

## Heptafluorobutyronitrile (C<sub>4</sub>F<sub>7</sub>N), Hydrolysis, a Density Functional Theory (DFT) Investigation

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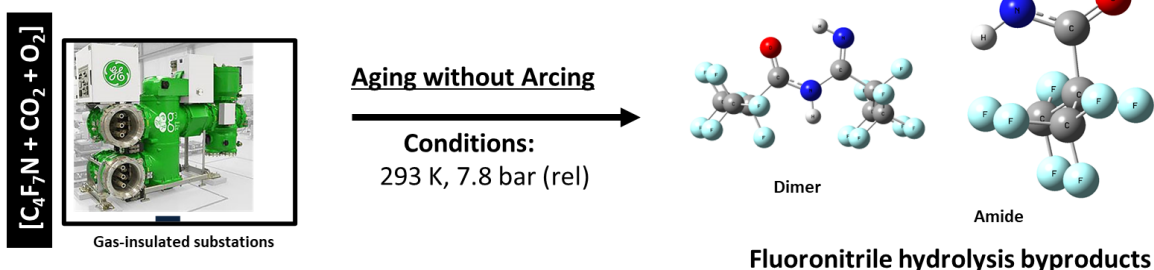
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Heptafluorobutyronitrile (C<sub>4</sub>F<sub>7</sub>N) has received much consideration as an effective substitute to sulfur hexafluoride (SF<sub>6</sub>) in the electrical industrial sector over the last decade. However, liability is the key to emerging technology, and the thermoelectric aging of the insulation gases may produce unavoidable consequences that raise concerns for the operator and human safety. Recently, numerous pieces of literature mentioned the production of crystals in the form of amide and dimer (ligand) generated from the aging of C<sub>4</sub>F<sub>7</sub>N with few water molecules. It was found that the hydrolysis of fluoronitrile chemical reactions initial with the production of amide (C<sub>4</sub>H<sub>2</sub>F<sub>7</sub>NO) and following, with the addition of C<sub>4</sub>F<sub>7</sub>N molecules, accelerates the reaction to produce dimer (C<sub>8</sub>H<sub>2</sub>F<sub>14</sub>N<sub>2</sub>O) and further is the possibility to generate various range of byproducts. Thermodynamically, C<sub>4</sub>F<sub>7</sub>NH<sub>2</sub>O + C<sub>4</sub>F<sub>7</sub>N → C<sub>8</sub>H<sub>2</sub>F<sub>14</sub>N<sub>2</sub>O is the favourable chemical reaction with a 23 kcal/mol energy barrier that generates a dimer molecule. Furthermore, in presence of paramagnetic ion (typically Cu (II)), a Cooper based complex (as purple crystals) may appear. Gibbs free energy at elevated temperature indicates the driving force is needed to accelerate the reaction except C<sub>8</sub>H<sub>2</sub>F<sub>14</sub>N<sub>2</sub>O + H<sub>2</sub>O → C<sub>12</sub>H<sub>2</sub>F<sub>21</sub>N<sub>3</sub>O, whose energy values throughout remain consistent. Theoretical calculations reveal the water acts as a strong catalytic that can abruptly reduce the energy barrier of the initial reaction from 59 to 10 kcal mol<sup>-1</sup> and open the pathway to generate other byproducts.

### Flowchart of fluoronitrile hydrolysis in industrial gas-insulated substation



## 1. Introduction

SF<sub>6</sub> is a well-known insulation gas, having the properties of excellent dielectric strength, arc quenching capability, chemical inertness, and low toxicity. These essential properties enable it an excellent choice to be used in high-voltage equipment such as Gas-Insulated Switchgear (GIS), Gas-Insulated Lines (GIL), Gas Circuit Breakers (GCB), Live Tank Breakers (LTB), and Dead Tank Breakers (DTB) from the past few decades. However, it has a global warming potential (GWP<sub>100-yr</sub>) about 24,300 times that of CO<sub>2</sub> with a 1000-year lifetime. Thus, it was restricted to be used in high-voltage equipment worldwide in the 1997 Kyoto Protocol and labelled as one of six global warming potential gases (Dervos and Vassiliou, 2000). Therefore, scientists conducted extensive research work to figure out the substitution of SF<sub>6</sub> gas, and eventually, a buffer gaseous blend containing CO<sub>2</sub> and O<sub>2</sub> with a few percent of C<sub>4</sub>F<sub>7</sub>N was introduced in the market by GE Vernova, Grid Solution (Kieffel *et al.*, 2017). Adding C<sub>4</sub>F<sub>7</sub>N in sufficient quantity will permit to have a bubble point curve in the right domain of P and T in comparison to CO<sub>2</sub>/O<sub>2</sub> binary system.

Chemical stability of the insulation gas with the interaction of metals and humidity is the crucial factor for its usage in high-voltage devices. Several literatures mention the qualitative and quantitative studies regarding the byproduct's identification under the thermoelectric stress of a g<sup>3</sup> (C<sub>4</sub>F<sub>7</sub>N – CO<sub>2</sub> – O<sub>2</sub>) gaseous mixture (Iddrissu *et al.*, 2021), (Li *et al.*, 2020), (Zhang *et al.*, 2019), (Ye *et al.*, 2022). Some common byproducts, CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, CF<sub>3</sub>CN, C<sub>2</sub>F<sub>5</sub>CN, and COF<sub>2</sub>, are identified by GC-MS and FTIR technology in different concentrations of g<sup>3</sup> gaseous blend. However, the interaction of fluoronitrile (C<sub>4</sub>F<sub>7</sub>N) with water results in distinct byproducts and points out the various kinds of crystals after the aging for a certain period.

Recently, Siemens Energy (JUHRE *et al.*, 2023) and Hitachi Energy (Donzel *et al.*, 2024) conducted the experimental study to deeply understand the crystal generation phenomena with fluoronitrile and humidity and also explore the catalytic effect of various kinds of desiccants. Different shapes of crystals, including amide and dimer, are noticed at the end of long-term tests in GIS/GIL with a g<sup>3</sup> gas mixture. Donzel *et al.*, (2024) (Donzel *et al.*, 2024) confirmed the melting points of amide (flakes-like crystals) and dimer (needle-like crystals) are 53 °C and 136 °C, respectively, by DSC measurement. Instead of removing or minimizing the humidity in the system, the desiccant also acts as a catalyst to accelerate the growth of crystals. Gao *et al.*, (2022) (Gao *et al.*, 2022) and his team proposed the 4 Å organic desiccant (CAS: 70955-01-0 ) as an alternative over the zeolite; though, experimental study close to industrial condition is still needed to benchmark the desiccants. Apart from the experimental work, Berteloot *et al.*, state the chemical reaction mechanism of fluoronitrile hydrolysis in which different kinds of byproducts are generated, including amid (C<sub>4</sub>H<sub>2</sub>F<sub>7</sub>NO) and dimer (C<sub>8</sub>H<sub>2</sub>F<sub>14</sub>N<sub>2</sub>O), molecules (Berteloot *et al.*, no date). Additionally, some initial reactions are also specified in the Siemens Energy CIGRE 2022 paper (JUHRE *et al.*, 2023).

In this study, we conduct a comprehensive simulation of the C<sub>4</sub>F<sub>7</sub>N hydrolysis reactions using Density Functional Theory (DFT), analyzing, and comparing the Gibbs free energy (ΔG) for the reactions involved in the mechanism. The role of water molecule increments affecting the energy barrier in the amide formation process is explored. Additionally, temperature influence up to 3000 K on the Gibbs free energy (ΔG) represent as energy barrier is estimated.

## 2. Methodology

DFT is one of the most effective tools to provide approximate solutions to the Schrodinger equation, the fundamental equation of quantum mechanics that describes any given chemical system. All the density functional theory (DFT) calculations were performed at the M062X hybrid functional (Zhao and Truhlar, 2008) and the combination of 6-311+G(d,p) basis sets (Krishnan *et al.*, 1980), (Cramer, 2004) for geometry optimization, employed in "Gaussian16" packages ([www.gaussian.com](http://www.gaussian.com)). Stationary points were established as minima with zero imaginary frequency. Each transition state was confirmed by the presence of one imaginary frequency at the same theory levels as employed for geometry optimization. The intrinsic reaction coordinate (IRC) calculations were carried out to confirm each transition state (TS) connecting with the two associated minima in the proposed mechanism. All the calculations are computed in ambient conditions (298.15 K and 1 atm) without solvation effect.

## 3. Results and discussion

Figure 1 illustrates the DFT-assisted reaction mechanism of fluoronitrile hydrolysis processes in the potential energy surface (PES) profile, and Table 1 presents the chemical reactions with the Gibbs free energies values. The first step involved the generation of an imidic acid (isomers) and amides following the hydration and tautomerization reactions.

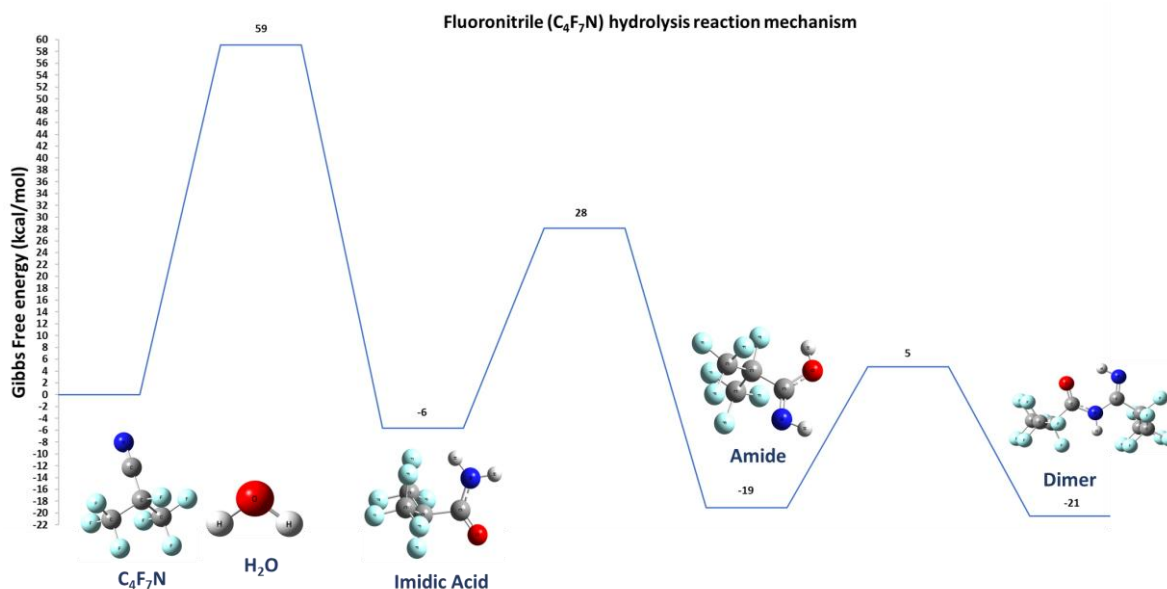


Figure 1: A complete chemical reaction mechanism of fluoronitrile hydrolysis

Table 1: Absorbed energy and reaction barrier (kcal/mol) of fluoronitrile ( $C_4F_7N$ ) hydrolysis reactions

#	Reactions symbol	Chemical Reaction	Relative Energy (kcal/mol)	Activation energy ( $\Delta G$ ) (kcal/mol)
1	Ra	$C_4F_7N + H_2O \rightarrow C_4F_7NH_2O$ (tautomer)	-5.6	59.1
2	Rb	(tautomer) $C_4F_7NH_2O \rightarrow C_4F_7NH_2O$	-13.4	33.8
3	Rc	$C_4F_7NH_2O + C_4F_7N \rightarrow C_8H_2F_{14}N_2O$	-1.48	23.8

The first reaction (Ra) step involved a nucleophilic attack by the water molecule on the protonated nitrile ( $-C\equiv N$ ) group of the fluoronitrile molecule to overcome the energy barrier of 59.1 kcal/mol, which undergoes the formation of an amidic acid with exothermic 5.6 kcal/mol energy. The highest energy barrier among all the reactions is reaction Ra and termed as the rate-determining step. Subsequently, the second step (Rb) is the isomerization of imidic acid, involving proton migration with a 34 kcal/mol barrier height to form a corresponding amide molecule ( $C_3F_7CONH_2$ ) with an overall exothermic energy of 13.4 kcal/mol, making it a more probable channel among all the hydrolysis reactions and also reported in the following literature (Yu and Wang, 2021), (Barbosa and Van Santen, 2000).

Consequently, the abundance of the  $C_4F_7N$  molecule in the system accelerates to the addition of another heptafluorobutyronitrile molecule and generates dimer. In the reaction (Rc), a dimer molecule is formed by the attack of a  $-CN$  bond from the fluoronitrile molecule on the  $-NH$  side of the amide, which needs an energy barrier of 23.8 kcal mol<sup>-1</sup>. Lower energy barrier in (Rc), subjecting it to thermodynamically more favourable than (Rb), and resulting in the formation of needle-like shape as mentioned in Hitachi Energy thermal aging tests (Donzel *et al.*, 2024). Additionally, these dimer molecules can trigger Cu-complex, a new violet crystal presented in the Kessler study (Kessler *et al.*, 2020).

Another approach with the interaction of up to four water molecules reduces the energy barrier of the reaction Ra from 59.1 to 10 kcal/mol (Figure 2). Which implies the strong catalysing effect of water in the crystal's generation phenomena. This suggests that the hydrogen bonding of the additional water molecules to the ( $C_3F_7CN-OH-H$ ) reactant complex greatly promotes the addition processes of more than one water molecule.  $C_3F_{10}O$  (Xiao *et al.*, 2017), NSCI (Zhen Guo, Cunyuan Zhao, David Lee Phillips, Evan G. Robertson, 2008), and aldehyde (Wang *et al.*, 2018), molecules are also showing the same behaviour. These theoretical investigations suggest the strict removal and through-monitored humidity value in the circuit breaker to prevent any kind of crystal formation, ensuring human and device safety.

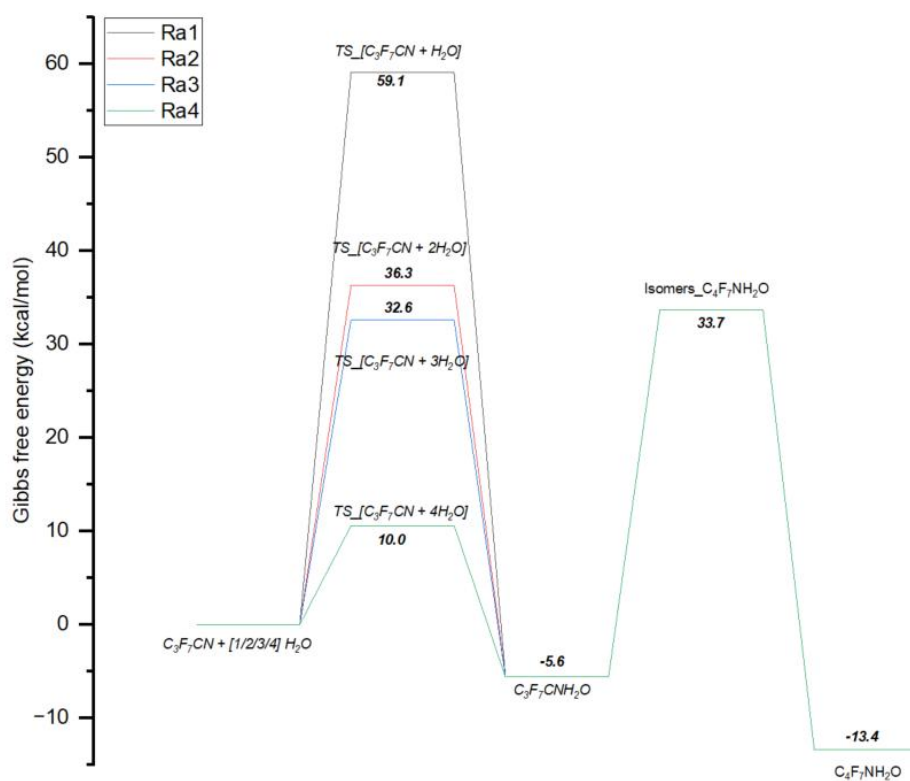


Figure 2: Reaction path of  $C_4F_7N$  with  $(n)H_2O$  water molecule relative to the energy of  $(-982,436603 \text{ a.u})$

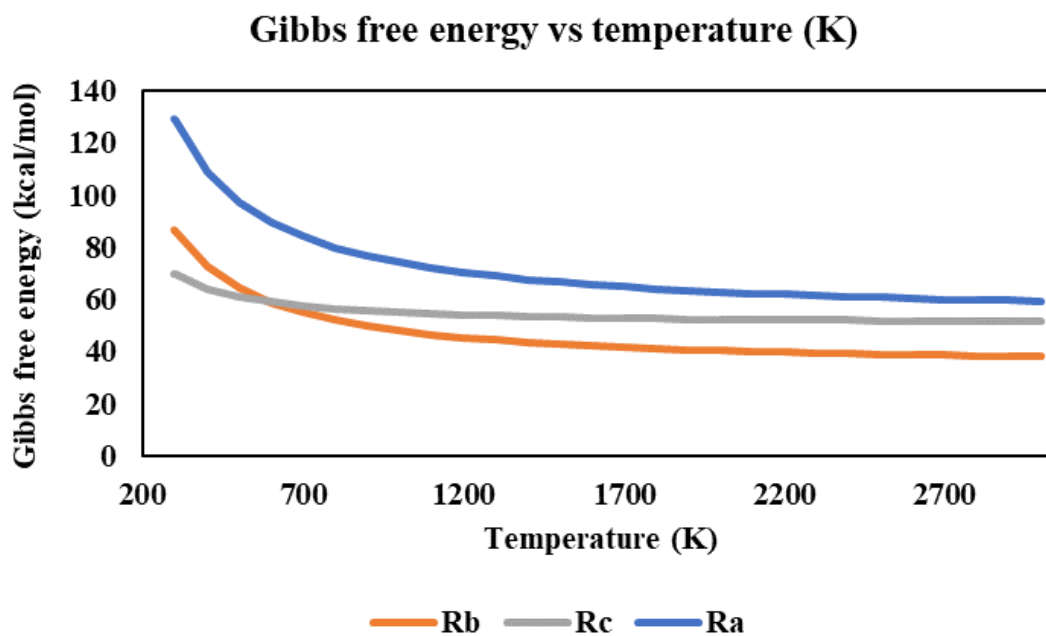


Figure 3: Variation of Gibbs free energy of fluoronitrile hydrolysis reactions under the influence of temperature (K)

Temperature rises above ambient conditions during arcing in the circuit breaker; therefore, it should be considered to determine the free energy at a higher temperature. Figure 3 illustrates the relationship between the Gibbs free ( $\Delta G$ ) energy within the temperature (K) range of 293 K to 3000 K through Gaussian thermochemistry data (Ochterski and Ph, 2000). All six chemical reactions have a Gibbs free energy value greater than zero, thereby implying that the fluoronitrile hydrolysis process cannot be carried out spontaneously. With the increment of temperature, the Gibbs free energy of reactions Ra, and Rb, abruptly decreases, while for reaction Rc, it remains consistently constant.

#### 4. Conclusion

In this study, a DFT-assisted theoretical study is conducted to explore the interaction between heptafluoroisobutryle ( $C_4F_7N$ ) and water and compute six chemical reactions. MO62X hybrid functional with the combination of 6-311+G(d,p) basis sets was utilized to compute the chemical reaction. All the molecular geometry is optimized, and the transition state is confirmed by the presence of one imaginary frequency. Amid ( $C_4H_2F_7NO$ ), and dimer ( $C_8H_2F_{14}N_2O$ ) are the main molecules produced through the hydrolysis of fluoronitrile. Among all the six-chemical reactions, the reaction (Ra) is termed a rate-determining step with an energy barrier of 59.1 kcal/mol. The energy value suddenly dropped to 10 kcal/mol from 59.1 kcal/mol by the addition of four water molecules in the first chemical reaction, indicating the small quantity of water is enough to initiate the reaction. Gibbs free energy ( $\Delta G$ ) in the temperature range from ambient to 3000 K, confirming that all the reaction is spontaneous except reaction Rd. The DFT-assisted study of fluoronitrile hydrolysis provided valuable insights into the reaction energies of all steps, advancing in the experimental design to optimize conditions and remove byproduct formation.

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