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Thermodynamics of aqueous perfluorooctanoic acid (PFOA) and 4,8-dioxa-3H-perfluorononanoic acid (DONA) from DFT calculations: Insights into degradation initiation

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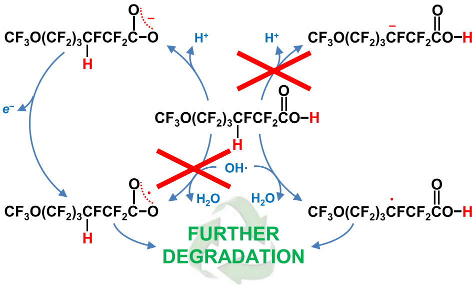
HIGHLIGHTS

- H-abstraction by OH· is thermodynamically favored on hydroperfluosurfactants.
- Conformational flexibility should be always considered for perfluoroether chains.
- A standard reduction potential of 2.2 V was estimated for $C_7F_{15}COO\cdot$ at DFT level.
- The pK_a of polyfluorocarboxylic acids is strongly influenced by substituents.

GRAPHICAL ABSTRACT



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ABSTRACT

Modern fluorosurfactants introduced during and after perfluoroalkyl carboxylates/sulfonates phase-out present chemical features designed to facilitate abatement, hence reducing persistence. However, the implications of such features on environmental partitioning and stability are yet to be fully appreciated, partly due to experimental difficulties inherent to the handling of their (diluted) aqueous solutions. In this work, rigorous quantum chemistry calculations were carried out in order to provide theoretical insights into the thermodynamics of hydroperfluorosurfactants in aqueous medium. Estimates of acid dissociation constant (pK_a), standard reduction potential (E^0), and bond dissociation enthalpy (BDE) and free energy (BDFE) were computed for perfluorooctanoic acid (PFOA), 4,8-dioxa-3H-perfluorononanoic acid (DONA) and their anionic forms *via* ensemble averaging at density functional theory level with implicit solvent models. A $\langle pK_a \rangle$ in the neighborhood of zero and a E^0 of about 2.2 V were obtained for PFOA. Predictions for the acidic function of DONA compare well with PFOA's, with a pK_a of 0.8–1.5 and a E^0 of 2.07–2.15 V. Deprotonation thus represents the dominant phenomenon at environmental conditions. Calculations indicate that H-abstraction of the aliphatic proton of DONA by a hydroxyl radical is the thermodynamically favored reaction path in oxidative media, whereas hydrolysis is not a realistic scenario due to the high dissociation constant. Short intramolecular interactions available to the peculiar hydrophobic tail of DONA were also reviewed, and the relevance of the full conformational space of the fluorinated side chain discussed.

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1. Introduction

Perfluorocarboxylic acids (PFCAs) fall in the chemical class of fully fluorinated carboxylic acids. Within this class, perfluorooctanoic acid (PFOA) was the compound with the largest number of applications in industry (Ameduri, 2009; Drobny, 2009; Grot, 2008; Moody and Field, 2000; Schultz et al., 2013). PFOA was in fact widely employed as surfactant in the synthesis of a variety of fluoropolymers, as hydrophobizing agent in outdoor clothing, etching agent on fused silica, as well as a component in fire-fighting foams. However, several studies demonstrated that PFOA and other perfluoroalkyl surfactants are bioaccumulative, carcinogenic, and toxic for liver, immune, and endocrine systems (Andersen et al., 2010; Lau et al., 2007; Post et al., 2012; Prevedouros et al., 2006; Sedlak, 2016; Ylinen et al., 1985). Thus, PFOA and perfluoroalkyl surfactants were listed as persistent organic pollutants under the Stockholm Convention, and their production was restricted and eventually discontinued in 2015. The decade preceding the phase out witnessed the introduction of several non-perfluoroalkyl PFOA alternatives (Wang et al., 2013; Zaggia and Ameduri, 2012). Furthermore, following the phase out decision, in order to address the recognized environmental threat posed by fluorosurfactants, a large number of approaches were considered and extensively tested to identify convenient techniques for their mineralization. In this context, PFOA was thoroughly adopted as the prototypical perfluoroalkyl emulsifier. Chemical, thermal, and photolytic stability of perfluorinated compounds are directly related to the high dissociation energy of C—F bonds (Amii and Uneyama, 2009; Avataneo et al., 2009; Lemal, 2004; Persico et al., 2013), which makes conventional degradation techniques rather inefficient. Advanced oxidation processes are thus required. These comprise Fenton and photo-Fenton treatments (Mitchell et al., 2014; Zepp et al., 1992), ozonization (Hoigne and Bader, 1983a, 1983b), photochemical treatments (Chen and Zhang, 2006; Hori et al., 2004; Li et al., 2017), photocatalytic techniques (Gatto et al., 2015; Sansotera et al., 2014), electrochemical oxidation (Niu et al., 2013, 2016), sonochemical degradation (Moriwaki et al., 2005), photolysis (Kochany and Bolton, 1992), and thermolysis (Krusic et al., 2005). Advanced reduction processes have also been proposed (Qu et al., 2014; Zhang et al., 2014; Vellanki et al., 2013; Song et al., 2013).

Improvement of abatement techniques toward higher efficiency and higher throughput requires a comprehensive understanding of the underlying mechanisms of degradation of PFOA. However, decomposition routes reported in literature were mainly speculated due to experimental limitations in the detection of degradation intermediates (Vecitis et al., 2009). Quantum chemistry methods were also considered as alternative approaches for the prediction of reaction mechanisms, as they were successfully applied to the study of other organic pollutants. However, despite the variety of degradation pathways proposed so far for PFOA (Kutsuna and Hori, 2007; Niu et al., 2013, 2016; Park et al., 2009; Sansotera et al., 2015), the very first few steps of the mechanism are largely agreed upon: acid dissociation followed by the oxidation of the resulting carboxylate to carboxyl radical.

The inherent difficulties associated with the study of such degradation processes are further aggravated by the absence of a general agreement on important chemical-physical properties of PFOA and of other perfluoroalkyl surfactants, such as their acid dissociation constant, pK_a, and the standard reduction potential of the corresponding carboxyl radical to a carboxylate anion, E^0. The appraisal of these quantities, *via* either computational prediction as attempted in this work, or experimental measurement, is valuable to the understanding of degradation mechanisms, to the identification of appropriate abatement processes, as well as to the design of environmentally-friendly alternatives. Working with aqueous solution of fluorinated surfactants, however, is reported to be a difficult task (Goss et al., 2006; Guo et al., 1991; López-Fontán et al., 2005; Kutsuna et al., 2012; Moroi et al., 2001) due to their scarce solubility in water, their tendency to aggregate in aqueous media even around picomolar concentrations, their habit to accumulate at air/water and glassware/water interfaces, and their preferential solvation by the alcoholic component of hydroalcoholic solvents. As such, a continued debate exists and several researchers reported markedly different results over a very short span of time.

The value of the pK_a rules the dissociation degree of the emulsifier, which is relevant in the context of transport processes between liquid and gas phases by directly influencing partition coefficients (Vierke et al., 2013). Spectroscopic measurements reported by Cheng et al. (2009) on micromolar aqueous perfluorooctanoate anion solutions, as well as computational analyses produced by Goss (2008) *via* popular thermochemistry codes SPARC and COSMO-RS, and by Rayne et al. (2009) and Rayne and Forest (2010a) *via* accurate solvation free energies at semi-empirical and DFT level, all agreed on a pK_a value for PFOA in the neighborhood of zero. In contrast, Burns et al. (2008) proposed a monomeric pK_a value of 3.8 by means of alkalimetric titration measurements performed in a methanol-water mixed solvent, after extrapolation to zero methanol and PFOA concentration.

Standard reduction/oxidation potentials represent a direct measure of the thermodynamic feasibility of an electrochemical half-reaction, and are consequently relevant to the oxidation step of the carboxylate species. As an example, the environmental persistence of halogenated aliphatic compounds has been found to correlate with their relative reduction potentials (Patterson et al., 2001; Totten and Roberts, 2001; van Pée and Unversucht, 2003). Unfortunately, to the best of the author's knowledge, an estimate of reduction potential in aqueous media has yet to be reported for PFOA. In this regard, however, it is possible to devise reasonable upper and lower limits based on experimental oxidation procedures detailed in the literature (Vecitis et al., 2009; Merino et al., 2016). On one hand, the hydroxyl radical is reportedly highly inefficient in the oxidation of PFOA, with a one-electron reduction potential of 1.9 V (Buxton et al., 1988). On the other hand, the sulfate radical, $SO_4{\cdot}^-$, exploiting a one-electron reduction potential of 2.3 V (Wardman, 1989), has been successfully employed in the degradation of several perfluorinated carboxylates in water, including PFOA (Hori et al., 2005).

Historically, almost all fluoropolymer manufacturers employed ammonium perfluorooctanoate (APFO) and other long-chain ammonium perfluorocarboxylates as emulsifiers. Following their phase out, most manufacturers developed their own alternatives. The large majority of these alternative surfactants is reportedly based on functionalized perfluoropolyethers (PFPEs), and, in some cases, by fluorotelomers and other partially hydrogenated species (Wang et al., 2013). However, due to relative novelty, little is currently known about the environmental fate and the potential toxicity of most of the APFO replacement compounds in production and in active usage across the globe. Among others, ammonium 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-(trifluorometoxy)propoxy)propanoate, commonly known as ammonium 4,8-dioxa-3H-perfluorononanoate (ADONA), from Dyneon—3M, is an interesting example of a partially hydrogenated perfluorooligoether (Gordon, 2011; Hintzer et al., 2007, 2010; VonHooks, 2013).

In the following sections, a number of computational predictions of acid dissociation constants and standard reduction potentials for PFOA and its conjugated base will be presented and critically validated based on literature. Subsequently, the results of similar calculations on acidic and aliphatic protons of 4,8-dioxa-3H-perfluorononanoic acid (DONA) will be discussed in details. An