THE JOURNAL OF
PHYSICAL CHEMISTRY A

Article

Cite This: *J. Phys. Chem. A* 2017, 121, 8675-8687

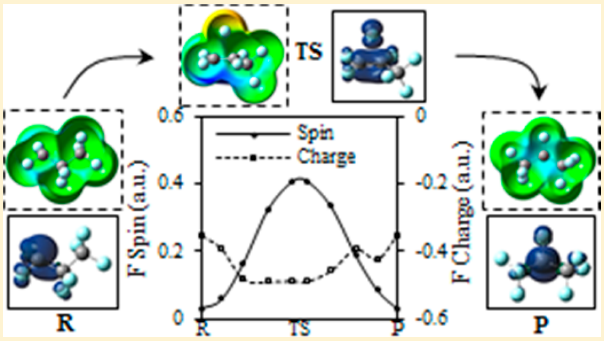
pubs.acs.org/JPCA

1,2-Fluorine Radical Rearrangements: Isomerization Events in Perfluorinated Radicals

Daniel J. Van Hoomissen and Shubham Vyas*

Department of Chemistry, Colorado School of Mines, Golden, Colorado 80401, United States

Supporting Information



ABSTRACT: Devising effective degradation technologies for perfluoroalkyl substances (PFASs) is an active area of research, where the molecular mechanisms involving both oxidative and reductive pathways are still elusive. One commonly neglected pathway in PFAS degradation is fluorine atom migration in perfluoroalkyl radicals, which was largely assumed to be implausible because of the high C−F bond strength. Using density functional theory calculations, it was demonstrated that 1,2-F atom migrations are thermodynamically favored when the fluorine atom migrated from a less branched carbon center to a more branched carbon center. Activation barriers for these rearrangements were within 19−29 kcal/mol, which are possible to easily overcome at elevated temperatures or in photochemically activated species in the gas or aqueous phase. It was also found that the activation barriers for the 1,2-F atom migration are lowered as much as by 10 kcal/mol when common oxidative degradation products such as HF assisted the rearrangements or if the resulting radical center was stabilized by vicinal π-bonds. Natural bond orbital analyses showed that fluorine moves as a radical in a noncharge-separated state. These findings add an important reaction to the existing knowledge of mechanisms for PFAS degradation and highlights the fact that 1,2-F atom shifts may be a small channel for isomerization of these compounds, but upon availability of mineralization products, this isomerization process could become more prominent.

1. INTRODUCTION

Perfluoroalkyl substances (PFASs) belong to an important class of anthropogenic chemicals that have been deemed contaminants of emerging concern due to their persistence and extreme resistivity to degradation.[1] Their persistence has led to their ubiquitous detection in aquatic environments,[1] and low concentrations detectable in drinking water have warranted increased study due to potential human exposure. Thus, the regulation of some of two widely utilized PFASs, including perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS), has become commonplace by regulatory agencies in both Europe and the United States.[2] However, elucidation of the molecular mechanisms involved in the degradation and remediation of PFAS compounds remains elusive and unclear in the literature.

The recalcitrant nature of PFASs has been attributed to the large C−F bond dissociation energy (>110 kcal/mol),[3] which contributes to the unique physiochemical properties of these compounds including unique sorption behavior,[4] vapor pressure, hydrophobicity, lipophobicity, helical carbon backbones,[5] and strong inductive effects on the pK_a of acidic or basic head groups.[3,6] Structural diversity in PFAS, including a wide variety of functional groups and variation of branched and linear structural isomers, has also contributed to difficulty in remediation and treatment.[1] These unique physiochemical properties have led to difficulties when employing a variety of common remediation techniques including tertiary water treatment, advanced oxidation techniques (AOTs), and reduction methodologies.[1,7−11] In most oxidation experiments involving PFAS samples, PFOA and its shorter chained analogues are commonly isolated as products. Consequently, many unregulated PFASs could have indirect impacts by producing more recalcitrant products during chemical transformations such as PFOA.[11,12] Chemical transformation from one PFAS compound to another in the context of remediation is also an active area of investigation, and several of these mechanisms remain unexplored to date.[10] Currently, AOTs including UV photolysis,[13−17] surface- and or metal-mediated photocatalysis,[18−22] sonolysis,[23−27] electrochemical decomposition,[28−32] and persulfate oxidation[12,33−37] have shown promise to degrade PFOA and other PFAS compounds, but so far, many have shown only lab-scale applicability.

The most commonly used technique for probing PFAS degradation products and identifying unknown PFAS compounds in a variety of matrixes is liquid chromatography coupled with mass spectrometry (LC/MS),[38−41] with electron spray ionization (ESI) in negative ion mode.[38] In these environments, PFOA and its longer and shorter chained

Received: September 6, 2017
Revised: October 12, 2017
Published: October 17, 2017

DOI: 10.1021/acs.jpca.7b08895

analogues are hypothesized to undergo 1,2-fluoride rearrangements after the suggested loss of CO_2, with these isomerizations being kinetically more favored than primary, secondary, and tertiary β-scission processes.[42] In fact, a number of mass spectrometry studies have been dedicated to 1,2-F rearrangements for a variety of fluorinated and perfluorinated compounds and have noted its importance in obtaining accurate results.[43−45] A combined Si−C/graphene reductive degradation approach showed that both perfluorinated carbon radical and anion alkyl chains are produced via quanfirmation exactive orbitrap mass spectrometry;[46] previous LC/MS/MS work (vide supra) indicates that these species could undergo fluoride rearrangements. This could imply that 1,2-F radical rearrangements could constitute a dominant kinetic pathway in the degradation of some PFAS in an oxidative environment, conceivably in persulfate oxidations, where a wide temperature range, oftentimes exceeding 50 °C, is utilized.[33,34,37]

1,2-Radical rearrangements involving hydrogen atoms,[47−50] and to a lesser extent with halogens such as chlorine,[51] have been studied extensively in a variety of chemical systems. Such rearrangements have become useful in understanding the mechanisms of various combustion reactions and reactions carried out in high-temperature/high-pressure environments.[52] The kinetic barriers of these rearrangements can exceed 60 kcal/mol in various conditions, for example, 1,2-H atom shifts in aryl radicals.[53] These reactions play an important role in hydrocarbon combustion and are important mechanistically because they affect the rate and product distribution of the combusted products.[54]

Conversely, in the early 1970s, 1,2-migrations of a fluorine atom were thought to be kinetically impossible, although rearrangements of a fluorine atom in carbenes and radical ions has been well documented.[55] The least investigated of the rearrangements, 1,2-fluorine atom shifts in radicals, have since been hypothesized or directly measured in a diverse consortium of chemical systems, both in the gaseous and the condensed phases.[56−59] For example, 1,2-fluorine shifts were observed in the condensed phase via NMR for the tertiary fluorine adjacent to a tertiary perfluorocarbanion.[60] Furthermore, F atom rearrangements in polyfluorinated cyclohexadienyl radicals generated by photochemical decomposition or heating of perfluoro-*p*-xylene and pentafluorobenzoyl peroxide was observed via electron paramagnetic resonance (EPR).[55,57,61] An early theoretical study by Fossey and Nedelec found the activation barriers for 1,2-F and 1,2-H shifts to be 107 and 88 kcal/mol respectively, indicating that these processes would not readily occur.[62] Surprisingly, further studies on the 1,2-migration of hydrogen and fluorine in $^{\bullet}CF_2{-}CHFT$ and $^{\bullet}CF_2{-}CFHT$ radicals, where T is a tritium atom, found that 1,2-F atom rearrangements had lower barriers than 1,2-H atom shifts.[63] A series of complementary theoretical studies utilizing INDO calculations also concluded that 1,2-F atom shifts were more likely than 1,2-H atom shifts in a variety of fluorinated ethyl radicals, cations, and anions.[64,65] Because of the controversy and elusiveness of the 1,2-F atom shift, coupled with urgency to understand the molecular mechanisms of PFAS transformations in the biosphere, it is extremely important to understand and quantify the kinetics of 1,2-F atom shifts. As 1,2-F atom shifts have been proposed for a variety of fluorinated and perfluorinated molecules, we posit that such transformations may take place during the PFAS degradation process or during their analytical measurement. As a result, a thorough investigation of these rearrangements is immediately warranted.

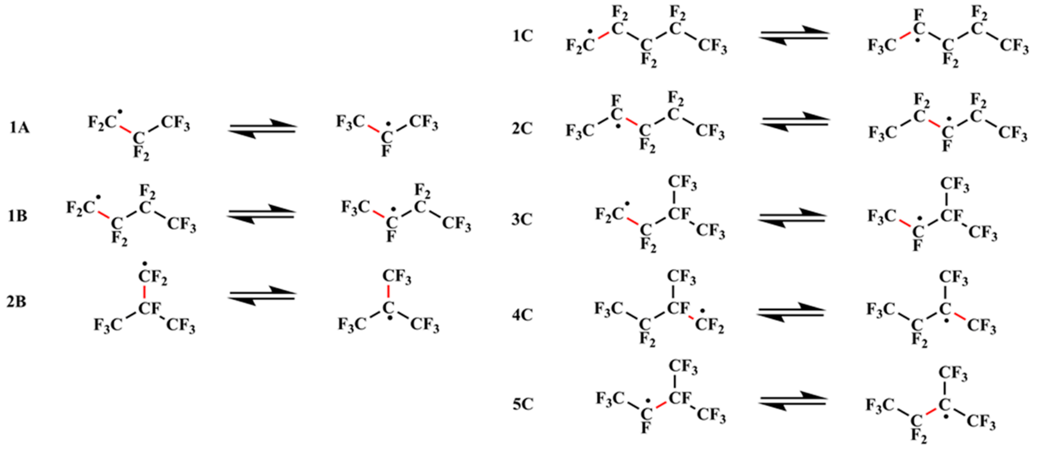
In this paper, we utilized electronic structure calculations to examine the 1,2-F atom shift for a variety of perfluorinated systems. As previously mentioned, experimental evidence for these shifts has already been demonstrated in both analytical detection (fluoride shift) and in high-energy environments; however, these studies did not formulate an understanding of 1,2-F radical rearrangements with a consistent and systematic approach. In our approach, we calculated the kinetic and thermodynamic parameters of 1,2-F atom rearrangements in radical perfluorinated molecules by varying the carbon chain length, the position of trifluoromethyl ($-CF_3$) substituents (isomer effects), the influence of adjacent conjugation, and possible assistance through small molecules. Furthermore, the nature of the F atom shift was explored through partial atomic charge calculations and spin population analysis to understand the nature of the migrating fluorine. A systemic approach to understand radical 1,2-F atom rearrangements and the affects named above to our knowledge has not been elucidated in the scientific literature.

2. COMPUTATIONAL METHODS

All of the calculations were performed using the Gaussian09 suite of programs.[66] Initial geometry optimizations for 1,2-F atom rearrangements were carried out using Becke's three-parameter hybrid exchange functional with the Lee−Yang−Parr correlation (B3LYP) functional.[67−70] In this work, extreme chemical accuracy is not of paramount concern as we are more interested in the trends elucidated through our systematic approach. Minimum energy structures were characterized by the absence of any imaginary frequency, while the transition states (TSs) were identified by the presence of one imaginary frequency. 1,2-F atom shifts from the TS structures were followed to the product and reactant local minima via intrinsic reaction coordinate (IRC) calculations.[71,72] For consistency and to obtain relatively accurate geometries and energies, the triple-ζ, CBSB7 (6-311G(2d,d,p)) basis set were used for all geometry optimizations, single-point calculations, and frequency calculations. Split valence basis sets were shown to comprise the best compromise between accuracy and computational efficiency for fluorine atom NMR chemical shifts using the GIAO method and the B3LYP functional.[5] This suggests that the CBSB7 basis set in concert with the B3LYP functional will be sufficient to describe the various systems herein. Previous theoretical investigations into these rearrangements observed that selection of the semiempirical method had a large impact on the rearrangement kinetics.[65] We posit that the same dependence is possible using a suite of DFT functionals; however, we have not investigated functional dependence in this work. Last, the Integral Equation Formalism Polarizable Continuum Model (IEF-PCM) of water (ε = 78.3553) was used to implicitly mimic an aqueous environment and was used in all geometry optimizations and frequency calculations.[73]

Using the potential energy surface and geometries from IRC calculations obtained at each TS, single-point calculations using the natural bond orbital (NBO 3.1, Gaussian 09(d)) method[74,75] were used to probe the partial atomic charge and spin densities of the atomic centers as the reaction proceeds. The total spin density from the NBO results was computed as the difference between the α and β spin densities for the atoms of interest.

Scheme 1. 1,2-F Atom Rearrangements in Perfluoropropyl (1A), Perfluorobutyl (1B, 2B), and Perfluoropentyl (1C−5C) Radical Systems[a]



[a]Bonds highlighted in red indicate the C−C bond over which the F atom migrates.

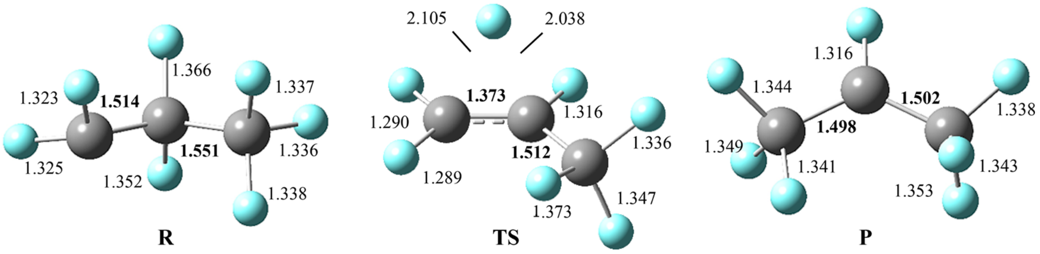


Figure 1. Reactant (R), three-membered ring transition state (TS), and product (P) geometries in the 1,2-F atom rearrangement of radical perfluoropropane. Bond lengths shown are in Å. The C−C bond lengths are shown in bold. All calculations were performed using the B3LYP(IEF-PCM)/CBSB7 level of theory.

Table 1. Thermodynamic Parameters, Enthalpy (ΔH) and Gibbs Free Energy (ΔG), As Calculated at the B3LYP(IEF-PCM)/CBSB7 Level of Theory for 1,2-F Atom Rearrangements Shown in Scheme 1[a]

	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\dagger}$	$\Delta G^{\dagger}$	ΔH°	ΔG°
1A	28.9	29.5	37.8	38.9	−8.8	−9.4
1B	27.8	27.8	38.2	39.1	−10.4	−11.3
2B	19.7	19.9	37.6	37.9	−17.9	−18.0
1C	28.9 (32.2)	29.3 (32.5)	38.7 (41.6)	39.9 (42.6)	−9.70 (−9.4)	−10.6 (−10.2)
2C	32.9 (34.8)	33.4 (35.5)	33.7 (35.6)	34.7 (36.4)	−0.70 (−0.8)	−1.30 (−0.9)
3C	27.2 (30.2)	26.9 (29.7)	39.1 (41.6)	40.4 (42.7)	−11.9 (−11.4)	−13.5 (−13.0)
4C	20.7 (23.6)	21.0 (23.9)	39.9 (42.0)	40.7 (42.8)	−19.2 (−18.4)	−19.7 (−19.0)
5C	29.0 (30.7)	30.1 (31.6)	37.7 (38.9)	37.9 (39.3)	−8.60 (−8.2)	−7.90 (−7.8)

[a]The forward activation barriers are represented by ‡, while the reverse activation barriers are denoted by †. Forward thermodynamic reaction energies are represented by °. Gas-phase results are given in parentheses for reactions **1C**−**5C** for comparison purposes calculated at the B3LYP/CBSB7 level of theory. Values are in kcal/mol.

3. RESULTS AND DISCUSSION

3.1. 1,2-F Atom Rearrangements in Perfluoroalkyl Radical Systems. 1,2-F atom rearrangements were studied in a series of perfluoroalkyl radical systems (Scheme 1). The nature of the carbon radical center on the chain (primary (1°) vs secondary (2°) vs tertiary (3°)) should have a prodigious impact on the kinetic and thermodynamic profiles of these rearrangements. The most internally consistent system is the perfluoropentyl system (**1C**−**5C**), whose linear and branched isomers comprise all of the possible 1,2-rearrangements: 1° to 2°, 1° to 3°, 2° to 2°, and 2° to 3° carbon centers. Perfluoropropyl (**1A**) and perfluorobutyl (**1B**−**2B**) are also included to compare any chain length dependency on the rearrangement. Furthermore, F atom rearrangements for longer chain length perfluoroalkanes, from C_5 to C_8, were used to investigate chain length dependency of 1° to 2° shifts as well as 2° to 2° shifts in C_8 compounds (vide infra).

For all of the cases considered, 1,2-F atom rearrangements in perfluoroalkyl radicals were found to proceed via a three-membered ring TS, as shown representatively for the perfluoropropyl radical in Figure 1. In the TS, the migrating fluorine is perpendicular to the plane of the carbon atoms, residing at the midpoint between the two atoms. Early computational investigations into free-radical migrations also predicted similar bridged intermediates for various atomic rearrangements such as chlorine and bromine.[62] During the F atom shift, the C−C bond length shrinks from a typical C−C

DOI: 10.1021/acs.jpca.7b08895
J. Phys. Chem. A 2017, 121, 8675−8687

single bond (1.54 Å) to 1.37 Å, indicating that the C−C has more double bond character. When comparing the reactant and product geometries, the C−F bond length does not change significantly, except for the C−F bonds connected to radical carbons (Figure 1). In the reactant conformation, the radical site has slightly smaller C−F bond lengths (1.325 and 1.323 Å) relative to other CF_2 (C−F ≈ 1.350 Å) and CF_3 units (C−F ≈ 1.330 Å). Similar results are observed for the product conformation, except for the slightly shorter radical C−F bond of 1.316 Å. In the perfluoropropyl system, the reaction of moving the F atom from the middle carbon to a terminal carbon atom is expected to be exothermic presumably because the product radical is stabilized by the two adjacent CF_3 groups and is a secondary carbon radical. In this case, the C−C bonds are each ~1.500 Å away, which is slightly shorter than the •C−C bond in the reactant (~1.510 Å). The combination of the shortening of the C−C bonds and the •C−F bonds in the product and reactant complex are contributing factors to the thermodynamic favorability of the 1,2-F shift in radical perfluoropropane.

Table 1 shows that 1,2-F atom shifts between the various carbons centers as shown in Scheme 1 are exothermic, with negligible differences observed between gas and implicit solvent calculations for **1C**−**5C** rearrangements. It is worth noting that the computed changes in enthalpy ($\Delta H°$) and Gibbs free energy ($\Delta G°$) values were generally within 1 kcal/mol, indicating that entropic effects were minimal in these systems. The degree of thermodynamic favorability was directly related to the change in the nature of carbon center bearing the radical site during the reaction; 1° to 2° is less favored than 1° to 3°, and 2° to 3° is similar in magnitude to 1° to 2°, and rearrangements without a change in the degree of carbon center (2° to 2°) are the least favored of the reactions in Table 1. The 2° to 2° rearrangements are nearly thermoneutral reactions, and show a predicable reversibility in forward and reverse activation energy barriers.

The kinetic parameters follow the same trends as the thermodynamic favorability, with gas-phase barrier energies typically 2−3 kcal/mol greater compared to those when an implicit solvent is utilized. The shifts with the greatest change in hyperconjugative groups between the product and reactant showed the greatest kinetic impetuous to rearrange. The values of the forward activation energy barriers for 1,2-F atom rearrangements involving structural isomers of the perfluoropentyl system indicate that the degree of branching has the largest effect on the forward activation barrier. The smallest activation barrier for 1,2-F atom rerrangments involves radical positions that have the largest change in radical order, illustrated by the barrier energies for the branched isomer of perfluorobutyl radical (**2B**). The smallest forward free energy barrier energy was approximately 20 kcal/mol for a 1° to 3° carbon radical shift (**2B**, Table 1). It is interesting to note that the largest barrier was for the F atom shift from a 2° center to another 2° radical center (**2C**, Table 1). The only difference between the two 2° radical centers is the position of carbon in the perfluoroalkyl chain. It is also important to observe that 1° to 2° (**1C**) and 2° to 3° radical transfers (**5C**) had similar activation barriers (28.9 vs 29.0 kcal/mol) due to the role of steric hindrance in the latter case.

On the basis of these results, we could predict that mutlihalogenated molecules bearing H, Cl, or Br may not significantly affect the kinetics and favorability of 1,2-F rearrangements as the change in carbon order is the most dominant factor in these isomerization processes. Many computational studies are dedicated to the 1,2-isomerization products of hydrofluorocarbons (HFCs), chlorofluorocarbons (CFCs), and other multihalogen alkanes in the gas phase as these molecules are subject to high-energy conditions in the upper atmosphere where these processes play a signifcant role in the transformation of these molecules. For example, dihalo shifts involving F−Cl,[76−78] Cl−Br,[79] and halogen−monovalent small-molecule rearrangements[80] are shown to be important in the transfromation of these refrigerants, e.g., involing HF or HCl elimination after 1,2-isomerization processes.[79,81,82] Although F atom rearrangements are likely processes in atmospheric conditions, the intent of this work is to relate these processes to common oxidation techniques used to remeditate PFASs in aqueous conditions, espeically the perfluorocarboxylic acids (PFCAs).

The activation energies and thermochemistries provided in Table 1 lend insight as to the degradation and stability of PFCAs in the environment. For instance, when PFCAs are degraded in an oxidative environment, shorter chain carboxylic acids are typically produced as products.[9] A strong oxidant, typically perfsulfate, is used to facilitate the electron transfer process producing a sulfate anion and an activated PFCA molecule. In the case of PFOA, immediately after the initial oxidation, CO_2 is released and perfluoroheptyl radical is produced. This is also observed from the perspective of LC/MS/MS techniques, but only for negatively charged species.[42] The barrier energies and thermodynamics associated with the 1,2-F atom shift provided in Table 1 indicate that these rearrangements could take place at elevated temperatures and in high-energy environments. Most persulfate oxidations are carried out at elevated temperatures, typically 80 °C; therefore, the probability of 1,2-F atom rearrangements occurring is higher under these conditions; however, the reaction with solvent molecules, other intermediate radicals such as hydroxyl radical, or oxygen will compete with these isomerization processes.

The propensity of certain structural isomers of PFASs, especially PFOA and PFOS, to degrade more than others has been highlighted in the relevant literature. Current literature suggests that branched isomers of PFASs are likely to undergo degradation at an increased rate compared to their linear analogues as the trend of stabilities of perfluoro carbanions was observed to be 3° > 2° > 1° for linear and branched PFOA in LC/MS/MS.[42] Furthermore, recent studies on the photolysis of PFOS utilizing VUV−graphene quantum dot/silicon carbide systems and PFOA using VUV−sulfite systems showed that branched PFOS structural isomers had degradation rate constants hundreds of times that of the linear analogues.[83,84] Our results as shown in Table 1 indicate that the radical produced at a less branched carbon has more kinetic drive to undergo rearrangement to the neighboring more branched carbon center. If a radical from an activated PFAS is present on a tertiary radical carbon, that carbon is unlikely to undergo any isomerization processes, at least from the perspective of 1,2-F rearrangements. The stabilization via hyperconjugation may provide further understanding of the degradation and fragmentation processes of branched PFAS. In a recent study, hyperconjugative interactions between σ_{C-C} and σ^*_{C-F} molecular orbitals were found to be a dominant factor in the helical nature of perfluoro-*n*-alkanes.[85] On the basis of our results from Table 1 and the literature, we anticipate a direct relationship between stabilization through hyperoconjugation at the site of a perfluorocarbon radical and its stability concerning further reaction. Such reactions have been suggested by many experimental studies and may include oxygen addition to the radical site,[86] hydrolysis,[16] and radical−radical terminations with other radical oxidants such as hydroxyl radicals.[33] To probe radical movement within the greater context of PFCA stability, 1,2-F atom rearrangements were computed for perfluoroalkanes with varied chain length and radical position.

To explore the impact of chain length on 1,2-F atom shifts, we investigated the 1° to 2 °F atom shifts in C_3−C_8 systems. Furthermore, 2° to 2° rearrangements were also investigated in the C_8 system to understand the possibility of radical migration through the perfluoroalkyl chain. The significance of these results was in turn understood from the context of perfluoroalkane helical structures. Reaction energetics from these computations are summarized in Table 2. It is clear that the chain length is not a significant factor in the favorability and kinetics of 1,2-F atom rearrangements. A small degree of thermodynamic stability is gained through larger chain lengths; however, the magnitude of the change is nearly insignificant after four carbon linear chains. Activation barriers for the shift are particularly unaffected by the presence of additional perfluorinated carbons, indicating that the state of the carbon radical (1°, 2°, etc.) in the reactant and TS has the greatest effect on the activation energy barrier for the reaction. The values computed in Table 2 allow us to evaluate the kinetic and thermodynamic favorability of propagating a radical through the chain. The last three entries in Table 2, namely, 8-2$^\bullet$, 8-3$^\bullet$, and 8-4$^\bullet$, correspond to 2°−2° 1,2-F atom shifts in a C_8 perfluoroalkyl chain where the shift initiates from the second, the third, and the fourth carbon, respectively. It is evident form these three entries in Table 2 that there is a mild impact of radical position along the carbon chain if one looks at the activation enthalpy of the reaction. However, the free energy of activation makes it clear that there is no impact of radical position at the rate of 1,2-F atom shift for these 2° to 2° shifts presumably due to favorable entropic contributions by gradual unfolding of the local helical structure. Consequently, this emphasizes that the 1,2-F atom rearrangement is typically only influenced by the local bonding environment, e.g., the carbons directly adjacent to the site of rearrangement.

Table 2. Thermodynamic Parameters, Enthalpy (ΔH) and Gibbs Free Energy (ΔG), for 1,2-F Atom Rearrangements for 1° to 2° Radicals with Varying Chain Length Perfluoroalkane Radical Linear Isomers[a]

chain length (C_n)	$\Delta H^\ddagger$	$\Delta G^\ddagger$	$\Delta H^\dagger$	$\Delta G^\dagger$	ΔH°	ΔG°
3	28.9	29.5	37.8	38.9	−8.8	−9.4
4	28.2	29.2	38.2	39.2	−10.0	−10.0
5	28.0	28.6	38.7	39.8	−10.7	−11.3
6	28.0	28.7	38.5	40.0	−10.6	−11.3
7	28.0	28.7	38.6	39.7	−10.6	−11.0
8	28.0	28.1	39.6	40.1	−11.6	−12.1
8-2$^\bullet$	33.4	34.1	34.6	35.6	−1.2	−1.4
8-3$^\bullet$	34.0	33.1	34.5	35.5	−0.5	−2.4
8-4$^\bullet$	34.7	35.6	34.7	33.4	0.0_4	2.1

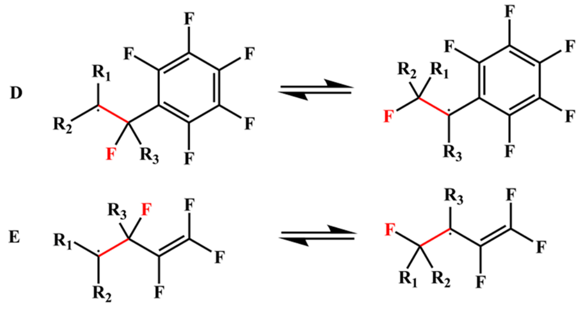
[a] The forward activation barriers are represented by ‡, while the reverse activation barriers bear †. Forward thermodynamic reaction energies are represented by °. N$^\bullet$ in the last three entries indicates the position of carbon from where the rearrangement begins. Values are in kcal/mol as calculated at the B3LYP(IEF-PCM)/CBSB7 level of theory.

The reversibility of the kinetic barriers in the case of 8-2$^\bullet$, 8-3$^\bullet$, and 8-4$^\bullet$ may be attributed to the near-equal electron withdrawal from the two adjacent carbons and is also reflected in the near-equilibrium conditions thermodynamically. The small fluctuations in these barriers could be due to dipole moment alterations as you propagate further into the chain. The near-zero favorability shown for the reaction may be attributed to the energy required to contort the chain from its lowest-energy conformation. It is evident that the degree of substituents, or rather the degree of σ-hyperconjugation in the product relative to the reactant, is a dominant factor in kinetic and thermodynamic favorability for these reactions; however, the degree to which π-conjugation affects the 1,2-F atom rearrangement requires further attention.

3.2. 1,2-F Atom Rearrangements in Conjugated Systems.

Numerous literature investigations have elucidated the chemical properties of conjugated perfluorinated molecules; however, F atom isomerization processes in these systems have not been subjected to a systematic study. Scheme 2 was formulated to investigate the impact of conjugation on 1,2-F atom shifts by using two model systems, allyl and benzyl systems.

Scheme 2. Radical 1,2-F Atom Rearrangements in Systems Containing Allyl (D) and Vinyl (E) Functional Groups[a]



[a] Bonds highlighted in red indicate the bond over which the F-atom migrates. R1, R2, and R3 substituents were modeled as CF_3 and .

The goal of investigating these conjugated systems was to determine if radical stabilization through π-conjugation affects the kinetic and thermodynamic properties of 1,2-F rearrangements to the same degree as seen with σ-conjugation in the previous section. To reiterate, 1,2-F migration have been proposed in the isomerization of aromatics such as in perfluorocyclohexadienyl radicals.[55] Furthermore, a few experimental gas-phase studies of perfluoroalkenes have proposed a 1,2-F atom rearrangement as a viable kinetic pathway. The first example concerns the photoisomerization of perfuoroallyl radical, where the authors computed a 4.3 kcal/mol barrier at the B3LYP/6-311G* level of theory, indicating that these rearrangements would be kinetically favorable processes under gas-phase conditions.[87] Second, the rearrangement process is also mentioned as a possible mechanism in the reaction of H atoms with perfluorobutadiene, although the authors omitted any significant discussion on this isomerization process.[88] In traditional nonperfluorinated systems such as triphenylmethyl radical, aromatic stabilization can result in long-term persistence of the radical due to steric hindrance and the ability of the radical character to delocalize onto the aromatic

Table 3. Thermodynamic Parameters, Enthalpy (ΔH) and Gibbs Free Energy (ΔG), for 1,2-F Atom Rearrangements for Radicals in Perfluorinated Conjugated Systems[a]

	substituent								
	R1	R2	R3	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\dagger}$	$\Delta G^{\dagger}$	ΔH°	ΔG°
1D	F	F	CF_3	16.0	16.1	41.1	40.6	−25.2	−24.5
2D	F	F	F	22.2	23.0	40.8	41.2	−18.5	−18.2
3D	CF_3	F	CF_3	25.6	26.6	41.2	41.4	−15.6	−14.8
4D	CF_3	CF_3	CF_3	30.1	30.6	36.2	36.5	−6.1	−5.8
5D	CF_3	F	F	25.8	27.2	34.2	34.1	−8.4	−6.9
6D	CF_3	CF_3	F	28.4	29.4	23.7	22.6	4.8	6.8
1E	F	F	CF_3	13.9	14.6	47.0	47.8	−33.1	−33.3
2E	F	F	F	21.8	22.2	44.0	44.7	−22.2	−22.5
3E	CF_3	F	CF_3	22.0	23.8	41.8	42.8	−19.8	−19.0
4E	CF_3	CF_3	CF_3	26.7	27.4	39.0	39.3	−12.3	−11.9
5E	CF_3	F	F	24.2	25.6	36.8	37.1	−12.6	−11.5
6E	CF_3	CF_3	F	28.1	29.3	26.8	27.7	1.4	1.6

[a] The forward activation barriers are represented by ‡, while the reverse activation barriers bear †. Forward thermodynamic reaction energies are represented by °. R1 and R2 substituents are located on the outer carbon, while the R3 substituent is adjacent to the conjugated part of the molecules, as shown in Scheme 2. Values are in kcal/mol as calculated at the B3LYP(IEF-PCM)/CBSB7 level of theory.

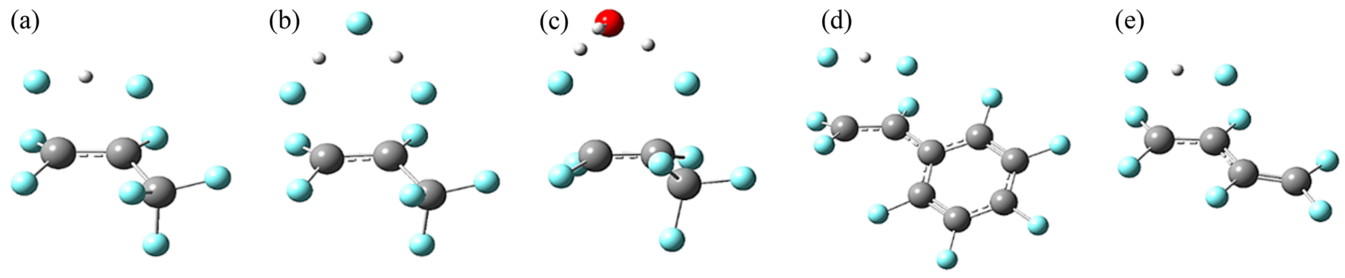


Figure 2. (a) TS conformations for 1,2-F atom rearrangement (a) in a perfluoropropyl system using HF assistance, (b) in a perfluoropropyl system using assistance by two molecules of HF, (c) in a perfluoropropyl system using HF and H_2O assistance, (d) in a perfluoroethylbenzyl system using HF assistance, and (e) in a perfluorobutenyl system using HF assistance. All calculations were performed using the B3LYP(IEF-PCM)/CBSB7 level of theory.

moieties. Therefore, the stabilization produced through conjugation could alter the persistence of perfluorinated substances containing conjugated groups and contribute to long-term stability. The substituents were chosen to evaluate whether π-conjugation or substitution at the radical carbon (σ-hyperconjugation) has a more dominant effect in these systems, which are shown in Scheme 2.

1,2-F atom rearrangements occurring adjacent to π-densities are likely to display a marked decrease in their forward barrier energies, at least when the product complex is forming either a benzyl (group D) or allyl radical (group E). The decrease in barrier energy for π-conjugated 1° to 2° shifts (**2D** and **2E**, Table 3) is approximately 7 kcal/mol less when compared to the analogous nonconjugated perfluoropropane case in Table 1. The decrease in barrier energies is also mirrored by an increase in reaction exothermicity, where the thermodynamic favorability increases by ~8 kcal/mol for benzyl-substituted molecules and ~12 kcal/mol for allyl substituents relative to the perfluoropropane case (Scheme 1 and Table 1). The increased favorability is not a commonality among all systems in Table 3. The position and number of the substituent groups play a significant role in determining the exothermicity of the fluorine atom migration. Steric hindrance by CF_3 groups near the rearrangement site contributed to the lower reaction favorability; however, this effect could be mitigated if the reactant radical position had no substituent CF_3 groups. For example, **1D** in Table 2 shows that the degree of branching in the conjugated rearranged product benefits from both stabilization through conjugation and a greater number of substituent CF_3 groups. This result is also mirrored in system **1E**, which is kinetically and thermodynamically more favored than **1D**. Overall, it was observed that allyl substituents affect the kinetics and thermodynamics of 1,2-F atom rearrangements to a greater degree than benzyl substituents. Our recent work on allyl and benzyl radicals compliments these results, where we identified that benzylic radicals do not effectively delocalize the radical relative to allyl radicals, leading to the conclusion that the latter is thermodynamically more stable.[89]

Table 3 provides an interesting contrast to the alkyl radical without any π-conjugation cases provided in Table 1. For example, rearrangement in **4D** shows a similar forward activation energy barrier to that of the primary to secondary shift encountered in cases of **1A** and **1C**, which suggests that stabilization through π-conjugation only provides a minimal amount of stabilization in group **D** systems while the benefit of hyperconjugation by increasing the number of contributing CF_3 could have equal or greater impact. Two interesting systems, **6D** and **6E**, show that moving to a less substituted carbon from a highly substituted carbon results in an endothermic reaction as well as that kinetic barriers are similar to 1° to 2° shifts in perfluoroalkyl systems from Table 1. However, if 2° to 2° shifts are compared between alkyl and allyl systems, the conjugation decreases the barrier by nearly 8 kcal/mol, indicating that conjugation still imparts a dominant kinetic drive to 1,2-F atom rearrangements, even if highly branched substituents like **4E** and **4D** show that the reaction becomes unfavorable under these conditions. These systems elucidate the importance of branching near the conjugated substituent and the type of conjugation present, i.e., allyl or benzyl substituents, which is in agreement with our previous results (vide supra).

3.3. Assisted 1,2-F Atom Rearrangements. Previous studies have shown the importance of small molecules in aqueous solution to assist 1,2-radical isomerizations. A notable case is the 1,2-H rearrangement of methoxyl and benzoxyl radicals, where it was shown experimentally[90] and theoretically[91] that water molecules play a significant role in lowering the activation barriers for the 1,2-H shift from an oxygen-centered radical to a carbon-centered radical. Thus, the possible role of solvent or foreign molecules in 1,2-F atom rearrangements cannot be ignored. The molecules aiding 1,2-F atom rearrangements depend on the solvent and molecular composition in which the rearrangement is taking place; however, they all share the ability to donate a F atom. For instance, in PFAS oxidation, it has been shown that HF and F^- are produced as the chain is truncated by CF_2 units through an unzipping mechanism[92] or through HF elimination from various PFAS intermediates.[33,37] Consequently, one or two molecules of HF or a combination of HF and H_2O were utilized to model assisted 1,2-F atom rearrangements with representative systems shown in Figure 2. It is conceivable that other PFAS molecules or intermediates could also facilitate the F atom shift; however, only small molecules were investigated in this work. During the degradation of PFAS, the F^- concentration increases with time and may create a new pathway for the oxidized PFAS, which may impact the degradation of PFAS with time. The concentration of HF will also be largely impacted by the pH of the solution (HF pK_a = 3.14) and will only build to appreciable concentrations in strongly acidic media.

The bond lengths for the TS structures in Figure 2a−c are shown in Figure S1 (Supporting Information). In general, the bond lengths for nonmigrating atoms are consistent in each case, within 2% for all structures investigated. Small deviations in bond length are noted for the migrating F atom above the second carbon position, the bond length increasing in the following series: $H_2O/HF < HF < 2HF$ (Figure S1). In the mono-HF catalyzed case, the HF molecule will orient itself perpendicular to the carbon−carbon bond, with the H atom more associated with the F atom above the first carbon position, its bond length approximately 10% elongated vs a noncomplexed HF molecule. As the F atom rearranges, it associates with the hydrogen of the HF molecule, while the fluorine atom originating from HF bonds with the first carbon center. The same mechanism is observed for the 2HF catalyzed case; however, the HF molecules no longer orient themselves perpendicular to the plane but rather in a plane that is 45° from normal (Figure S1). The same tilt in assisting molecules is also observed for H_20/HF catalyzed rearrangements. All of the small-molecule catalyzed rearrangements investigated in this work all proceed in a concerted fashion. Analysis of the charge and spin profiles provided in the subsequent section (section 3.4) imply that the bonds between the substrate and assisting molecules are made and broken homolytically.

Thermodynamic and kinetic parameters for 1,2-F atom shifts assisted by small molecules are summarized in Table 4. It is clear that small-molecule assistance to the 1,2-F atom rearrangement can influence kinetic barriers by a large degree.

Table 4. Thermodynamic Parameters, Enthalpy (ΔH) and Gibbs Free Energy (ΔG), for 1,2-F Atom Rearrangements for Radicals in Perfluorinated Alkyl Systems with or without Solvent Assistance[a]

system	$\Delta H^‡$	$\Delta G^‡$	$\Delta H^†$	$\Delta G^†$	$\Delta H°$	$\Delta G°$
1A-no assistance	28.9	29.5	37.8	38.9	−8.8	−9.4
1A-HF/H_2O	25.1	29.8	35.4	41.4	−10.2	−11.6
1A-HF	21.5	25.4	30.9	34.8	−9.4	−9.4
1A-2HF	19.2	22.8	29.2	33.6	−10.0	−10.8
2D-no assistance	22.2	23.0	40.8	41.2	−18.5	−18.2
2D-HF	15.5	18.1	33.7	36.8	−18.2	−18.7
2E-no assistance	21.8	22.2	44.0	44.7	−22.2	−22.5
2E-HF	11.8	13.7	33.7	36.5	−21.9	−22.8

[a] The forward activation barriers are represented by ‡, while the reverse activation barriers bear †. Forward thermodynamic reaction energies are represented by °. Values are in kcal/mol as calculated at the B3LYP(IEF-PCM)/CBSB7 level of theory.

However, the reaction enthalpy is mostly unaffected by changes in the degree of assistance because the initial and final states of the 1,2-rearrangements remain unchanged. In cases with alkyl radicals, one and two HF molecules have a larger effect on the barrier energies than a combination of HF and H_2O molecules. When H_2O and HF assist the 1,2-rearrangement, the barrier decreases by 3.8 kcal/mol, while a decrease of 7.4 and 9.7 kcal/mol is computed for one and two HF assistance, respectably. This result indicates that although water may influence the kinetic barriers of the reaction, the shift is more likely to occur when assisted by one or two HF molecules. At lower concentrations of HF, it is more likely that HF and H_2O assistance will be the dominant reaction. Moreover, adding an extra HF molecule to the rearrangement makes a smaller difference compared to adding just a single HF molecule, not to mention it would involve a significant entropic penalty; therefore, rearrangements involving three HF molecules were not investigated.

Although not shown in Table 4, modeled rearrangements involving two HF molecules were attempted in allylic and benzylic systems; however, an identical TS to the alkyl case was not located in these cases due to the assumed repulsion of HF molecules by the π-cloud. Likewise, the combined HF/H_2O shifts were not investigated in these systems; it is anticipated that computed barriers would fall within the unassisted and assisted cases for both systems. The HF-assisted rearrangement in systems **2D** and **2E** nevertheless has a similar magnitude of effect as in the two HF case in alkyl systems, which indicates that HF assistance could be a much more prominent factor in systems containing π-conjugation. The HF assistance in allylic and benzylic radicals is significant, with computed $\Delta H^‡$ decreasing by about 6.5 and 10 kcal/mol when compared to the unassisted case (Table 3), respectably.

To further investigate the impact of assistance on 1,2-F atom shifts, we investigated 1° to 2° shifts in various perfluoroalkyl systems with varied chain length. Reaction energetics for various chain length alkyl systems as shown in Table 5 reassert a previous conclusion that 1,2-F rearrangements are mostly affected by the local bonding environment as both the TS barrier energies and reaction favorability are mostly unaffected by the presence of additional carbons. It is also reaffirmed that the order of the carbon radical (primary, secondary, etc.) in the reactant and TS have the greatest effect on the activation energy barriers and favorability of the rearrangement. Similar

DOI: 10.1021/acs.jpca.7b08895
J. Phys. Chem. A 2017, 121, 8675−8687

Table 5. Thermodynamic Parameters, Enthalpy (ΔH) and Gibbs Free Energy (ΔG), for HF- and 2HF-Assisted 1,2-F Atom Rearrangements for 1° to 2° Radicals with Varying Chain Length Perfluoroalkane Radical Linear Isomers[a]

chain length	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta H^{\dagger}$	$\Delta G^{\dagger}$	ΔH°	ΔG°
3−HF	21.5	25.4	30.9	34.8	−9.4	−9.4
3−2HF	19.2	22.8	29.2	33.6	−10.0	−10.8
4−HF	21.9	25.7	32.3	36.0	−10.5	−10.4
4−2HF	21.6	25.5	30.9	35.4	−9.3	−9.8
5−HF	22.2	26.5	32.4	36.9	−10.2	−10.4
5−2HF	20.5	24.2	31.2	36.0	−10.7	−11.8
6−HF	22.3	25.7	32.4	36.3	−10.1	−10.6
6−2HF	20.6	25.0	31.4	36.2	−10.8	−11.2
7−HF	22.3	25.8	32.4	36.6	−10.1	−10.9
7−2HF	20.6	24.4	31.4	36.5	−10.9	−12.1
8−HF	22.3	26.5	33.0	35.8	−10.7	−9.4
8−2HF	20.6	24.6	31.4	35.7	−10.8	−11.1
8-2*−HF	27.6	32.4	28.3	32.5	−0.7	−0.1
8-2*−2HF	27.9	32.4	28.5	32.4	−0.6	0.0
8-3*−HF	29.2	33.5	30.3	34.6	−1.1	−1.1
8-3*−2HF	29.5	34.4	29.6	34.8	−0.1	−0.4
8-4*−HF	29.4	33.9	29.4	33.9	0.0	0.0
8-4*−2HF	29.7	34.4	29.7	35.1	−0.1	−0.6

[a] The * symbol indicates the radical carbon on which the rearrangement begins. The forward activation barriers are represented by ‡, while the reverse activation barriers bear †. Forward thermodynamic reaction energies are represented by °. Values are in kcal/mol as calculated at the B3LYP(IEF-PCM)/CBSB7 level of theory.

results are noticed for the assisted shifts with one and two HF molecules. Although a simple reaction, these calculations suggest that electronic structure calculations on PFAS systems with radicals can be successfully truncated to smaller carbon systems, without sacrificing significant computational accuracy or conclusions. However, this may not be generalizable for all reactions and not for other properties such as van der Waals interactions, which should scale with the length of the chain increasing.

The thermodynamic favorability of unassisted and assisted F atom shifts only minimally increased as the carbon chain was elongated. Moreover, thermodynamic favorability of fluorine migration when one or two HF molecule provide assistance does not significantly change when compared to the unassisted case. Nonetheless, the barrier energy of the reaction does have slight dependence on chain length when barrier energies are compared. As the chain length increases past C_4, the difference between the one and two HF-assisted cases remains unchanged (Tables 5 and 2). This indicates that the presence of a longer chain does not significantly impact the ability to recruit HF molecules to the site of rearrangement. For the 2° to 2° shifts shown in Table 5, the addition of a second HF molecule results in no appreciable decrease in the forward activation energy barrier, and the location of the 2° to 2° shift also has no impact if one or two HF molecules facilitates the reaction. This may be due to the F^- repulsion between the fluorine on the perfluoroalkane chain and the hydrogen fluoride molecule assisting the rearrangement. The same is not true for the reverse reaction, which involves the movement from a secondary radical to a primary radical.

3.4. Nature of Migrating Fluorine: Charge and Spin Analysis.

Discussion so far suggests that 1,2-F atom shifts are plausible in activated perfluoroalkyl radicals; however, it is not clear if the fluorine atom migrates as a neutral atom or as an anion. Being the most electronegative atom in the periodic table, fluorine may migrate as a F^- ion, a possibility that may direct the elucidation of mechanistic pathways in the reductive degradation of these compounds. Investigations of 1,2-F rearrangements in organic reactions suggest that fluorine can rearrange with a variety of charge and spin profiles, for example, through carbocation and radical intermediates in fluoroepoxides[93,94] and in complicated sequences involving multiple steps for fluorine atoms on aromatic rings.[58] To investigate the nature of migrating fluorine, partial atomic charges and total spin densities were obtained by analyzing the SCF electron spin density and electrostatic potentials, shown in Figure 3, for various geometries through rearrangement.

Figure 3a shows that the rearranging fluorine atom in the perfluoropropyl system gains a noticeable amount of charge as it proceeds through the TS to the product conformation. In the rearranged product, the electrostatic potentials of the bound fluorines are equal by a qualitative visual inspection. Qualitatively, isosurface maps of the electrostatic potential suggest that the fluorine atom gains a noticeable amount of negative charge as it proceeds through the TS. In the case of one and two HF-assisted F atom transfers, the electrostatic density in Figure 3b,c, respectively, suggests that the charge localization is similar in the TS but with sharing of the negative charge between the migrating fluorine and the fluorine donated by the HF molecule(s). The charge density does not seem to change near the carbon radicals in the product and reactant complexes in the HF-assisted cases; however, small amounts of negative electrostatic potential are observed in the reactant and in the product. As shown previously in Figure 1, the fluorine is the most dissociated from the rest of the molecule in the TS, with bond lengths exceeding 2 Å; therefore, it is expected that charge localization on the migrating fluorine(s) would be the greatest at this point during the reaction, which is observed for all 1,2-F transfers shown in Figure 3. The insignificant increase in the fluorine atomic charge density in the TS indicates that the fluorine atom does not migrate via a charge-separated state. Nonetheless, the charge is not the only factor in these rearrangements as the SCF derived spin density provides us insight into the actual radical transfer taking place in all three rearrangements.

From the perspective of spin, Figure 3a shows that the majority of excess α spin resides on the first carbon in the reactant and on the second carbon in the product, which is not an unexpected result and confirms that radical migration takes place. In the TS, the spin density in Figure 3a is shared equally among the three atoms involved in the 1,2-F rearrangement, indicating that the fluorine also possesses some radical character as it migrates across the C−C bond. The distribution of the excess α spin is not as stark in the TSs of HF-assisted rearrangements, indicating that the radical character may be more localized on the carbon centers and less localized on the moving fluorine atoms. The charge and spin profiles of HF catalyzed rearrangements involve a mechanism in which the fluorine originating from the perfluoralkyl chain is exchanged with a fluorine from the small molecules through homolytic bond breaking/making. As these isosurfaces were constructed using the Mulliken populations, which is arguably a qualitative and error-prone technique,[95] we performed NBO analysis on similar systems to explore this effect further, as shown in Figure

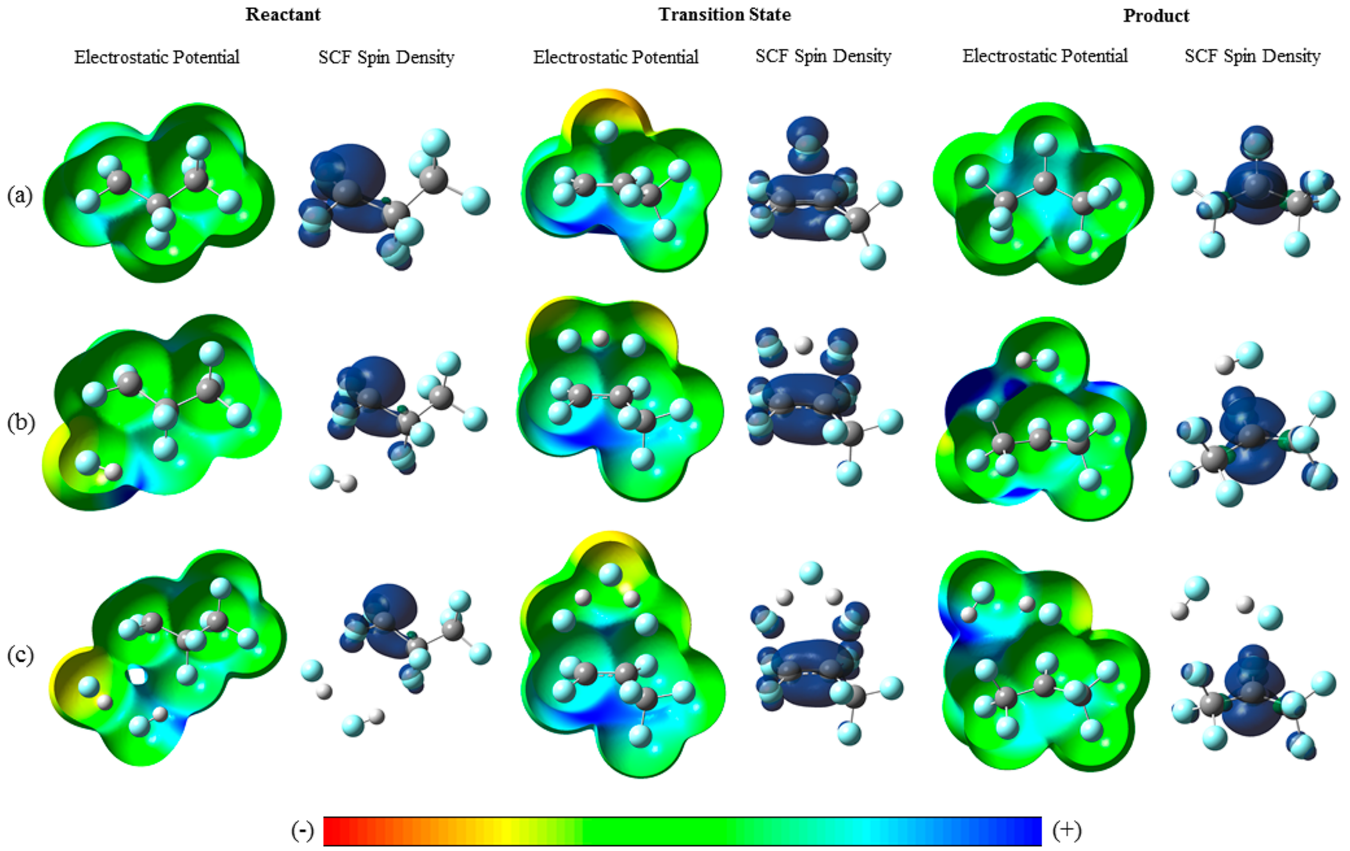


Figure 3. Electrostatic potential mapped onto the total electron density (isoval = 0.002) and the reactant, TS, and product conformations and the corresponding (α−β) spin density distributions (isoval = 0.004) for (a) 1,2-F rearrangement, (b) HF-assisted 1,2-F rearrangement , and (c) two HF-assisted 1,2-F rearrangement in radical perfluoropropane. The qualitative scale for the charge distribution is shown above. All calculations were performed at the B3LYP(IEF-PCM)/CBSB7 level of theory.

4, to gain a quantitative understanding of the spin density and partial atomic charge associated with the migrating fluorine.

Partial atomic charges and atomic spin densities afforded through NBO analysis shows that the fluorine atom migration does not proceed through a charged-separated state for all three cases (Figure 4). The partial atomic charge on the fluorine atom does not significantly increase as the fluorine migrates to a more energetically favorable position; however, the atomic spin density on the fluorine atom changes markedly as it proceeds through the TS and downhill toward the product. This is somewhat contrary to the qualitative results provided in Figure 3, which appeared to have more partial charge localized on the fluorine in the TS.

In the case of the unassisted rearrangement, the reactant complex shows that a partial atomic charge between the two carbons is not significantly different. As the F atom shift occurs, the charge on the primary carbon (C1) increases and the secondary carbon (C2) decreases. In the product complex, the charge is consistent with the amount of fluorine atoms bound to the carbons. As the fluorine shifts to the secondary carbon position, a small amount of negative charge builds up, which then decreases as the secondary carbon radical is established in the product complex. The atomic spin density results show that the majority of excess α spin is localized on the primary carbon (C1) in the reaction. As the rearrangement begins, the spin density on the primary carbon (C1) decreases while the secondary carbon (C2) and fluorine atom spin densities increase. At the TS, the total excess α spin density on the fluorine is approximately 0.4 au, while the primary and secondary carbons carry approximately 0.3 au spin each. Once the F atom is transferred to the primary carbon center, the spin is completely situated at the secondary carbon. The trends in atomic spin density and atomic charge density provided in Figure 4a are consistent with the fluorine atom moving as a radical.

If the fluorine moved as F^-, more charge would be associated with the fluorine atom as the isomerization process occurs; however, partial atomic charge on the fluorine atom at the TS is not significantly different from the charges in the product and reactant. Furthermore, the observed bell-shaped curve for atomic spin density as the reaction proceeds reinforces our conclusion that F moves as a radical. As with the unassisted case, analyses of the assisted 1,2-F atom shifts (Figure 4b,c) also show the charge between the two carbons is nearly identical as two fluorines are bound by each carbon. As the HF-assisted 1,2-F shift occurs, the charge on the primary carbon (C1) increases and that of the secondary carbon (C2) decreases. In the product complex, the charge is consistent with the amount of fluorine atoms bound to the carbons. The fluorine associated with the carbon in the reactant complex (F2) gains a small amount of negative charge as the fluorine associates more with the hydrogen of the assisting HF molecule. The charge of the fluorine atoms remains unchanged as the reaction proceeds; however, the fluorine originally associated with the HF molecule loses a small amount of charge as it makes a bond with the primary carbon (C2). The charge on the hydrogen atom(s) was unchanged throughout the rearrangement process in both HF-assisted cases, indicating covalent binding between

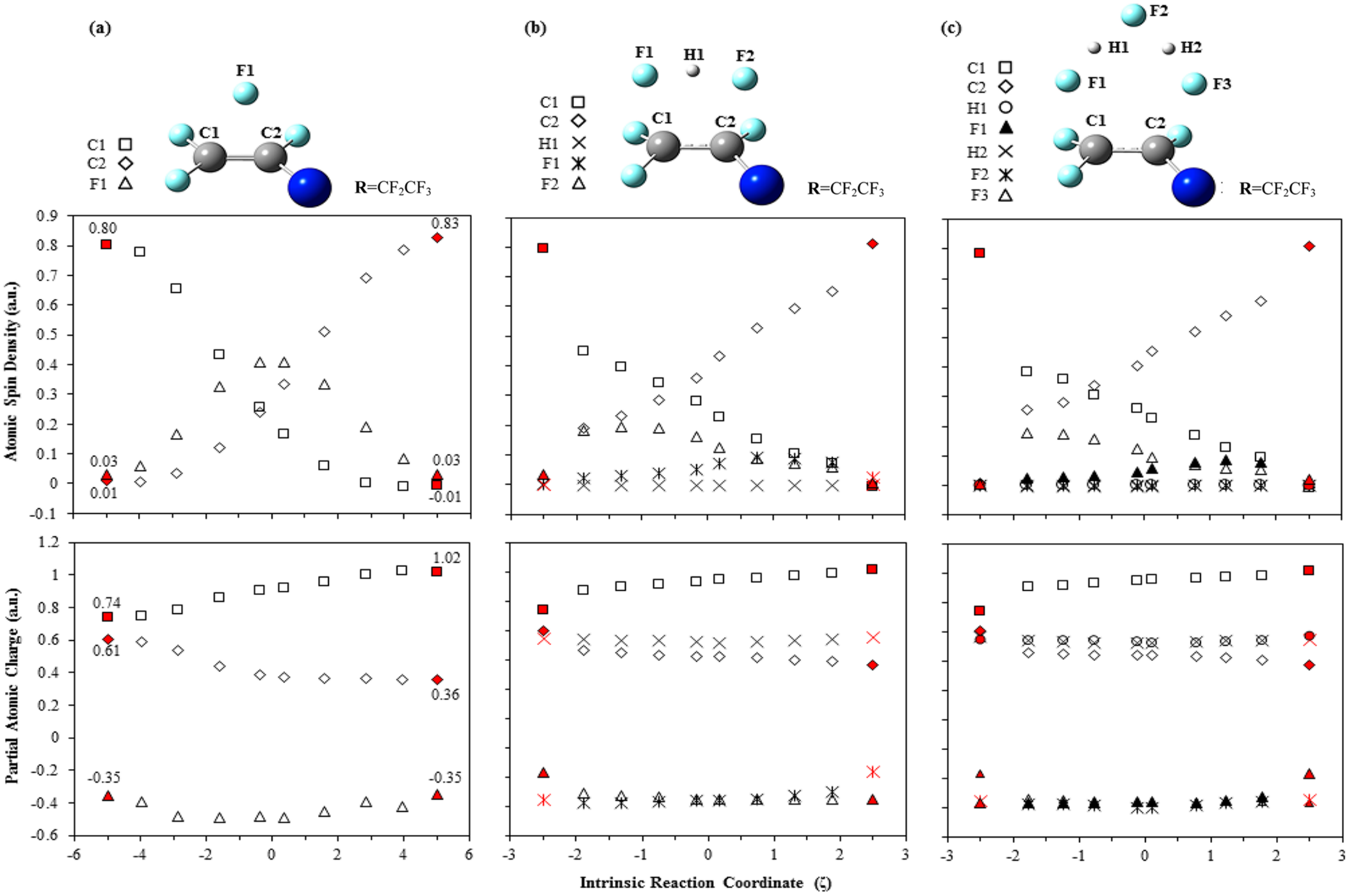


Figure 4. Partial atomic spin densities and total spin for points along the IRC as calculated at the B3LYP(IEF-PCM)/CBSB7 level of theory in the (a) 1,2-F rearrangement, (b) HF-assisted rearrangement, and (c) two HF-assisted rearrangement in perfluorobutane. Values in (a) are shown for visualization purposes. The red points represent NBO calculation on the optimized product and reactant complexes.

the fluorines and hydrogens. The charge profile of both HF-assisted shifts (Figure 4b,c) shows that the moving fluorine atoms have the same charge as the unassisted case. The three-membered ring structure in the HF catalyzed TS becomes a five-membered ring structure for the 2HF catalyzed case where the fluorine atoms are much less associated with the carbons; however, more charge is not localized on the nonassociated fluorine atoms.

4. CONCLUSIONS AND INSIGHT INTO THE MECHANISM PFAS DEGRADATION

A detailed and systematic investigation of 1,2-F atom migration in the context of PFASs leads us to conclude that associated activation energy barriers and reaction thermodynamics are directly related to the number of substituents around the carbon radical of interest between the reactant and product complexes. In most cases, the 1,2-F atom rearrangement is an exothermic, kinetically controlled process when more substituents (CF_3 groups) can stabilize the product radical relative to the reactant radical. This observation is attributed to the hyperconjugation interactions provided through the substituents, or in other words, 1,2-F atom shifts are thermodynamically favorable if the radical center in the product is more substituted than the radical center in the reactant.

The 1,2-F atom rearrangements are suggested to occur for a variety of perfluorinated substances; however, chain length was not observed to play a major role in the kinetic and thermodynamic profiles after four carbons were situated in a linear chain. Because 2° to 2° 1,2-F atom rearrangements are thermoneutral, F atom shifts in linear perfluoroalkanes are plausible, which could have wide implications in the degradation mechanisms and structural characteristics of these linear chains including β-scission of carbon−carbon bonds. For example, the degradation of various PFOA or PFOS isomers in oxic or anoxic environments could be reasoned through the ability for 1,2-F atom rearrangements to occur.

Hyperconjugation and the degree of branching was also observed to play a major role in the kinetics and favorability of perfluorinated substances containing benzylic and allylic functionalities. The degree of branching and the availability of the radical site to access nearby π-conjugation were a major factor in both thermodynamic and kinetic favorability. In general, in conjugated molecules with minimal CF_3 branching, the 1,2-F atom rearrangements were both more favored and had less activation energies, with allylic functionalities having slightly more favorable enthalpies of reaction and lower barrier energies, indicating that these rearrangements are more likely in these systems. Increasing the degree of CF_3 substitution in these conjugated molecules showed that hyperconjugation and conjugation can have similar magnitudes of effect due to steric factors and the ability to delocalize the radical near the rearrangement site. Steric factors and the relative degree of spin delocalization also contributed to making the allylic case slightly more thermodynamically and kinetically favored rearrangements compared to the benzyl analogues.

Assisted fluorine atom migration through one or two HF molecules and a combination of H_2O and HF lowered activation energy barriers for 1,2-F atom rearrangements in all cases explored, which led to the conclusion that solvent or mineralization products may facilitate the 1,2-F atom rearrangement further, particularly in aqueous systems with a combination of low pH and high amounts of F^-. In an oxidative degradation scheme, the experimentally suggested mechanisms for PFOA degradation suggest that as more and more HF is produced through elimination reactions the 1,2-F atom shift could be more prevalent as the time of treatment increases. The kinetics of these rearrangements in aqueous solution would also be temperature-dependent, with higher temperatures favoring faster kinetics for 1,2-F atom rearrangements.

Partial atomic charges and spin density analyses suggest that unassisted and small-molecule-assisted 1,2-F atom rearrangements occur via a fluorine radical intermediate. NBO results show that the partial atomic charge on the migrating fluorine does not change significantly throughout the rearrangement process, even in the case of small-molecule catalyzed rearrangements, indicating homolytic bond cleavage and a concerted mechanism.

We predict that 1,2-F atom rearrangements could be prominent isomerizations in radical species of perfluorinated molecules. Our study suggests that these reactions play a major role in high-energy and high-temperature environments. These isomerization processes may be a missing link in understanding defluorination rates, environmental fate and transport, and analytical detection and quantification of these compounds. Therefore, these isomerization events should be considered in most degradation PFASs processes, especially those that utilize high-energy/high-temperature techniques involving UV/VUV photons, sonolysis, and pyrolysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b08895.

All optimized molecular geometries utilized in this work (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: svyas@mines.edu. Phone: +1-303-273-3632.

ORCID

Shubham Vyas: 0000-0002-5849-8919

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors gratefully acknowledge the allocated computational resources at the high-performance computing facility at Colorado School of Mines and financial support from the National Science Foundation (CHE-1710079).

■ REFERENCES

(1) Rayne, S.; Forest, K. Perfluoroalkyl sulfonic and carboxylic acids: A critical review of physicochemical properties, levels and patterns in waters and wastewaters, and treatment methods. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2009**, *44*, 1145−1199.

(2) *EPA Lifetime health advisories and health effects support documents for perfluorooctanoic acid and perfluorooctane sulfonate*; Environmental Protection Agency, 2016; Vol. *81*, 33250−33251.

(3) Goss, K. U. The pK(a) values of PFOA and other highly fluorinated carboxylic acids. *Environ. Sci. Technol.* **2008**, *42*, 456−458.

(4) Goss, K. U.; Bronner, G. What is so special about the sorption behavior of highly fluorinated compounds? *J. Phys. Chem. A* **2006**, *110*, 9518−9522.

(5) Liu, Z. Z.; Goddard, J. D. Predictions of the fluorine NMR chemical shifts of perfluorinated carboxylic acids, CnF2n+1COOH (n = 6−8). *J. Phys. Chem. A* **2009**, *113*, 13921−13931.

(6) Rayne, S.; Forest, K. Theoretical studies on the pK(a) values of perfluoroalkyl carboxylic acids. *J. Mol. Struct.: THEOCHEM* **2010**, *949*, 60−69.

(7) Arvaniti, O. S.; Stasinakis, A. S. Review on the occurrence, fate and removal of perfluorinated compounds during wastewater treatment. *Sci. Total Environ.* **2015**, *524-525*, 81−92.

(8) Yang, S. Y.; Zhang, Y. T.; Zheng, D. Advanced reduction processes: a novel technology for water treatment. *Prog. Chem.* **2016**, *28*, 934−941.

(9) Merino, N.; Qu, Y.; Deeb, R. A.; Hawley, E. L.; Hoffmann, M. R.; Mahendra, S. Degradation and removal methods for perfluoroalkyl and polyfluoroalkyl substances in water. *Environ. Eng. Sci.* **2016**, *33*, 615−649.

(10) Rahman, M. F.; Peldszus, S.; Anderson, W. B. Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: A review. *Water Res.* **2014**, *50*, 318−340.

(11) Anumol, T.; Dagnino, S.; Vandervort, D. R.; Snyder, S. A. Transformation of polyfluorinated compounds in natural waters by advanced oxidation processes. *Chemosphere* **2016**, *144*, 1780−1787.

(12) Sun, B.; Ma, J.; Sedlak, D. L. Chemisorption of perfluorooctanoic acid on powdered activated carbon initiated by persulfate in aqueous solution. *Environ. Sci. Technol.* **2016**, *50*, 7618−7624.

(13) Zhang, T. L.; Pan, G.; Zhou, Q. Temperature effect on photolysis decomposing of perfluorooctanoic acid. *J. Environ. Sci.* **2016**, *42*, 126−133.

(14) Giri, R. R.; Ozaki, H.; Morigaki, T.; Taniguchi, S.; Takanami, R. UV photolysis of perfluorooctanoic acid (PFOA) in dilute aqueous solution. *Water Sci. Technol.* **2011**, *63*, 276−282.

(15) Chen, J.; Zhang, P. Photodegradation of perfluorooctanoic acid in water under irradiation of 254 and 185 nm light by use of persulfate. *Water Sci. Technol.* **2006**, *54*, 317−325.

(16) Qu, Y.; Zhang, C. J.; Li, F.; Chen, J.; Zhou, Q. Photo-reductive defluorination of perfluorooctanoic acid in water. *Water Res.* **2010**, *44*, 2939−2947.

(17) Qu, Y.; Zhang, C. J.; Chen, P.; Zhou, Q.; Zhang, W. X. Effect of initial solution pH on photo-induced reductive decomposition of perfluorooctanoic acid. *Chemosphere* **2014**, *107*, 218−223.

(18) Gu, Y. R.; Dong, W. Y.; Luo, C.; Liu, T. Z. Efficient reductive decomposition of perfluorooctanesulfonate in a high photon flux UV/sulfite system. *Environ. Sci. Technol.* **2016**, *50*, 10554−10561.

(19) Song, Z.; Tang, H. Q.; Wang, N.; Zhu, L. H. Reductive defluorination of perfluorooctanoic acid by hydrated electrons in a sulfite-mediated UV photochemical system. *J. Hazard. Mater.* **2013**, *262*, 332−338.

(20) Wang, Y.; Zhang, P. Y. Enhanced photochemical decomposition of environmentally persistent perfluorooctanoate by coexisting ferric ion and oxalate. *Environ. Sci. Pollut. Res.* **2016**, *23*, 9660−9668.

(21) Wang, Y.; Shi, X. Y. Photochemical degradation of perfluorocarboxylic acids induced by ferric ion: effects of pH and carbon chain. *Huaxue Xuebao* **2014**, *72*, 682−688.

(22) Li, M. J.; Yu, Z. B.; Liu, Q.; Sun, L.; Huang, W. Y. Photocatalytic decomposition of perfluorooctanoic acid by noble metallic nanoparticles modified TiO2. *Chem. Eng. J.* **2016**, *286*, 232−238.

(23) Fernandez, N. A.; Rodriguez-Freire, L.; Keswani, M.; Sierra-Alvarez, R. Effect of chemical structure on the sonochemical degradation of perfluoroalkyl and polyfluoroalkyl substances (PFASs). *Environ. Sci.: Water Res. Technol.* **2016**, *2*, 975−983.

(24) Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T.; Hoffmann, M. R. Kinetics and mechanism of the sonolytic conversion of the aqueous perfluorinated surfactants, perfluorooctanoate (PFOA), and perfluorooctane sulfonate (PFOS) into inorganic products. *J. Phys. Chem. A* **2008**, *112*, 4261−4270.

(25) Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T.; Hoffmann, M. R. Enhancement of perfluorooctanoate and perfluorooctanesulfonate activity at acoustic cavitation bubble interfaces. *J. Phys. Chem. C* **2008**, *112*, 16850−16857.

(26) Moriwaki, H.; Takagi, Y.; Tanaka, M.; Tsuruho, K.; Okitsu, K.; Maeda, Y. Sonochemical decomposition of perfluorooctane sulfonate and perfluorooctanoic acid. *Environ. Sci. Technol.* **2005**, *39*, 3388−3392.

(27) Lee, Y. C.; Chen, M. J.; Huang, C. P.; Kuo, J.; Lo, S. L. Efficient sonochemical degradation of perfluorooctanoic acid using periodate. *Ultrason. Sonochem.* **2016**, *31*, 499−505.

(28) Zhuo, Q. F.; Luo, M. Q.; Guo, Q. W.; Yu, G.; Deng, S. B.; Xu, Z. C.; Yang, B.; Liang, X. L. Electrochemical oxidation of environmentally persistent perfluorooctane sulfonate by a novel lead dioxide anode. *Electrochim. Acta* **2016**, *213*, 358−367.

(29) Zhuo, Q.; Deng, S.; Yang, B.; Huang, J.; Yu, G. Efficient electrochemical oxidation of perfluorooctanoate using a Ti/SnO2-Sb-Bi anode. *Environ. Sci. Technol.* **2011**, *45*, 2973−2979.

(30) Yang, B.; Jiang, C. J.; Yu, G.; Zhuo, Q. F.; Deng, S. B.; Wu, J. H.; Zhang, H. Highly efficient electrochemical degradation of perfluorooctanoic acid (PFOA) by F-doped Ti/SnO2 electrode. *J. Hazard. Mater.* **2015**, *299*, 417−424.

(31) Niu, J. F.; Li, Y.; Shang, E. X.; Xu, Z. S.; Liu, J. Z. Electrochemical oxidation of perfluorinated compounds in water. *Chemosphere* **2016**, *146*, 526−538.

(32) Lin, H.; Niu, J.; Ding, S.; Zhang, L. Electrochemical degradation of perfluorooctanoic acid (PFOA) by Ti/SnO2-Sb, Ti/SnO2-Sb/PbO2 and Ti/SnO2-Sb/MnO2 anodes. *Water Res.* **2012**, *46*, 2281−2289.

(33) Yin, P. H.; Hu, Z. H.; Song, X.; Liu, J. G.; Lin, N. Activated persulfate oxidation of perfluorooctanoic acid (PFOA) in groundwater under acidic conditions. *Int. J. Environ. Res. Public Health* **2016**, *13*, 602.

(34) Lee, Y.-C.; Lo, S.-L.; Kuo, J.; Lin, Y.-L. Persulfate oxidation of perfluorooctanoic acid under the temperatures of 20−40 degrees C. *Chem. Eng. J.* **2012**, *198-199*, 27−32.

(35) Lee, Y.; Lo, S.; Kuo, J.; Hsieh, C. Decomposition of perfluorooctanoic acid by microwaveactivated persulfate: Effects of temperature, pH, and chloride ions. *Front. Environ. Sci. Eng.* **2012**, *6*, 17−25.

(36) da Silva-Rackov, C. K. O.; Lawal, W. A.; Nfodzo, P. A.; Vianna, M.; do Nascimento, C. A. O.; Choi, H. Degradation of PFOA by hydrogen peroxide and persulfate activated by iron-modified diatomite. *Appl. Catal., B* **2016**, *192*, 253−259.

(37) Liu, C. S.; Higgins, C. P.; Wang, F.; Shih, K. Effect of temperature on oxidative transformation of perfluorooctanoic acid (PFOA) by persulfate activation in water. *Sep. Purif. Technol.* **2012**, *91*, 46−51.

(38) Villagrasa, M.; Lopez de Alda, M.; Barcelo, D. Environmental analysis of fluorinated alkyl substances by liquid chromatography-(tandem) mass spectrometry: a review. *Anal. Bioanal. Chem.* **2006**, *386*, 953−972.

(39) de Voogt, P.; Saez, M. Analytical chemistry of perfluoroalkylated substances. *TrAC, Trends Anal. Chem.* **2006**, *25*, 326−342.

(40) Rotander, A.; Karrman, A.; Toms, L. M. L.; Kay, M.; Mueller, J. F.; Gomez Ramos, M. J. Novel fluorinated surfactants tentatively identified in firefighters using liquid chromatography quadrupole time-of-flight tandem mass spectrometry and a case-control approach. *Environ. Sci. Technol.* **2015**, *49*, 2434−2442.

(41) Trier, X.; Granby, K.; Christensen, J. H. Tools to discover anionic and nonionic polyfluorinated alkyl surfactants by liquid chromatography electrospray ionisation mass spectrometry. *J. Chromatogr. A* **2011**, *1218*, 7094−7104.

(42) Arsenault, G.; McAlees, A.; McCrindle, R.; Riddell, N. Analysis of perfluoroalkyl anion fragmentation pathways for perfluoroalkyl carboxylates and sulfonates during liquid chromatography/tandem mass spectrometry: evidence for fluorine migration prior to secondary and tertiary fragmentation. *Rapid Commun. Mass Spectrom.* **2007**, *21*, 3803−3814.

(43) Wang, H. Y.; Gao, Y.; Zhang, F.; Yu, C. T.; Xu, C.; Guo, Y. L. Mass spectrometric study of the gas-phase difluorocarbene expulsion of polyfluorophenyl cations via F-atom migration. *J. Am. Soc. Mass Spectrom.* **2013**, *24*, 1919−1926.

(44) Marotta, E.; Paradisi, C. Isomerization and dissociation of C2 × 5+ and C2 × 4+center dot ions (X = Cl, F) from chlorofluoroethanes in an ion trap mass spectrometer. *J. Mass Spectrom.* **2002**, *37*, 1280−1286.

(45) Gao, Y.; Wang, H. Y.; Zhang, X.; Cheng, J. S.; Zhang, F.; Guo, Y. L. Gas-phase fluorine migration reactions in the radical cations of pentafluorosulfanylbenzene (Aryl-SF5) and benzenesulfonyl fluoride (Aryl-SO2F) derivatives and in the 2,5-xylylfluoroiodonium ion. *J. Mass Spectrom.* **2014**, *49*, 481−489.

(46) Huang, D. H.; Yin, L. F.; Niu, J. F. Photoinduced hydrodefluorination mechanisms of perfluorooctanoic acid by the SiC/graphene catalyst. *Environ. Sci. Technol.* **2016**, *50*, 5857−5863.

(47) Kunz, M.; Rétey, J. Evidence for a 1,2 shift of a hydrogen atom in a radical intermediate of the methylmalonyl-CoA mutase reaction. *Bioorg. Chem.* **2000**, *28*, 134−139.

(48) Madden, K. P.; Bernhard, W. A. A 1,2 hydrogen shift and other thermally induced free radical reactions in X-irradiated methyl.α.-D-glucopyranoside single crystals. An ESR-ENDOR study. *J. Phys. Chem.* **1980**, *84*, 1712−1717.

(49) Viana, R. B.; Varela, J. J. G., Jr.; Tello, A. C. M.; Savedra, R. M. L.; da Silva, A. B. F. The 1,2-hydrogen shift reaction for monohalogenophosphanes PH2X and HPX (X = F, CI). *Mol. Phys.* **2016**, *114*, 2999−3014.

(50) Gordon, A. S.; Tardy, D. C.; Ireton, R. Ethyl radical isomerization. A 1,2-hydrogen (deuterium) shift in the pyrolysis of 1,1,1-trideuterioethane. *J. Phys. Chem.* **1976**, *80*, 1400−1404.

(51) Neumann, B.; Zipse, H. 1,2-chlorine atom migration in 3-chloro-2-butyl radicals: a computational study. *Org. Biomol. Chem.* **2003**, *1*, 168−172.

(52) Zhu, L.; Bozzelli, J. W.; Kardos, L. M. Thermochemical properties, ΔfH°(298), S°(298), and Cp°(T), for n-butyl and n-pentyl hydroperoxides and the alkyl and peroxy radicals, transition states, and kinetics for intramolecular hydrogen shift reactions of the peroxy radicals. *J. Phys. Chem. A* **2007**, *111*, 6361−6377.

(53) Brooks, M. A.; Scott, L. T. 1,2-shifts of hydrogen atoms in aryl radicals. *J. Am. Chem. Soc.* **1999**, *121*, 5444−5449.

(54) Wang, K.; Villano, S. M.; Dean, A. M. Reactivity-structure-based rate estimation rules for alkyl radical H atom shift and alkenyl radical cycloaddition reactions. *J. Phys. Chem. A* **2015**, *119*, 7205−7221.

(55) Kobrina, L. S.; Kovtonyuk, V. N. Rearrangements with migration of a fluorine atom. *Russ. Chem. Rev.* **1988**, *57*, 62.

(56) So, S. P. 1,2-Fluorine shift rearrangement of 1,1,1-trifluoromethylcarbene to trifluoroethylene. *J. Phys. Chem.* **1993**, *97*, 11908−11911.

(57) Kovtonyuk, V. N.; Kobrina, L. S.; Volodin, A. M. ESR study of the 1,2-migration of F atoms in polyfluorinated radicals. *Russ. Chem. Bull.* **1995**, *44*, 95−98.

(58) Pretali, L.; Dondi, D.; D'Angelantonio, M.; Manet, I.; Fasani, E.; Monti, S.; Bovio, B.; Albini, A. A fluorine 1,2-migration via aryl cation/radical/radical anion/radical sequence. *Org. Lett.* **2013**, *15*, 3926−3929.

(59) Luo, T.; Zhang, R.; Zhang, W.; Shen, X.; Umemoto, T.; Hu, J. B. divergent rearrangements of cyclopropyl-substituted fluoroepoxides involving C-F bond cleavage and formation. *Org. Lett.* **2014**, *16*, 888−891.

(60) Farnham, W. B. Fluorinated carbanions. *Chem. Rev.* **1996**, *96*, 1633−1640.

(61) Kobrina, L. S. Radical reactions of aromatic polyfluorocompounds. *Russ. Chem. Rev.* **1977**, *46*, 348.

(62) Fossey, J.; Nedelec, J.-Y. Theoretical study of free-radical migrations. *Tetrahedron* **1981**, *37*, 2967−2976.

(63) Kotaka, M.; Sato, S. 1,2-Fluorine atom migration in the 1,1,2-trifluoroethyl radical. *J. Chem. Soc., Chem. Commun.* **1986**, *24*, 1783−1784.

(64) Kotaka, M.; Sato, S.; Shimokoshi, K. INDO study of 1,2-fluorine atom migration in 1,2-difluoroethyl and 1,1,2-trifluoroethyl radicals. *J. Fluorine Chem.* **1987**, *37*, 387−396.

(65) Kotaka, M.; Sato, S.; Shimokoshi, K. Indo study of 1,2-fluorine atom migration in 1,1,2,2-tetrafluoroethyl radical, cation and anion. *J. Fluorine Chem.* **1988**, *41*, 371−382.

(66) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson; et al.. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.

(67) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648.

(68) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−789.

(69) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *J. Phys. Chem.* **1994**, *98*, 11623−11627.

(70) Vosko, S. H.; Wilk, L.; Nusair, M. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. *Can. J. Phys.* **1980**, *58*, 1200−1211.

(71) Hratchian, H. P.; Schlegel, H. B. Using Hessian updating to increase the efficiency of a Hessian based predictor-corrector reaction path following method. *J. Chem. Theory Comput.* **2005**, *1*, 61−69.

(72) Fukui, K. The path of chemical-reactions - the IRC approach. *Acc. Chem. Res.* **1981**, *14*, 363−368.

(73) Tomasi, J.; Mennucci, B.; Cancès, E. The IEF version of the PCM solvation method: an overview of a new method addressed to study molecular solutes at the QM ab initio level. *J. Mol. Struct.: THEOCHEM* **1999**, *464*, 211−226.

(74) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO* version 3.1; 1992.

(75) Weinhold, F. Natural bond orbital analysis: A critical overview of relationships to alternative bonding perspectives. *J. Comput. Chem.* **2012**, *33*, 2363−2379.

(76) Everett, W. C.; Holmes, B. E.; Heard, G. L. A computational study of the threshold energies of the 1,2-FCl interchange reaction of chlorofluoroethanes. *Can. J. Chem.* **2010**, *88*, 1112−1117.

(77) Enstice, E. C.; Duncan, J. R.; Setser, D. W.; Holmes, B. E. Unimolecular reactions in the CF3CH2Cl < -> CF2ClCH2F system: isomerization by interchange of Cl and F atoms. *J. Phys. Chem. A* **2011**, *115*, 1054−1062.

(78) Solaka, S. A.; Boshamer, S. E.; Parworth, C. L.; Heard, G. L.; Setser, D. W.; Holmes, B. E. Isomerisation of CF2ClCH2Cl and CFCl2CH2F by interchange of Cl and F atoms with analysis of the unimolecular reactions of both molecules. *ChemPhysChem* **2012**, *13*, 869−878.

(79) Friederich, L.; Duncan, J. R.; Heard, G. L.; Setser, D. W.; Holmes, B. E. Unimolecular reactions of CH2BrCH2Br, CH2BrCH2Cl, and CH2BrCD2Cl: identification of the cl-br interchange reaction. *J. Phys. Chem. A* **2010**, *114*, 4138−4147.

(80) Kim, J. S.; Brandt, L. M.; Heard, G. L.; Holmes, B. E. Computational study of the threshold energy for the 1,2-interchange of X and R (X, R = halogens, pseudohalogens, and monovalent hydrocarbon groups) on CH2XCH2R. *Can. J. Chem.* **2016**, *94*, 1038−1043.

(81) Ferguson, J. D.; Johnson, N. L.; Kekenes-Huskey, P. M.; Everett, W. C.; Heard, G. L.; Setser, D. W.; Holmes, B. E. Unimolecular rate constants for HX or DX elimination (X = F, Cl) from chemically activated CF3CH2CH2Cl, C2H5CH2Cl, and C2D5CH2Cl: Threshold energies for HF and HCl elimination. *J. Phys. Chem. A* **2005**, *109*, 4540−4551.

(82) Heard, G. L.; Holmes, B. E. 1,2-FCl rearrangement as an intermediate step in the unimolecular 1,3-HCl elimination from chlorofluoropropanes. *J. Phys. Chem. A* **2001**, *105*, 1622−1625.

(83) Gu, Y.; Liu, T.; Zhang, Q.; Dong, W. Efficient decomposition of perfluorooctanoic acid by a high photon flux UV/sulfite process: Kinetics and associated toxicity. *Chem. Eng. J.* **2017**, *326*, 1125−1133.

(84) Huang, D.; Yin, L.; Lu, X.; Lin, S.; Niu, Z.; Niu, J. Directional electron transfer mechanisms with graphene quantum dots as the electron donor for photodecomposition of perfluorooctane sulfonate. *Chem. Eng. J.* **2017**, *323*, 406−414.

(85) Cormanich, R. A.; O'Hagan, D.; Bühl, M. hyperconjugation is the source of helicity in perfluorinated n-alkanes. *Angew. Chem., Int. Ed.* **2017**, *56*, 7867−7870.

(86) Sansotera, M.; Persico, F.; Rizzi, V.; Panzeri, W.; Pirola, C.; Bianchi, C. L.; Mele, A.; Navarrini, W. The effect of oxygen in the photocatalytic oxidation pathways of perfluorooctanoic acid. *J. Fluorine Chem.* **2015**, *179*, 159−168.

(87) Baskir, E. G.; Korolev, V. A.; Nefedov, O. M. Photo-isomerization of the perfluoroallyl radical: a FTIR matrix-isolation study. *Mendeleev Commun.* **2000**, *10*, 125−126.

(88) Hu, X.; Goumri, A.; Marshall, P. The kinetics of the reaction of H atoms with C4F6. *J. Phys. Chem. A* **2001**, *105*, 11220−11225.

(89) Van Hoomissen, D. J.; Vyas, S. Impact of conjugation and hyperconjugation on the radical stability of allylic and benzylic systems: A theoretical study. *J. Org. Chem.* **2017**, *82*, 5731−5742.

(90) Konya, K. G.; Paul, T.; Lin, S.; Lusztyk, J.; Ingold, K. U. laser flash photolysis studies on the first superoxide thermal source. first direct measurements of the rates of solvent-assisted 1,2-hydrogen atom shifts and a proposed new mechanism for this unusual rearrangement. *J. Am. Chem. Soc.* **2000**, *122*, 7518−7527.

(91) Fernández-Ramos, A.; Zgierski, M. Z. Theoretical study of the rate constants and kinetic isotope effects of the 1,2-hydrogen-atom shift of methoxyl and benzyloxyl radicals assisted by water. *J. Phys. Chem. A* **2002**, *106*, 10578−10583.

(92) Niu, J.; Lin, H.; Gong, C.; Sun, X. Theoretical and experimental insights into the electrochemical mineralization mechanism of perfluorooctanoic acid. *Environ. Sci. Technol.* **2013**, *47*, 14341−14349.

(93) Luo, T.; Zhang, R.; Shen, X.; Zhang, W.; Ni, C.; Hu, J. Bronsted acid-catalyzed 1,2-fluorine migration with fluoroepoxides. *Dalton Trans.* **2015**, *44*, 19636−19641.

(94) Czarnowski, J. The 1,2-fluorine atom migration in the epoxide of 1,1-dichlorodifluoroethene. The infrared spectrum of dichloro-fluoroacetyl fluoride. *J. Fluorine Chem.* **1990**, *47*, 193−198.

(95) Gómez-Jeria, J. S. An empirical way to correct some drawbacks of mulliken population analysis. *J. Chil. Chem. Soc.* **2009**, *54*, 482−485.