

# Cl-Initiated oxidation of *N*-ethyl-perfluoroalkanesulfonamides: A theoretical insight into the experimentally observed products

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## Abstract

Theoretical calculations at the B3LYP level of theory were performed to investigate the Cl-initiated oxidation of the *N*-ethyl-perfluorobutanesulfonamide ( $C_4F_9SO_2-NH-CH_2CH_3$ ; NEtFBSA). We studied in particular the thermodynamic aspects of the possible oxidation reactions so to obtain a first indication on the conceivably preferred pathways and on the structure and stability of the observed products. The reactions of Cl with the model compound  $CF_3SO_2-NH-CH_2CH_3$  produce the three primary radicals  $CF_3SO_2-N-CH_2CH_3$  (**1**),  $CF_3SO_2-NH-CHCH_3$  (**2**), and  $CF_3SO_2-NH-CH_2CH_2$  (**3**). Both **2** and **3** react exoergically with  $O_2$  and eventually form the ketone  $CF_3SO_2-NH-C(O)-CH_3$  and the aldehyde  $CF_3SO_2-NH-CH_2-C(O)-H$ , respectively. The addition of  $O_2$  to the N atom of **1** is instead endoergic, but the radical can exoergically react with  $RO_2$  with formation of  $CF_3SO_2-N(O)-CH_2CH_3$ ,  $CF_3SO_2-O-N-CH_2CH_3$ , and/or  $CF_3SO_2-N-O-CH_2CH_3$ . These three intermediates may in turn react with  $HO_2$  to produce, at least in principle, the four neutral products  $CF_3SO_2-N(OH)-CH_2CH_3$ ,  $CF_3SO_2-N(O)H-CH_2CH_3$ ,  $CF_3SO_2-O-NH-CH_2CH_3$ , and  $CF_3SO_2-NH-O-CH_2CH_3$ . This explains the proposed formation of a mixture of isomeric products of general formula  $C_4F_9SO_2N(C_2H_5OH)$  from the Cl-initiated oxidation of NEtFBSA.  $CF_3SO_2-N(O)-CH_2CH_3$  and  $CF_3SO_2-O-N-CH_2CH_3$  may also dissociate into  $CH_3CH_2-NO$  and  $CF_3SO_2$  and/or  $CF_3$ . This suggests that the sulfonamide radicals  $C_nF_{2n+1}SO_2-N-CH_2CH_3$ , once oxidized, could be direct precursors of perfluoroalkancarboxylic acids *via*  $C_nF_{2n+1}SO_2$  and  $C_nF_{2n+1}O_2$ . The formation of  $C_nF_{2n+1}SO_3-O-N-CH_2CH_3$  by reaction of  $C_nF_{2n+1}SO_2-N-CH_2CH_3$  with  $O_2$ , while exoergic, is not supported by the experiments on the Cl-initiated oxidation of NEtFBSA.

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## 1. Introduction

Perfluoroalkanesulfonates (PFSAs,  $CF_3(CF_2)_nSO_3^-$ ) and perfluoroalkancarboxylates (PFCAs,  $CF_3(CF_2)_nCO_2^-$ ), extensively used for over 40 years in a number of applications [1,2], have been recently detected as persistent contaminants of wildlife [3], including species in the remote Arctic zones [4]. The physical and chemical properties of PFSAs and PFCAs are, however, only little compatible with atmospheric transport, and two hypotheses have been

proposed to explain the observation of PFSAs and PFCAs far from major production and emission areas. First, water-soluble compounds such as the shorter-chain PFCAs may be transported directly by sea currents or by means of sea-spray [2,3,5]. Alternatively, persistent PFSAs and PFCAs may be formed by “in situ” oxidation of suitable volatile precursors which undergo long-range atmospheric transport far from their point(s) of emission. This hypothesis, recently corroborated by novel experiments [6,7], was first suggested [8] by the detection in ambient air of industrially-employed perfluoroalkane compounds such as the fluorotelomer alcohols  $C_nF_{2n+1}C_2H_4OH$  ( $n = 6, 8, 10$ ) and the *N*-substituted perfluorooctanesulfonamides  $C_8F_{17}$

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SO<sub>2</sub>-NH-CH<sub>2</sub>CH<sub>3</sub>, C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>-N(CH<sub>3</sub>)-CH<sub>2</sub>CH<sub>2</sub>OH, and C<sub>8</sub>F<sub>17</sub>SO<sub>2</sub>-N(CH<sub>2</sub>CH<sub>3</sub>)-CH<sub>2</sub>CH<sub>2</sub>OH. Subsequent studies [9–12] established that the atmospheric fate of the fluorotelomer alcohols includes substantial long-range atmospheric transport and gas-phase production of PFCAs. More recently, using the Cl atom as a surrogate of OH, Mabury, Wallington, and co-workers investigated the Cl-initiated oxidation of the two model compounds *N*-methyl-perfluorobutanesulfonamidoethanol (C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>-N(CH<sub>3</sub>)-CH<sub>2</sub>CH<sub>2</sub>OH) [13], and *N*-ethyl-perfluorobutanesulfonamide (C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>-NH-CH<sub>2</sub>CH<sub>3</sub>; NEtFBSA) [14]. In particular, liquid chromatography/tandem mass spectrometry (LC/MS/MS) experiments showed that the products obtained from NEtFBSA included the ketone C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>-NH-C(O)-CH<sub>3</sub> and the aldehyde C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>-NH-CH<sub>2</sub>-C(O)-H, obtained from the oxidation of the ethyl group of NEtFBSA, the aldehyde C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>-NH-C(O)-H, obtained from the oxidation of C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>-NH-CH<sub>2</sub>-C(O)-H, and a species whose anion was identified as C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>-N-(C<sub>2</sub>H<sub>5</sub>O)<sup>-</sup> by high-resolution MS but whose structure remained tentative. Another aldehyde or ketone probably arising from this unknown compound was also detected, together with the sulfonamide C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>-NH<sub>2</sub>. Perfluorobutanesulfonate was not revealed above the level of the blank, while the three PFCAs C<sub>3</sub>F<sub>7</sub>CO<sub>2</sub><sup>-</sup>, C<sub>2</sub>F<sub>5</sub>CO<sub>2</sub><sup>-</sup>, and CF<sub>3</sub>CO<sub>2</sub><sup>-</sup> were detected in all samples. While the formation of C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>-NH-C(O)-CH<sub>3</sub> and C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>-NH-CH<sub>2</sub>-C(O)-H can be explained by typical reaction sequences [15] commenced by H-atoms abstraction from the ethyl group of NEtFBSA, the “unknown” product reasonably arises from the oxidation of the primary N-radical C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>-N-CH<sub>2</sub>CH<sub>3</sub>. The atmospheric fate of the amine radicals R<sub>1</sub>-N-R<sub>2</sub> has however received only limited attention [16], and, in particular, neither experimental nor theoretical studies have been reported on the structure and stability of the products arising from the oxidation of the sulfonamide radicals R<sub>1</sub>-SO<sub>2</sub>-N-R<sub>2</sub>. We therefore decided to undertake a theoretical investigation on the Cl-initiated oxidation of the model compound CF<sub>3</sub>SO<sub>2</sub>-NH-CH<sub>2</sub>CH<sub>3</sub>. As noted previously [14], the length of the perfluorinated chain is not expected to have a substantial effect on the reactivity of perfluoroalkanesulfonamides. Our calculations describe in particular the thermodynamic aspects of the possible Cl-initiated oxidation reactions of the *N*-ethyl-perfluoroalkanesulfonamides so to obtain a first indication on the conceivably preferred pathways and on the structure and stability of the observed products.

## 2. Computational methods

The quantum chemical calculations were performed using the Unix version of the Gaussian03 [17] set of programs. The geometries of the investigated molecules and radicals were optimized using the hybrid exchange correlation functional B3LYP, which combines the Becke’s three-terms exchange functional [18,19] with the non-local corre-

lation functional of Lee, Yang, and Parr [20], in conjunction with the 6-31++G(d,p) basis set [21]. The total energies were subsequently refined by B3LYP/6-311++G(2df,2pd) single-point calculations. All the stationary points located on the B3LYP/6-31++G(d,p) potential energy surface, obtained by unconstrained gradient procedures [22–25], were unambiguously characterized as energy minima by calculating their harmonic vibrational frequencies. The unscaled values were also used to evaluate the zero-point energies and the vibrational contribution to the thermal correction (TC), obtained at 298.15 K by standard statistical mechanics formulas [26]. The overall TC term was finally obtained by adding the translational (3/2 *RT*) and rotational (*RT* or 3/2 *RT*) contributions at this temperature. The total entropies were calculated using the B3LYP/6-31++G(d,p) harmonic frequencies and moments of inertia.

## 3. Results and discussion

Scheme 1 shows the most relevant elementary steps of our proposed mechanism of the Cl-initiated gas-phase oxidation of CF<sub>3</sub>SO<sub>2</sub>-NH-CH<sub>2</sub>CH<sub>3</sub>. The products indicated by boxes are the corresponding analogues of those experimentally observed from the Cl-initiated oxidation of NEtFBSA [14]. For any unimolecular or bimolecular reaction, the positive or negative quoted values are the enthalpy ( $\Delta H$ ) and the free energy change ( $\Delta G$ ) calculated from the data listed in Table 1. The relevant optimized geometric parameters of selected intermediates (particularly those involved in the oxidation of the sulfonamide radical CF<sub>3</sub>SO<sub>2</sub>-N-CH<sub>2</sub>CH<sub>3</sub>) are shown in Fig. 1.

### 3.1. H-atom abstraction from CF<sub>3</sub>SO<sub>2</sub>-NH-CH<sub>2</sub>CH<sub>3</sub>: formation of the primary radicals

The primary reactions of the Cl-initiated oxidation of NEtFBSA were proposed to be the H-atom abstraction from the carbons of the ethyl moiety and from the nitrogen atom [14]. Consistently, from Scheme 1, the reaction of Cl with any H atom of CF<sub>3</sub>SO<sub>2</sub>-NH-CH<sub>2</sub>CH<sub>3</sub> is exoergic by 5–14 kcal mol<sup>-1</sup> and produces the three isomeric radicals **1** (from NH), **2** (from CH<sub>2</sub>), and **3** (from CH<sub>3</sub>). All these species are true minima on the doublet B3LYP/6-31++G(d,p) potential energy surface, and, at the B3LYP/6-311++G(2df,2pd)//B3LYP/6-31++G(d,p) level of theory, their order of stability is **2** > **1** > **3**. The secondary C-radical **2** is therefore more stable than the primary radical **3** (this is likely due to the ability of the lone pair on N to stabilize the radical center) and their formation from CF<sub>3</sub>SO<sub>2</sub>-NH-CH<sub>2</sub>CH<sub>3</sub> does not produce appreciable structural changes. The formation of the sulfonamide radical **1** results as well in essentially unchanged bond distances, while the C–N–S bond angle reduces by nearly 8 degrees. We note also the symmetry change of the skeletal conformation from C<sub>1</sub> to C<sub>s</sub>.

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