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A theoretical study on the pyrolysis of perfluorobutanoic acid as a model compound for perfluoroalkyl acids

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ABSTRACT

The potential energy surface is mapped out for all plausible reactions in the self-decomposition of perfluorobutanoic acid ($CF_3CF_2CF_2COOH$) as a model compound for the notoriously toxic and bio-accumulative perfluoroalkyl acids. Initial decomposition of perfluorobutanoic acid is found to be controlled by HF elimination and the formation of an α-lactone intermediate. The fate of this intermediate is predicted to be dominated by two competing channels, namely formation of pentafluoropropanoyl fluoride (CF_3CF_2COF) and the closed-shell singlet CF_3CF_2CF:. Direct elimination of CO_2 through decarboxylation is found to be retarded by strong hyperconjugation effects induced by fluorine atoms on the carbon chain. The results presented herein provide insightful information towards a comprehensive understanding of the decomposition of perfluoroalkyl acids in thermal systems.

The scientific community has begun to explore a new class of polyfluorinated compounds, the perfluoroalkyl acids (PFCAs), in terms of their origins, health impacts and environmental occurrence. This new frontier in environmental chemistry has gained increasing scientific and regulatory interest in recent years.[1] PFCAs are detected ubiquitously in various environmental matrices in urban areas and in regions as remote as the Arctic.[2] These compounds tend to bio-accumulate in living tissues with no proven degradation pathways under conditions encountered in biotic and abiotic media. The environmental persistency of these compounds enables long-range oceanic and atmospheric transport. PFCAs are believed to cause serious health problems, including propensity to cause certain types of cancer, as is evident from tests on animals in laboratories. Currently, the largest proportion of PFCAs is believed to be emitted into the environment via the production and the use of fluorinated products.[3] However, a significant portion of perfluoroalkyl acids is believed to be produced from the degradation of larger fluorinated compounds such as fluorinated polymers.

As fluorine-based products are usually deployed at the peak point of their thermal stability, there has been a growing interest since the early 1970s to investigate the thermal degradation of fluoropolymers and the subsequent emission of PFCAs. In fact, pyrolysis of product-based fluoropolymers has proven to be a viable option for their recycling.[4] For instance, Ellis et al.,[5] found that the thermolysis of different commercial fluoropolymers produced a wide range of PFCAs. Accordingly, there is a need to understand the decomposition behaviour of PFCAs at elevated temperatures. Thermal decomposition of perfluorooctanoic acid (PFOA)[6] and ammonium perfluorooctanoate[7] (APFO) has been investigated by NMR spectroscopy. In the case of perfluorooctanoic acid,[6] it was found that the thermal decomposition was dominated by elimination of HF and the subsequent formation of 1*H*-perfluoroheptane. Notably, the decomposition rate of PFOA was found to be strongly accelerated by the addition of crushed quartz to the reactor, indicating plausible catalysed activation.

There is a consensus of opinion in the literature that the length of the perfluorinated carbon chain (i.e., *n* from 4 to 14) does not alter the prominent physical and chemical properties of PFCAs.[1] To this end, this contribution addresses theoretically the unimolecular decomposition of perfluorobutanoic acid ($n = 4$) as a model compound for PFCAs. The results presented herein should be instrumental in the pursuit of understanding the fate and the transformation of PFCAs in thermal systems.

All structural and energy calculations were carried out using the GAUSSIAN03[8] suite of programmes. The potential energy surface for the unimolecular decomposition of perfluorobutanoic was explored using the G3MP2B3[9] composite method. The G3MP2B3 method performs initial optimisation and frequency calculations at the B3LYP/6-31G(d)[10] level followed by accurate single point energy calculations. All transition structures were linked to their corresponding reactants and products by performing intrinsic reaction coordinate (IRC) calculations. Rate constant calculations were carried out using the CHEMRATE programme.[11] Reaction rate constants at atmospheric pressure were obtained from RRKM theory.[12] The

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collisional energy transfer is described using an exponential-down model with $\Delta E_{down} = 200\ cm^{-1}$. This value is chosen to mimic the nature of He as a weak collider.[13] The Lennard–Jones parameters used for perfluorobutanoic acid were adopted from the corresponding values of C_3F_8, $\sigma = 4.705$ Å and $k/\varepsilon_b = 383.05$ K.[14]

Unimolecular decomposition of perfluorobutanoic acid

The potential energy surface (PES) for the unimolecular decomposition of perfluorobutanoic acid (**M**) is shown in Figure 1. The geometries of the transition structures are depicted in Figure 2. As shown in Figure 1, the PES exhibits seven distinct initial decomposition pathways. The three considered barrierless β C–C bond fissions are highly endoergic in the range 85.3–93.7 kcal/mol. The reverse reactions are also barrierless. Furthermore, the bond dissociation enthalpies for O–H (89.0 kcal/mol) and C–F (121.0 kcal/mol) are also very energy demanding. Accordingly, direct bond scissions are most likely to be of rather minor importance in the decomposition of PFCAs.

Direct elimination of a CO_2 molecule, could take place through two routes as shown in the upper part of Figure 1. In the first route, a CO_2 molecule departs the **M** moiety simultaneously with transfer of the hydroxy hydrogen atom to form 1,1,1,2,2,3,3-heptafluoropropane (**M1**). The transition structure (TS1) resides 77.3 kcal/mol above the initial reactant and the reaction is exoergic by 16.2 kcal/mol. The second decarboxylation route is characterised by the four-centre transition structure, TS2. TS2 resembles migration of the hydroxy H atom to the trifluoromethyl group with the subsequent elimination of perfluoroethene (**M2**) and CO_2. The energy barrier of TS2 amounts to 96.2 kcal/mol. The formation of trifluoroacetic acid (**M3**) and perfluoroethene (**M2**) via the transition state TS3 is associated with the highest energy requirement (129.2 kcal/mol) among the seven plausible initial channels. In comparison with acetic acid,[15] or its derivatives[16] such as $NH_2C(O)CH_2$– and CF_3CH_2–, the apparent high reaction barrier associated with direct decarboxylation can be interpreted based on stabilisation of the carbon chain by hyperconjugation induced by fluorine atoms.[17]

Elimination of a molecule of HF through the five-membered transition structure TS4 is the most favourable initial channel with an activation barrier of 54.2 kcal/mol. This finding is in accord with experimental observations from the pyrolysis of fluoroacetic acid[18] and perfluorooctanoic acid[6] where HF molecules were reported to be the dominant initial channels. The importance of HF elimination as the dominant initial channel has also been reported in previous theoretical studies on the self-decomposition of fluoroacetic acid.[19,20] The products of this channel, namely, HF and the α-lactone intermediate **M10** lie 35.1 kcal/mol above the initial reactant. The analogous epoxide intermediate of CF_2CO_2 was also considered to be an important intermediate in the pyrolysis of fluoroacetic acid following HF elimination.[20] It is worthwhile mentioning that α-lactones are normally very transient species in solution. However, bulky perfluorinated α-lactones are reported to be stable at room temperature.[21,22] In solution, α-lactones are formed by internal SN2-like backside ionic displacement.[21,22]

The fate of the intermediate **M10** appears to be controlled by two reactions with comparable activation energies, namely expulsion of CO_2 and CO molecules via TS5 and TS6, respectively. Formation of the closed-shell singlet carbene **M11** and a molecule of CO_2 from **M10** requires an activation energy of 13.8 kcal/mol. This

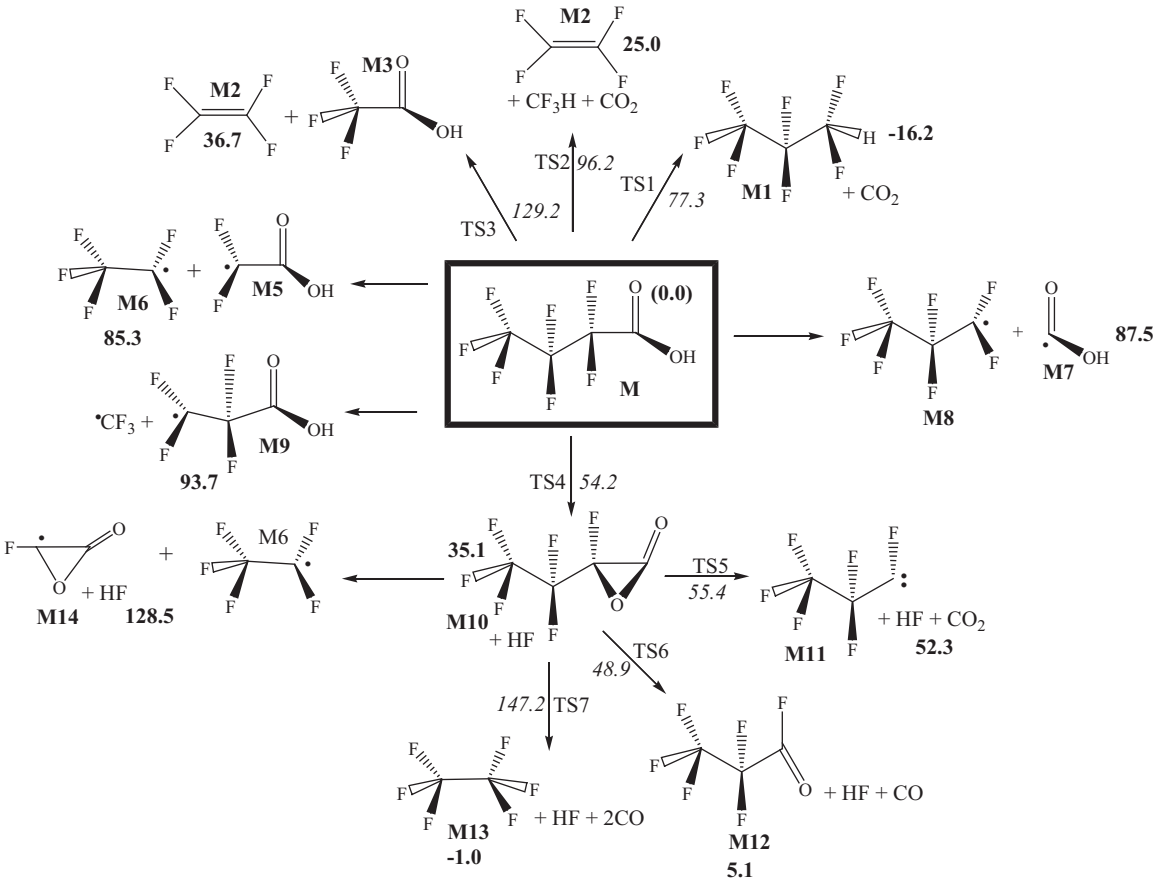

Figure 1. Potential energy surface for the unimolecular decomposition of perfluorobutanoic acid (**M**). Values in bold and italic are reaction and activation energies; respectively, at 0 K. All values in reference to the initial reactant (**M**).

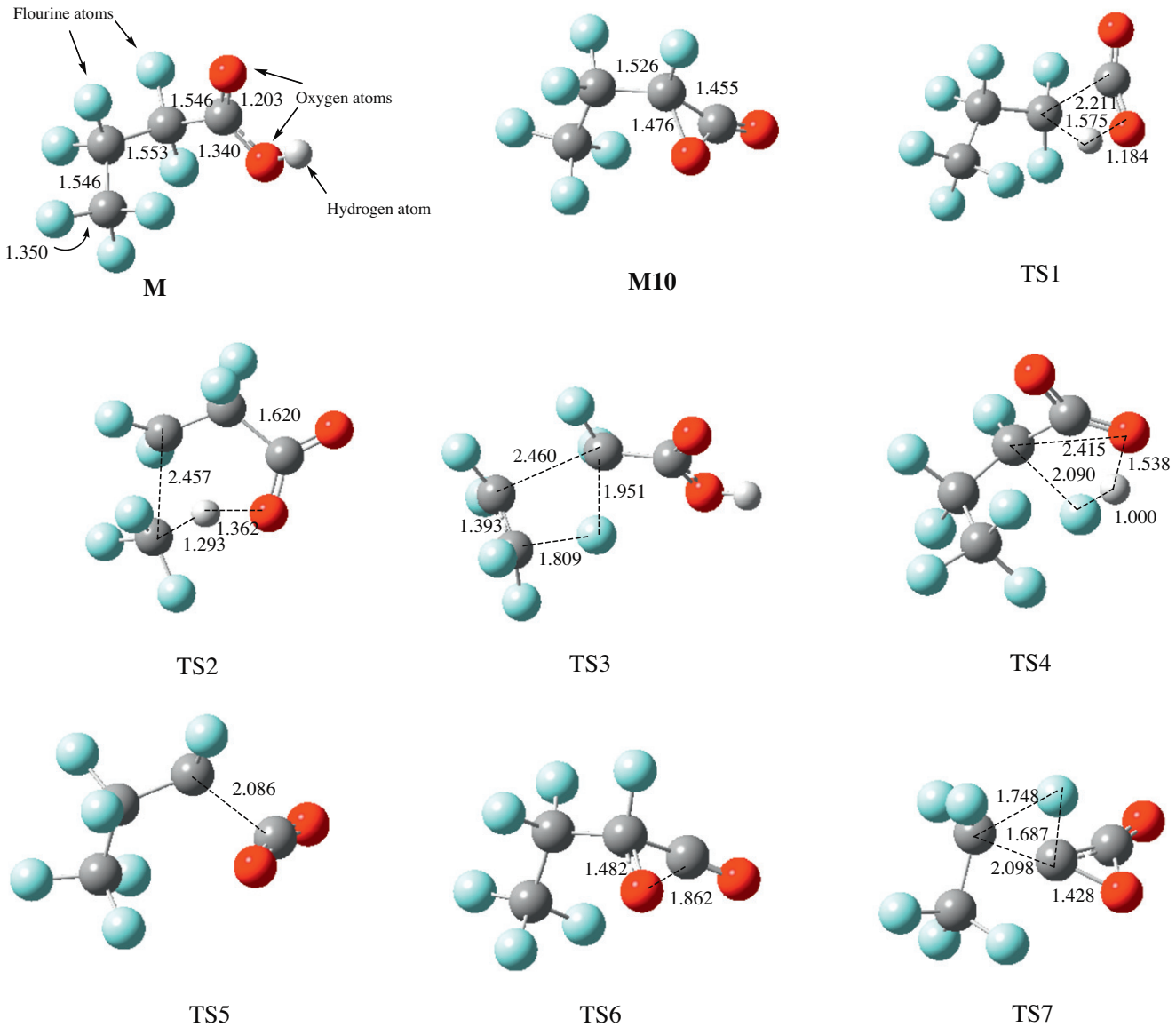

Figure 2. Geometries for the optimised structures of **M** and **M10** and the transition structures. Distances are in Å.

activation energy is lower by only 6.5 kcal/mol than the corresponding value required for the formation of 2,2,3,3,3-pentafluoropropanoyl fluoride (**M12**) and a molecule of CO. The other two exit channels for the **M10** moiety are most likely to be of negligible importance in view of their excessive energy requirements.

Kinetic considerations

Considering the energetic trends given in the PES of Figure 1, reaction rate constants are calculated for the perceptible controlling reactions of the unimolecular decomposition of M (**M** → **M10** + **HF**), (**M10** → **M11** + CO_2) and (**M10** → **M12** + CO). The reaction rate parameters are given in Table 1. The three reactions are found to be highly pressure independent at all temperatures. Branching ratios based on the high pressure limit are plotted in Figure 3 for the two channels available for **M10**. Pentafluoropropanoyl fluoride (**M12**) is predicted to be the dominant channel during the pyrolysis of perfluorobutanoic acid at temperatures as high as 1300 K. Beyond this temperature, entropic factors favour the formation of the intermediate **M11**. Nevertheless, the reaction leading to the formation of **M11** contributes notably at low and intermediate temperatures. For instance, branching ratios for the formation of **M11** reach 5%, 10% and 26% at 600 K, 700 K and 900 K, respectively. The calculated predominance for the formation of CO and **M11** is in qualitative agreement with earlier work on the

Table 1
Arrhenius rate parameters for important reactions[a]

	A[b] (s^{-1})	n[c]	E_a[d] (cal mol^{-1})
M → **M10** + HF	3.5×10^{37}	−7.53	63,000
	2.3×10^{12}	0.33	54,700
M10 → **M11** + CO_2	1.7×10^{29}	−7.15	17,500
	1.7×10^{13}	0.35	20,900
M10 → **M12** + CO	2.5×10^{26}	−5.47	13,700
	3.2×10^{12}	0.24	14,400

[a] Reactions at 1 atm and high-P limit.
[b] Pre-exponential Arrhenius factor.
[c] Factor for temperature-dependency.
[d] Activation energy.

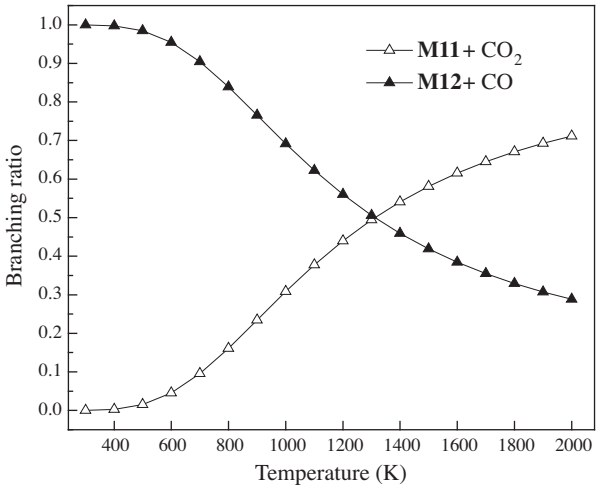

Figure 3. Branching ratios for the two competing channels; **M10** → **M11** + CO_2 and **M10** → **M12** + CO.

thermolysis of fluoroacetic acid. It was found that the overall activation energy for the formation of CO (43.7 kcal/mol) was lower than the corresponding value for CO_2 (47.4 kcal/mol).[23] Decomposition of fluoroacetic acid was found to produce appreciable concentrations of CF_3COF that is an analogous structure to that of **M12**.[24]

However, the calculated energetic and rate constants do not support the experimental results of Kursic et al.,[6] in which 1*H*-perfluoroheptane (**M1**) was found to be the dominant product from the pyrolysis of perfluorooctanoic acid between 628 K and 658 K. In fact the authors had admitted that their gas phase system was highly prone to heterogeneous and surface assistance by the reactor walls which were made of quartz. It is well-known that many commonly used reactor walls such as zeolite, alumina and silica surfaces[25] exhibit profound surface acivation. The catalyst-assisted formation of CO_2 from the thermolysis of fluoroacetate was also considered by Ashworth and Harrison.[18] One possible hypothesis is that chemical/physical adsorption of perfluorooctanoic acid via its carboxylic oxygen would weaken the C–C bond and facilitate decarboxylation.[16] A study will be carried out in due course to investigate the effect of reactor walls on accelerating the rate of decarboxylation using model compounds for quartz and silica.

In conclusion, unimolecular decomposition of perfluorobutanoic acid is found to afford the α-lactone intermediate **M10** and HF as the prominent initial products. Further decomposition of **M10** results predominantly in the formation of pentafluoropropanoyl fluoride (CF_3CF_2COF) throughout the low and intermediate temperature regions. The plausible catalytic-assisted decarboxylation process to 1,1,1,2,2,3,3-heptafluoropropane warrants further investigation.

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