULLIKEN[28] program package. The traditional Hartree−Fock (HF)[29−31] ab initio method was used. In addition, the MB3LYP DFT method (see ref 32) available within the MULLIKEN program package was used.

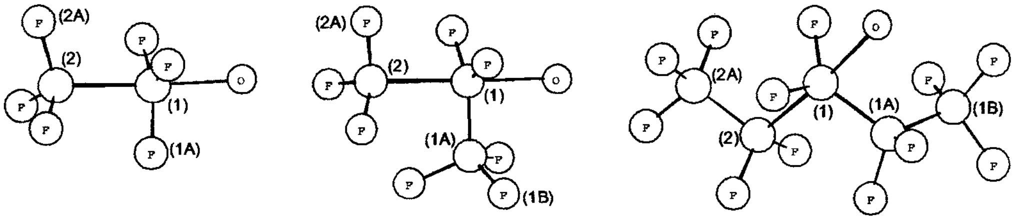
In our previous paper dealing with hydrocarbons,[27] having structures related to the molecules studied here, we carried out a variety of numerical experiments that allow us now to be more efficient in this work. There we used a variety of accurate computational methods, including MP2, G1, G2, and CBS-QB3 type calculations. We also explored the effect of adding extensive basis sets. We found that the more accurate computational methods, using extended basis sets, gave results for related molecules that were reliably predicted by a combination of Hartree−Fock (HF) and DFT calculations employing moderate basis sets (3-21G and 6-31+G(d,p)). To be precise, we found that the HF and DFT methods (with moderate bases) would always bracket, from above and below, respectively, the most accurate results. Therefore in this paper we find it to be efficient to restrict ourselves, in the study of these structure related compounds, to calculations of HF and DFT type. The conclusions we draw will only depend on the assumption that here, too, the most accurate energies are bracketed by the two types of calculation, as before.

For all the calculations Gaussian-type basis sets were employed (see Tables 1 and 2). The explanation and abbreviations of the basis sets can be found in ref 33.

The geometries of all reactants, products, and transition states have been optimized at the levels of theory mentioned above. For all the triplet species, i.e., the transition states and $O(^3P)$, an unrestricted wave function was implemented and examined for spin contamination, which was found to be inconsequential. No symmetry constraints were imposed for optimizations of the transition states. Vibrational frequencies have been calculated using the same approximation to characterize the nature of stationary points and to determine zero-point energy (ZPE) corrections. All the stationary points have been positively identified for either minimum energy with no imaginary frequencies or for transition states with one imaginary frequency. In the cases where it was not clear (from the analysis of vibrational modes) whether a transition structure is connecting the desired reactants and products, intrinsic reaction coordinate (IRC) analysis was carried out in order to confirm that.

In the study we report here, a question arises of whether results of small molecules relate to analogous results on larger molecules, and molecules attached to surfaces. On qualitative grounds, we would expect the effects studied to be "near sighted", i.e., to be localized to a small region of the target molecule. From a quantitative point of view, previous calculations show, for example, in hydrocarbon chains, that chain-breaking activation energy becomes rather constant as a function of chain length. This effect is reflected in the results of Table 2 in this paper, wherein the chain-breaking activation energy is the same for C_3F_8 and C_5F_{12}. Concerning surface effects, again

TABLE 1: Structural Parameters (Ångstroms and Degrees) for the Transition States of O(^{3}P) Reactions with C_2F_6, C_3F_8, and C_5F_{12}, Where in the Case of C_3F_8 and C_5F_{12} the Oxygen Atom Attacks the Center Carbon Atom[a]



model molecule	theory[a,b]	r_{O-1}	r_{1-2}	a_{O-1-2}	a_{O-1-1A}	a_{1-2-2A}	$d_{2-1-1A-1B}$	$d_{O-1-1A-1B}$
C_2F_6	HF/3-21G	2.914	2.746	174.2	81.9	102.7		
C_3F_8		2.974	2.725	175.5	79.8	93.5	−122.3	61.1
C_5F_{12}								
C_2F_6	MB3LYP/6-31+G(d,p)	1.765	1.920	176.7	92.5	107.8		
C_3F_8		1.830	2.011	173.4	85.2	102.6	−103.3	71.0
C_5F_{12}		1.873	2.066	172.8	84.7	109.3	99.2	−74.6

[a] The HF results fail to converge for C_5F_{12}. [b] See refs 29−31 for HF and ref 32 for MB3LYP methods and formalism. [c] See ref 33 for definitions and nomenclature of basis sets.

TABLE 2: Total Energies (au) and Activation Barriers (kcal/mol) for the Transition States of O(^{3}P) Reactions with C_2F_6, C_3F_8, and C_5F_{12}, Where in the Case of C_3F_8 and C_5F_{12} the Oxygen Atom Attacks the Center Carbon Atom[a]

model molecule	theory[b,c]	E_{TS}	E_{model}	E_O	E_a
C_2F_6	HF/3-21G	−742.98149	−668.74490	−74.39366	98.6
	HF/3-21G (0 K)	−742.95561	−668.71264	−74.39366	94.6
C_3F_8	HF/3-21G	−978.47485	−904.20508	−74.39366	77.7
	HF/3-21G (0 K)	−978.43497	−904.15945	−74.39366	74.1
C_5F_{12}	HF/3-21G				
	HF/3-21G (0 K)				
C_2F_6	MB3LYP/6-31+G(d,p)	−749.95470	−675.04639	−75.03772	81.2
	MB3LYP/6-31+G(d,p) (0 K)	−749.92822	−675.01763	−75.03772	79.8
C_3F_8	MB3LYP/6-31+G(d,p)	−987.67601	−912.74698	−75.03772	68.2
	MB3LYP/6-31+G(d,p) (0 K)	−987.63678	−912.70611	−75.03772	67.2
C_5F_{12}	MB3LYP/6-31+G(d,p)	−1463.07482	−1388.14563	−75.03772	68.1
	MB3LYP/6-31+G(d,p) (0 K)	−1463.01145	−1388.08061	−75.03772	67.1

[a] The HF results fail to converge for C_5F_{12}. [b] See refs 29−31 for HF and ref 32 for MB3LYP methods and formalism. [c] See ref 33 for definitions and nomenclature of basis sets.

because of "nearsightedness" we assume near neighbor polymer molecules would not play a significant role in the results of an atom approaching a given polymer molecule. We have not quantified this, but one would expect that the potential energy barriers in question would be dominated by the electron clouds of the individual target molecules, as opposed to the statistical collection of molecules which form the surface.

Computational Results

Chain-breaking reactions of O(^{3}P) with C_2F_6, C_3F_8, and C_5F_{12}, where in the case of C_3F_8 and C_5F_{12}, O(^{3}P) attacks the central carbon atom, were studied in this work. The key geometric parameters computed by HF and DFT methods of the transition state structures for these reactions are presented in Table 1. The classical and vibrational adiabatic (zero-point corrected) reaction barriers obtained by HF and DFT methods are presented in Table 2. As is the case with the alkane analogues that we studied previously,[27] there is no experimental evidence that would suggest any information about the structures of the transition states or the energy barriers associated with these reactions.

The appearance of the transition state structure for O(^{3}P) reaction with C_2F_6, is similar to that of O(^{3}P) reaction with C_2H_6. The oxygen atom is almost aligned with the two carbon atoms. C1 and three fluorine atoms attached to it lie in a plane, while C2 and its three fluorine atoms form a pyramidal shape.

Turning our attention to HF results only, a major difference between the hydrogenated and fluorinated analogues is observed for the partially formed (O−C1) and partially broken (C1−C2) bonds of the transition state structure. The O−C1 bond length is 2.914 and 2.005 Å for C_2F_6 and C_2H_6 cases, respectively. Also, the C1−C2 bond length is 2.746 and 2.372 Å for the same respective cases.

Considering the results of MB3LYP DFT only, the bond length values calculated for C_2F_6 are very similar to those in the case of C_2H_6, i.e., 1.765 Å for the O−C1 bond and 1.920 Å for the C1−C2 bond.

The fluorinated case differs from the hydrogenated case in two ways. First, highly electronegative fluorine atoms withdraw some electron density from the carbon atom that is being attacked by oxygen and, therefore, the oxygen atom would have to be slightly closer to the carbon atom in order for a bonding interaction to take place. Second, there is a repulsive interaction between highly electronegative fluorine atoms and the oxygen atom. These two interactions have opposite effects on the bond lengths. The latter effect seems to be strongly favored by the HF method, which does not account for electron correlation. These results emphasize that electron correlation is especially important in complex systems, such as transition states that involve bond breaking and forming. Since DFT methods do account for electron correlation the results obtained by the use of these methods are likely to be more trustworthy in this case.

The two effects described above offer a possible explanation for the high activation energy for the fluorinated case, i.e., 94.6 and 79.8 kcal/mol as obtained with the use of HF and DFT methods, respectively. On the basis of our previous experience[27] with C_2H_6, we believe that these two numbers are high and low bounds for the activation energy of the reaction.

The transition state structures for the reactions of $O(^3P)$ with C_3F_8 and C_5F_{12}, obtained with the use of the MB3LYP DFT method, are similar to what we would expect on the basis of our experience with the $O(^3P)$ reactions with alkanes.[27] The bonds that are being broken and formed are slightly longer than in the C_2F_6 case, and the O−C1−C2 angle is slightly smaller due to the repulsion between the oxygen atom and the groups attached to the carbon atom that is being attacked by $O(^3P)$. We were unable, however, to obtain the result for the C_5F_{12} case with the use of HF method due to convergence problems which, we believe, arose because of the unrealistically long partially broken and formed bonds.

The activation energy values for the reactions of $O(^3P)$ with C_3F_8 and C_5F_{12}, obtained with the use of MB3LYP DFT method, are 67.2 and 67.1 kcal/mol, respectively. The activation energy value for the reaction of $O(^3P)$ with C_3F_8 obtained with the use of HF method, is 74.1 kcal/mol. The similarity of the two DFT results encourages us to estimate the activation energy value for longer fluoropolymer chains at ∼67−75 kcal/mol.

Discussion and Conclusions

Since our estimate of the activation energy for the chain-breaking reactions of $O(^3P)$ with fluoropolymer chains is ∼67−75 kcal/mol, we conclude that such reactions are possible under LEO conditions where the oxygen atoms possess translational energy relative to a spacecraft on the order of ∼100 kcal/mol. Not all of the total kinetic energy is available to surmount the reaction barrier. However, even after the total kinetic energy is reduced by the center-of-mass kinetic energy (∼25 kcal/mol), there remains sufficient kinetic energy (∼75 kcal/mol) associated with the interparticle distance coordinate to make the reaction possible.[34] Not only is the peak of the experimental energy distribution (∼103.8 kcal/mol) sufficient to allow the reaction, but moreover, one must remember there is a spread about the peak. Therefore in the high-energy tail of the distribution will be found particles with relative kinetic energies as high as 125 kcal/mol (using a full width at half-maximum estimate). Thus we conclude the chain-breaking mechanism is a possible one. (Experiments[35] have shown mass spectra of fragments emitted from the surface of fluorinated polymers under AO attack, which would be consistent with a chain-breaking mechanism, although we are aware that the scission fragments could conceivably also be produced by UV light, employed in the experiment.) This result offers a simple explanation for why exposure to low-energy AO does not seem to cause erosion in fluoropolymers: the oxygen atoms do not possess enough energy to overcome the activation barrier of the reaction.

It is interesting to note, however, that we did observe fluoropolymer erosion by neutral AO alone in low-energy plasma asher experiments.[21] Although AO kinetic energy in plasma ashers is only ∼1 kcal/mol at the distribution peak (based upon the temperature conditions of the experiment), we have noticed that in addition to fluoropolymer erosion, there was also etching of a glass window covering the experimental chamber. Since glass etching could be caused by high-energy AO, we conclude such would be consistent with the existence of a high-energy tail AO in plasma ashers, and that such a high-energy tail might be responsible for erosion in fluoropolymers during our experiment.[36]

Another significant implication of our computational results is the (previously dismissed) possibility that the degradation by AO alone could be the most important contributor to fluoropolymer erosion in LEO. It is worth noting that bond breaking by AO attack, even if it should occur as suggested by the theoretical calculations of this paper, is not by that fact alone guaranteed either to lead to the macroscopic degradation which does occur or to be the rate determining step for that process. However, as we indicate in our ref 27, a plausible picture can be built for such macroscopic degradation, on the basis of the chain-breaking mechanism.[37] If AO alone truly is the most important contributor to fluoropolymer erosion in LEO, then accurate ground-based simulation of LEO erosion rates for fluoropolymers would be possible with only the use of neutral AO beams having an AO energy distribution comparable to that of the LEO environment, without simultaneous UV exposure. If such testing, however, would produce the fluoropolymer erosion rates lower than those observed in LEO, it would then be suggestive that AO/UV synergy does contribute to the erosion.

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(34) The total kinetic energy (KE) of the interacting particles may be transformed into a sum of center-of-mass KE and reduced mass KE. The center-of-mass KE is conserved in the collision. Therefore the total KE is reduced by that amount. In gas−surface scattering a binary collision model is utilized in which the collision is viewed as occurring at the position of an assumed effective mass for the target molecule on the surface. [Harris, J. In *Dynamics of Gas−Surface Interactions*; Rettner, C. T., Ashfold, M. N. R., Eds.; Royal Society of Chemistry: Cambridge, U.K., 1991]. To estimate the total mass of the center-of-mass, an estimate is required of the effective surface mass for the target particle. In the scattering of 5 eV fluorine atoms from a fluorinated silicon surface, Minton and co-workers [*J. Phys. Chem. A* **1997**, *101*, 6549] found an effective surface mass of 31 amu. Also, in the cited ref 11, Minton and Garton report an effective surface mass of roughly 40 amu for the interaction of 5 eV oxygen atoms with a saturated hydrocarbon surface. Assuming an effective surface mass of 40 amu for the oxygen atom collision with the fluoropolymer surface, the center-of-mass collision energy of 4.5 eV oxygen atoms would be approximately 75 kcal/mol.

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(36) It is important to note, we do not claim to explain why conclusions of earlier experiments, for example, of refs 18 and 21−24, may or may not be erroneous. Our main interest here is to study, by theoretical methods, the characteristics of only one mechanism, viz., chain breaking by direct attack of C−C bonds by O(^{3}P). Given such study, we do point out that the main experimental results may be given an interpretation at least consistent with the theoretical results. We are aware many other mechanisms could be invoked, perhaps also consistent with the experimental results, but each such additional proposed mechanism would require its own additional study. In this paper, only chain breaking is the object of study.

(37) In our ref 27 we described how chain breaking in hydrocarbons might result in an efficient degradation pathway, and diagrams were employed, to supplement the discussion of degradation. The premise we invoke is that short chain fragments produced by carbon−carbon bond breaking via backbone oxidation can be volatile if they are sufficiently short and that the dominant cause for mass loss is volatilization of these short fragments. Consistent with this, we have degraded FEP Teflon using X-rays to cause chain scission and have found that, in sufficiently high doses, a liquid formed on the Teflon, which we believe was simply a collection of low molecular weight scission fragments.