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14. ABSTRACT

Poly- and perfluoroalkyl substances (PFAS) are man-made compounds that are widely used in numerous commercial and industrial applications. Perfluorocarboxylic acids (PFCAs) are a commonly used class of PFAS extensively used in aqueous film-forming foams (AFFFs). Due to both the environmental persistence and toxicity of these species, the removal and destruction of PFAS/PFCAs have garnered significant attention from the research community, specifically with a focus on long chain species such as perfluorooctanoic acid (PFOA). The most common method of PFAS treatment is via adsorption onto granular activated carbon (GAC) followed by incineration at high temperatures. However, a fundamental chemical understanding of this thermal decomposition process as well as the byproducts formed is still not well known. This presentation will discuss the unimolecular decomposition of PFOA as well as some of its simpler analogues, trifluoroacetic acid (TFA) and perfluoropropanoic acid (PFPA) via theoretical gas phase kinetics studies utilizing potential energy surfaces (PESs) developed using density functional theory (DFT) methods.

15. SUBJECT TERMS

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Theoretical Gas Phase Kinetics of Perfluorocarboxylic Acid(PFCA) decomposition

ROBERT BUSZEK, CTR

Jacobs, Edwards Air Force Base

RQRP 8/25/2021

Computational modeling and AI/ML for degradation, destruction and removal of per- and polyfluoroalkyl substances (PFASs)

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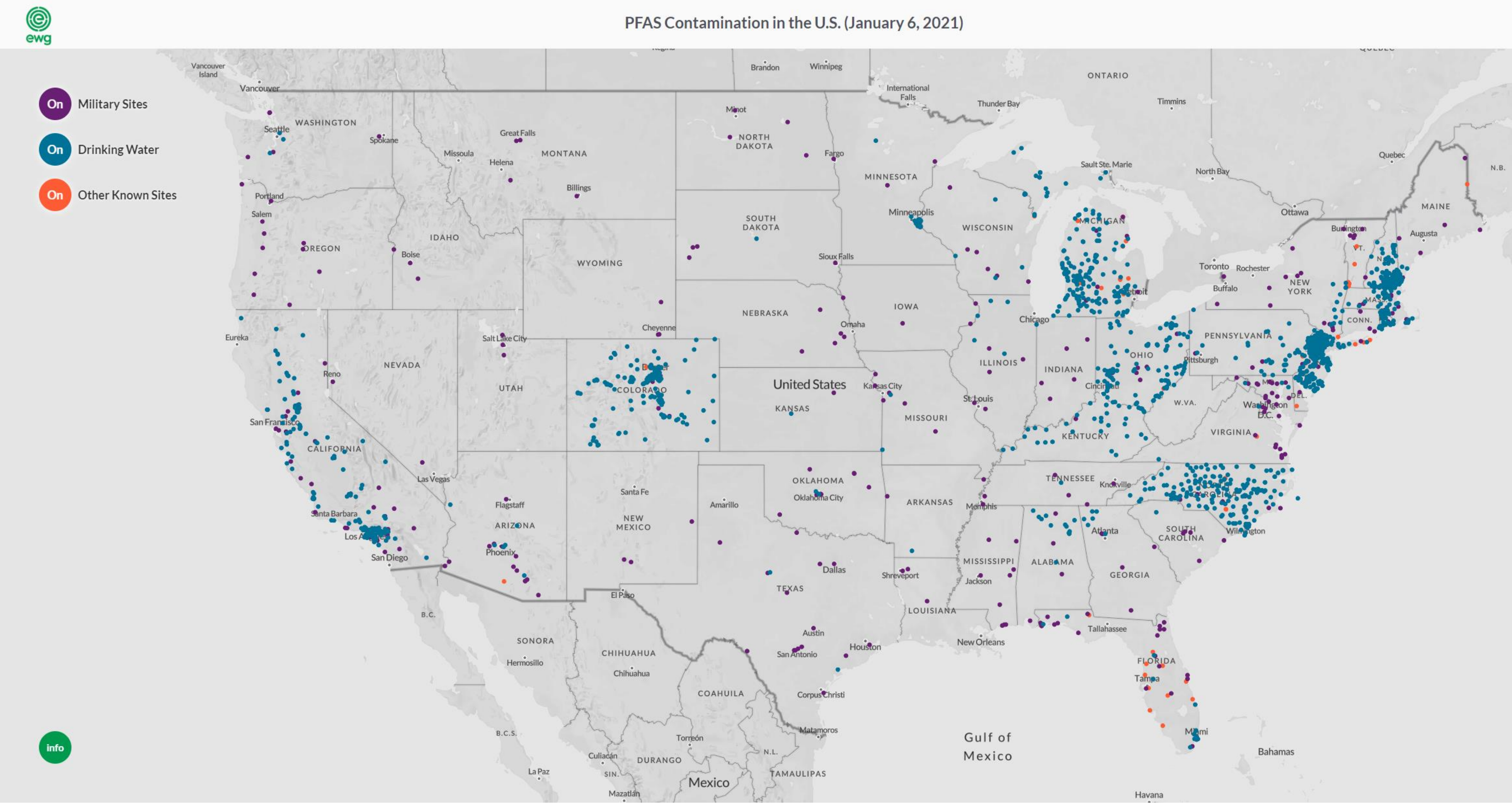
PFAS Sources

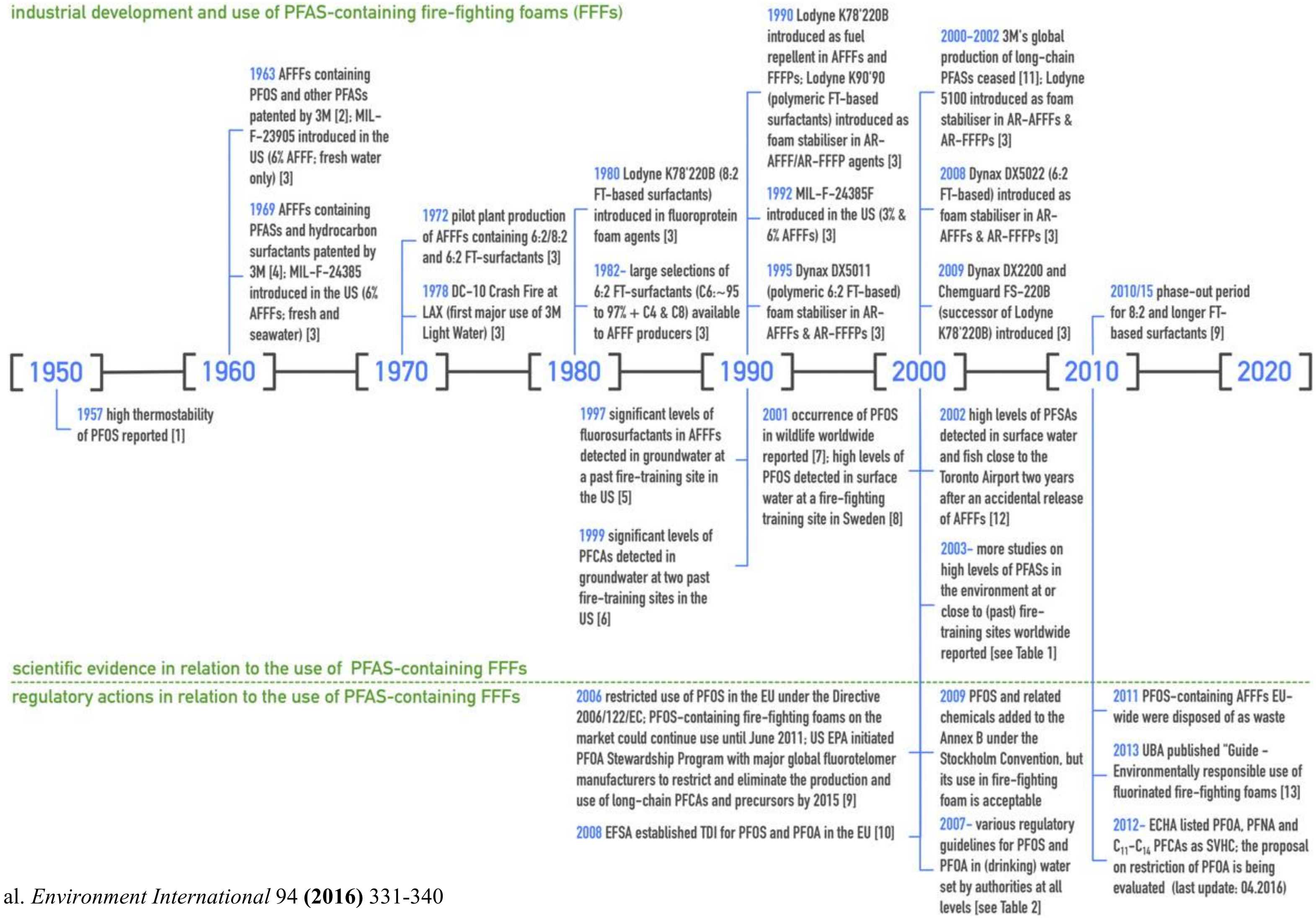
https://www.defence.gov.au/environment/pfas/pfas.asp

PFAS Contamination



https://www.ewg.org/interactive-maps/pfas_contamination/map/

Aqueous Film Forming Foams (AFFFs)



industrial development and use of PFAS-containing fire-fighting foams (FFFs)

1963 AFFFs containing PFOS and other PFASs patented by 3M [2]; MIL-F-23905 introduced in the US (6% AFFF; fresh water only) [3]

1969 AFFFs containing PFASs and hydrocarbon surfactants patented by 3M [4]; MIL-F-24385 introduced in the US (6% AFFFs; fresh and seawater) [3]

1972 pilot plant production of AFFFs containing 6:2/8:2 and 6:2 FT-surfactants [3]

1978 DC-10 Crash Fire at LAX (first major use of 3M Light Water) [3]

1980 Lodyne K78'220B (8:2 FT-based surfactants) introduced in fluoroprotein foam agents [3]

1982- large selections of 6:2 FT-surfactants (C6:~95 to 97% + C4 & C8) available to AFFF producers [3]

1990 Lodyne K78'220B introduced as fuel repellent in AFFFs and FFFPs; Lodyne K90'90 (polymeric FT-based surfactants) introduced as foam stabiliser in AR-AFFF/AR-FFFP agents [3]

1992 MIL-F-24385F introduced in the US (3% & 6% AFFFs) [3]

1995 Dynax DX5011 (polymeric 6:2 FT-based) foam stabiliser in AR-AFFFs & AR-FFFPs [3]

2000–2002 3M's global production of long-chain PFASs ceased [11]; Lodyne 5100 introduced as foam stabiliser in AR-AFFFs & AR-FFFPs [3]

2008 Dynax DX5022 (6:2 FT-based) introduced as foam stabiliser in AR-AFFFs & AR-FFFPs [3]

2009 Dynax DX2200 and Chemguard FS-220B (successor of Lodyne K78'220B) introduced [3]

2010/15 phase-out period for 8:2 and longer FT-based surfactants [9]

[1950]—[1960]—[1970]—[1980]—[1990]—[2000]—[2010]—[2020]

1957 high thermostability of PFOS reported [1]

1997 significant levels of fluorosurfactants in AFFFs detected in groundwater at a past fire-training site in the US [5]

1999 significant levels of PFCAs detected in groundwater at two past fire-training sites in the US [6]

2001 occurrence of PFOS in wildlife worldwide reported [7]; high levels of PFOS detected in surface water at a fire-fighting training site in Sweden [8]

2002 high levels of PFSAs detected in surface water and fish close to the Toronto Airport two years after an accidental release of AFFFs [12]

2003- more studies on high levels of PFASs in the environment at or close to (past) fire-training sites worldwide reported [see Table 1]

scientific evidence in relation to the use of PFAS-containing FFFs

regulatory actions in relation to the use of PFAS-containing FFFs

2006 restricted use of PFOS in the EU under the Directive 2006/122/EC; PFOS-containing fire-fighting foams on the market could continue use until June 2011; US EPA initiated PFOA Stewardship Program with major global fluorotelomer manufacturers to restrict and eliminate the production and use of long-chain PFCAs and precursors by 2015 [9]

2008 EFSA established TDI for PFOS and PFOA in the EU [10]

2009 PFOS and related chemicals added to the Annex B under the Stockholm Convention, but its use in fire-fighting foam is acceptable

2007- various regulatory guidelines for PFOS and PFOA in (drinking) water set by authorities at all levels [see Table 2]

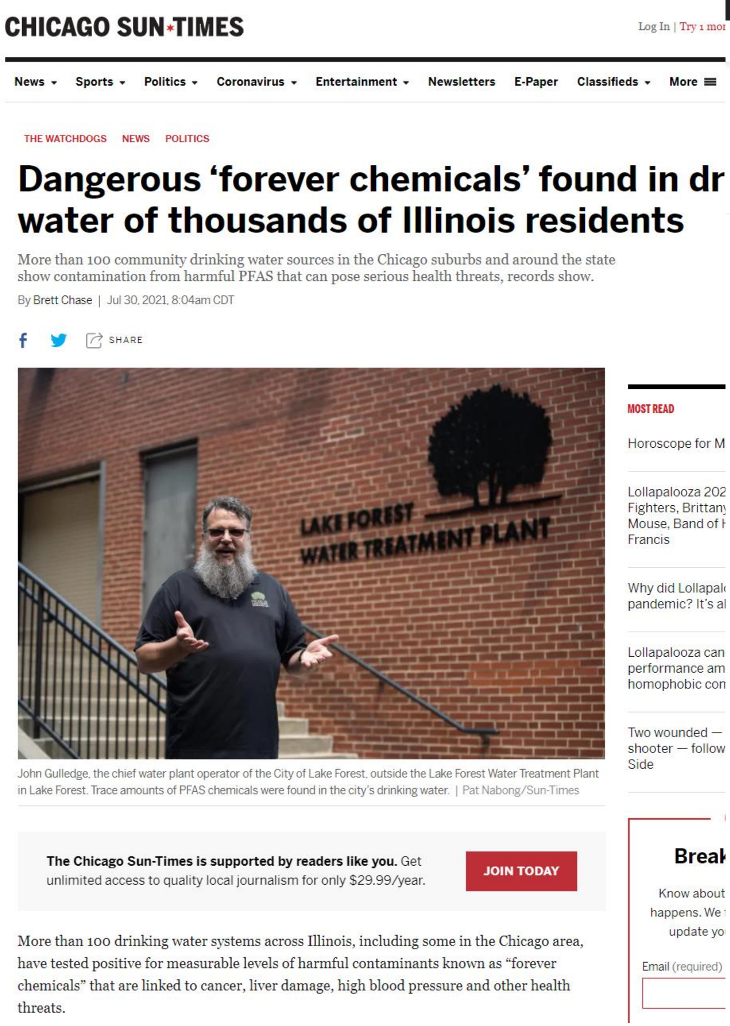
2011 PFOS-containing AFFFs EU-wide were disposed of as waste

2013 UBA published "Guide – Environmentally responsible use of fluorinated fire-fighting foams [13]

2012- ECHA listed PFOA, PFNA and C_{11}-C_{14} PFCAs as SVHC; the proposal on restriction of PFOA is being evaluated (last update: 04.2016)

I.T. Cousins et al. *Environment International* 94 **(2016)** 331-340

In the News



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THE WATCHDOGS NEWS POLITICS

Dangerous ‘forever chemicals’ found in dr water of thousands of Illinois residents

More than 100 community drinking water sources in the Chicago suburbs and around the state show contamination from harmful PFAS that can pose serious health threats, records show.

By Brett Chase | Jul 30, 2021, 8:04am CDT

SHARE

John Gulledge, the chief water plant operator of the City of Lake Forest, outside the Lake Forest Water Treatment Plant in Lake Forest. Trace amounts of PFAS chemicals were found in the city’s drinking water. | Pat Nabong/Sun-Times

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More than 100 drinking water systems across Illinois, including some in the Chicago area, have tested positive for measurable levels of harmful contaminants known as “forever chemicals” that are linked to cancer, liver damage, high blood pressure and other health threats.

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Break

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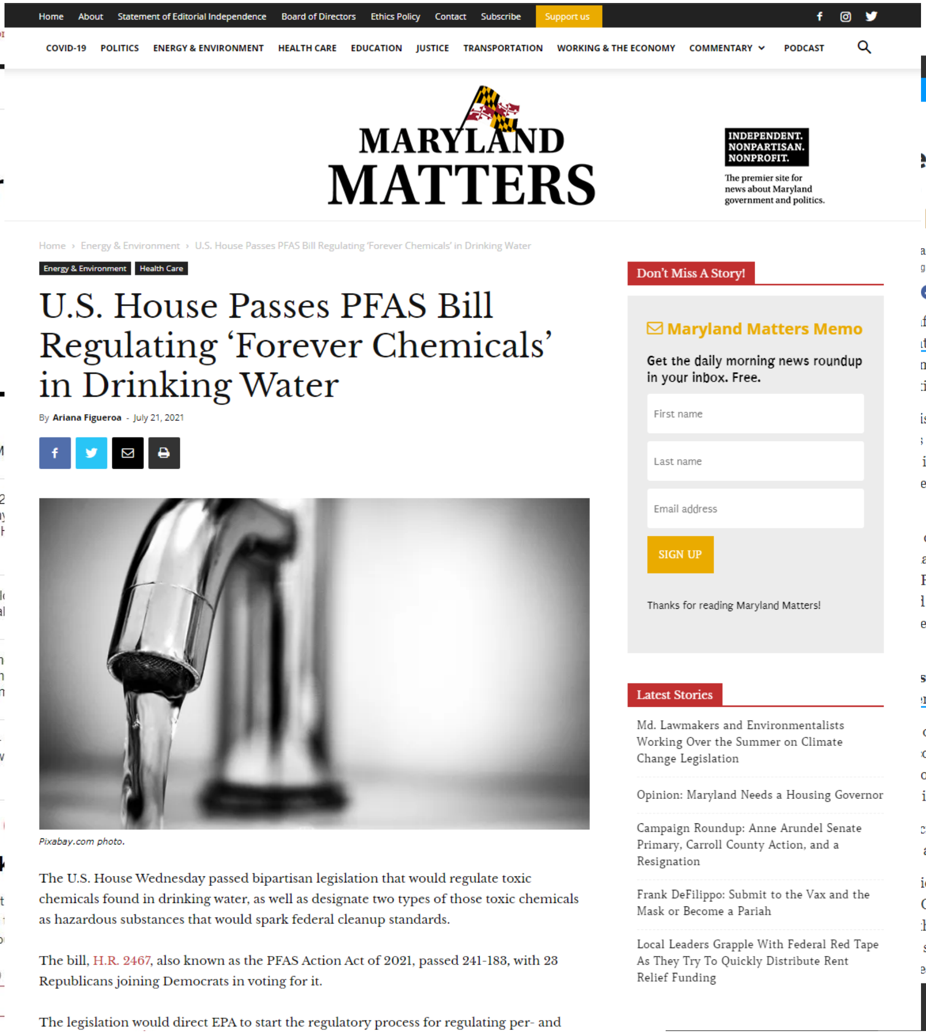

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Energy & Environment Health Care

U.S. House Passes PFAS Bill Regulating ‘Forever Chemicals’ in Drinking Water

By **Ariana Figueroa** - July 21, 2021

Pixabay.com photo.

The U.S. House Wednesday passed bipartisan legislation that would regulate toxic chemicals found in drinking water, as well as designate two types of those toxic chemicals as hazardous substances that would spark federal cleanup standards.

The bill, H.R. 2467, also known as the PFAS Action Act of 2021, passed 241-183, with 23 Republicans joining Democrats in voting for it.

The legislation would direct EPA to start the regulatory process for regulating per- and

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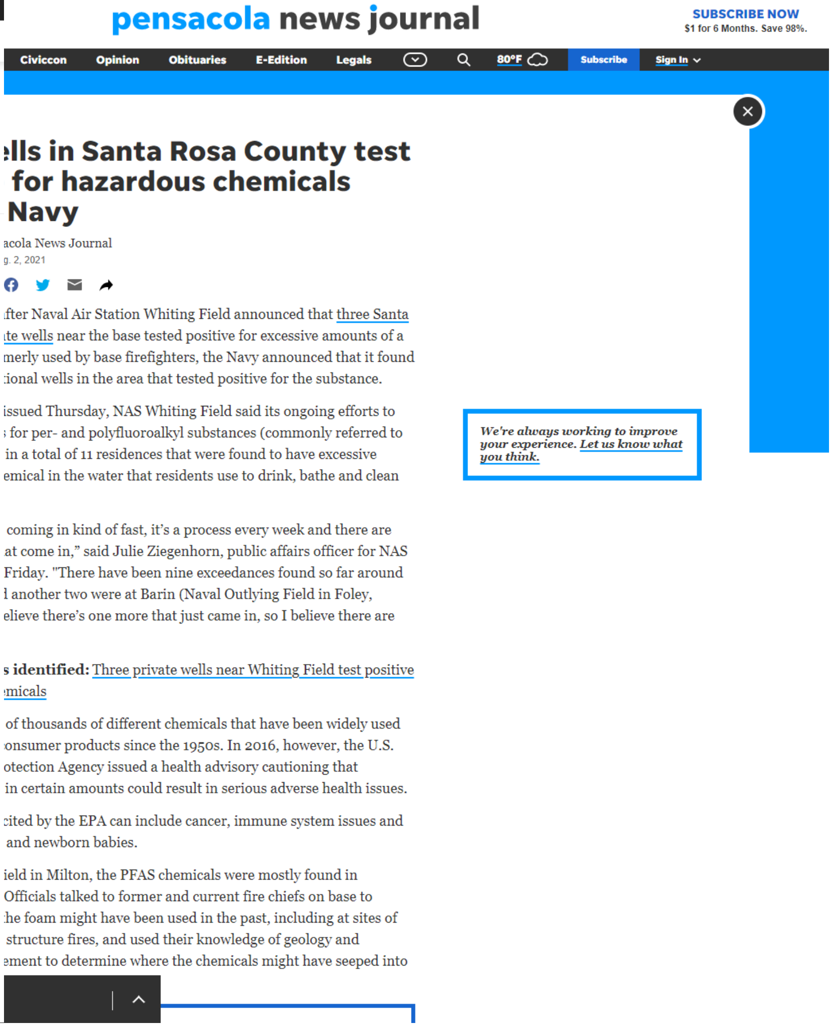
- Local Leaders Grapple With Federal Red Tape As They Try To Quickly Distribute Rent Relief Funding



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ells in Santa Rosa County test for hazardous chemicals Navy

acola News Journal
g. 2, 2021

fter Naval Air Station Whiting Field announced that three Santa te wells near the base tested positive for excessive amounts of a merly used by base firefighters, the Navy announced that it found tional wells in the area that tested positive for the substance.

issued Thursday, NAS Whiting Field said its ongoing efforts to for per- and polyfluoroalkyl substances (commonly referred to in a total of 11 residences that were found to have excessive emical in the water that residents use to drink, bathe and clean

coming in kind of fast, it’s a process every week and there are at come in,” said Julie Ziegenhorn, public affairs officer for NAS Friday. "There have been nine exceedances found so far around l another two were at Barin (Naval Outlying Field in Foley, elieve there’s one more that just came in, so I believe there are

s identified: Three private wells near Whiting Field test positive micals

of thousands of different chemicals that have been widely used onsumer products since the 1950s. In 2016, however, the U.S. otection Agency issued a health advisory cautioning that in certain amounts could result in serious adverse health issues.

cited by the EPA can include cancer, immune system issues and and newborn babies.

ield in Milton, the PFAS chemicals were mostly found in Officials talked to former and current fire chiefs on base to he foam might have been used in the past, including at sites of structure fires, and used their knowledge of geology and ement to determine where the chemicals might have seeped into

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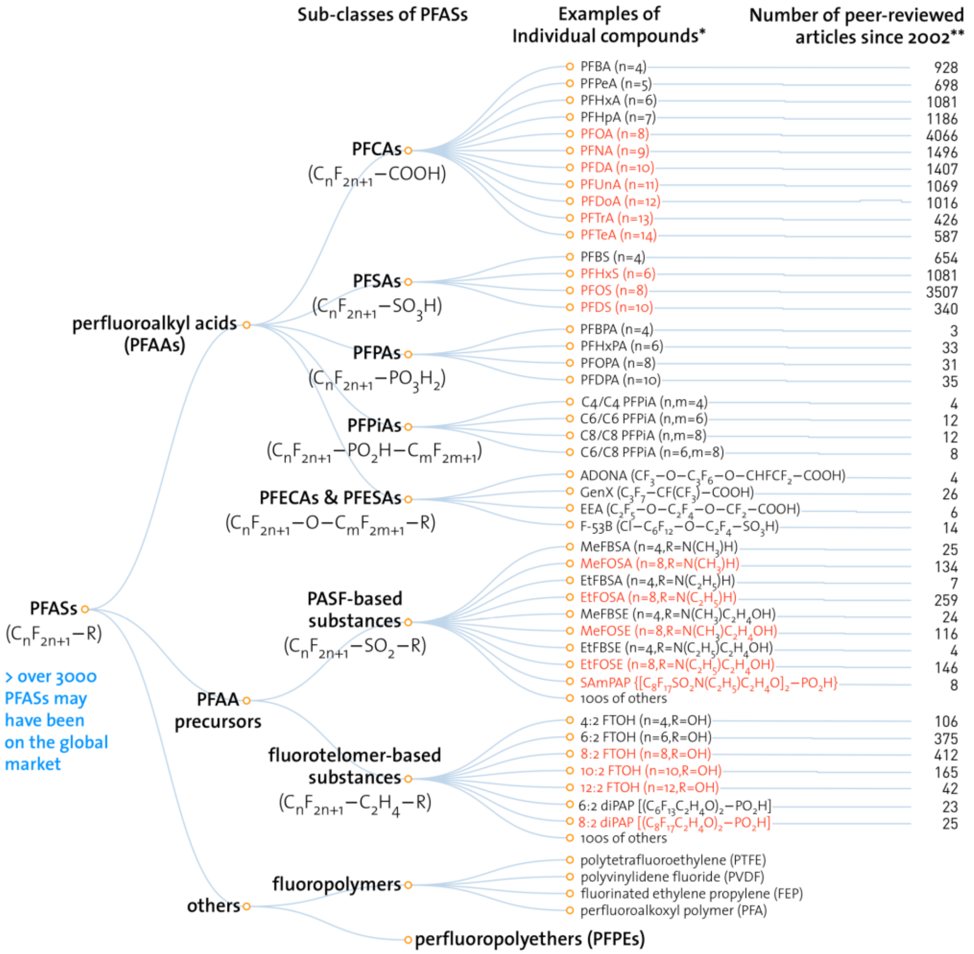
PFAS Species



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* PFASs in **RED** are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/1AN).

** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016.

Z. Wang et al. *Environ. Sci. Technol. 51* **(2017)** 2508-2518

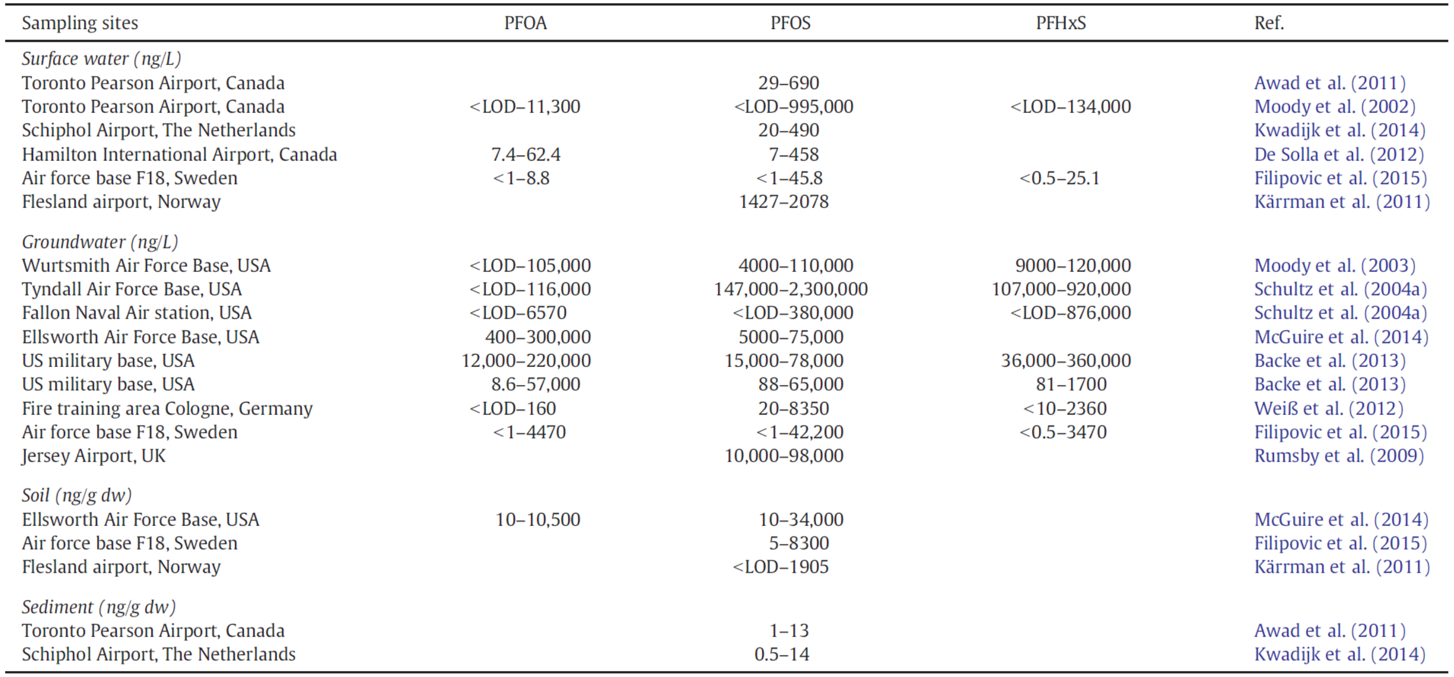


Table 1

Measured concentrations of selected examples of PFASs in the environmental media at sites where fire-fighting foams have been used or spilled. LOD = limit of detection.

Sampling sites	PFOA	PFOS	PFHxS	Ref.
Surface water (ng/L)				
Toronto Pearson Airport, Canada		29–690		Awad et al. (2011)
Toronto Pearson Airport, Canada	<LOD–11,300	<LOD–995,000	<LOD–134,000	Moody et al. (2002)
Schiphol Airport, The Netherlands		20–490		Kwadijk et al. (2014)
Hamilton International Airport, Canada	7.4–62.4	7–458		De Solla et al. (2012)
Air force base F18, Sweden	<1–8.8	<1–45.8	<0.5–25.1	Filipovic et al. (2015)
Flesland airport, Norway		1427–2078		Kärrman et al. (2011)
Groundwater (ng/L)				
Wurtsmith Air Force Base, USA	<LOD–105,000	4000–110,000	9000–120,000	Moody et al. (2003)
Tyndall Air Force Base, USA	<LOD–116,000	147,000–2,300,000	107,000–920,000	Schultz et al. (2004a)
Fallon Naval Air station, USA	<LOD–6570	<LOD–380,000	<LOD–876,000	Schultz et al. (2004a)
Ellsworth Air Force Base, USA	400–300,000	5000–75,000		McGuire et al. (2014)
US military base, USA	12,000–220,000	15,000–78,000	36,000–360,000	Backe et al. (2013)
US military base, USA	8.6–57,000	88–65,000	81–1700	Backe et al. (2013)
Fire training area Cologne, Germany	<LOD–160	20–8350	<10–2360	Weiß et al. (2012)
Air force base F18, Sweden	<1–4470	<1–42,200	<0.5–3470	Filipovic et al. (2015)
Jersey Airport, UK		10,000–98,000		Rumsby et al. (2009)
Soil (ng/g dw)				
Ellsworth Air Force Base, USA	10–10,500	10–34,000		McGuire et al. (2014)
Air force base F18, Sweden		5–8300		Filipovic et al. (2015)
Flesland airport, Norway		<LOD–1905		Kärrman et al. (2011)
Sediment (ng/g dw)				
Toronto Pearson Airport, Canada		1–13		Awad et al. (2011)
Schiphol Airport, The Netherlands		0.5–14		Kwadijk et al. (2014)

I.T. Cousins et al. *Environment International* 94 **(2016)** 331-340

PFAS Treatment

- Incineration
  - Temperatures of 600 - 1000 ºC[1]
- Sorption onto Granular Activated Carbon (GAC)
- Extremely active research area generating many novel methods
  - Adsorption
  - Filtration
  - Sono-chemical Destruction
  - Electrochemical Oxidation
  - Photolytic Oxidation
  - e^- Beam destruction
  - Plasma Based Methods
  - Biological Methods
  - Treatment Trains
  - Others

---

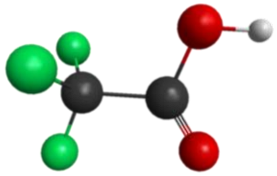
[1] Mills, Marc A., D. Bless, K. Dasu, D. P. Siriwardena, AND A. Dinal. Thermal Treatment of PFAS in Environmental Media: A review of the state-of-the-science. Workshop: Thermal state of the Science, Cincinnati,OH, February 25, 2020

Objectives

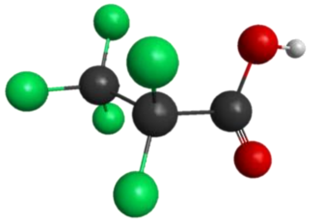
- What is the Mechanism for thermal Decomposition of PFCAs?
- What byproducts can we expect to be formed?
- Does this change with respect to chain length or temperature?

Theoretical Methods

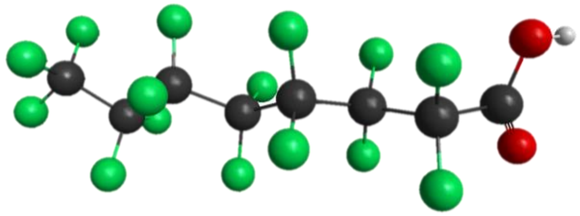
PFCA Models



C2 Trifluoroacetic Acid (TFA)



C3 Perfluoropropanoic Acid (PFPA)



C8 Perfluorooctanoic Acid (PFOA)

Energetics

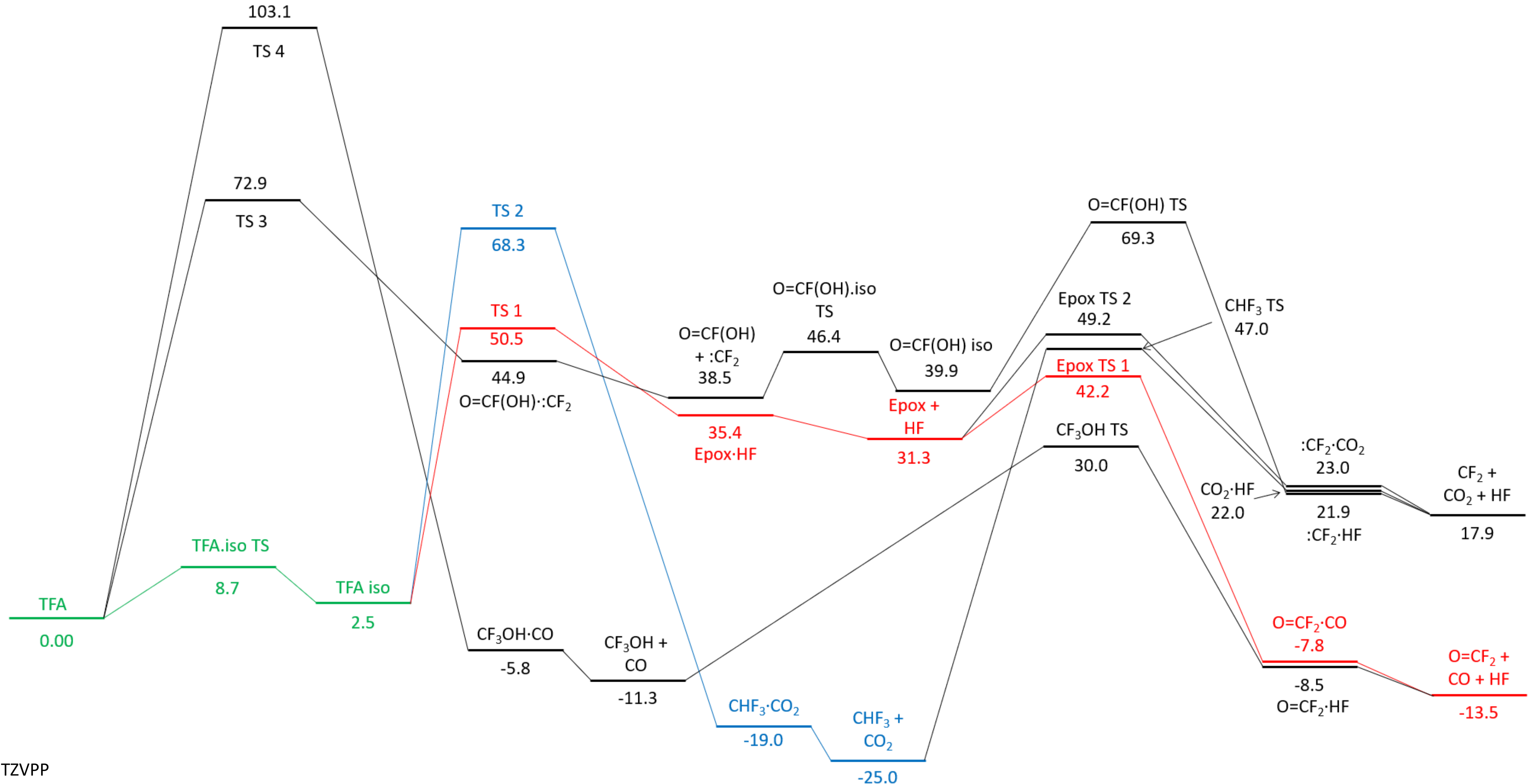
- Density Functional Theory (DFT)
    - *M06-2X-D3alt/def2TZVPP
- All ground state minima and transition states are confirmed via the diagonalization of the mass weighted hessian matrix
- Transition states are further verified to connect products and reactants through intrinsic reaction coordinate (IRC) computations

Kinetics

- Transition State Theory (TST)
    - Arkane (RMG)
- Calculated at temperatures ranging from 298 -1500 K at 50K intervals
- Tunneling corrections included based on the asymmetric Eckart model

*D3alt refers to D3 dispersion corrections with the parameters in GAMESS edited to resemble those in Gaussian16

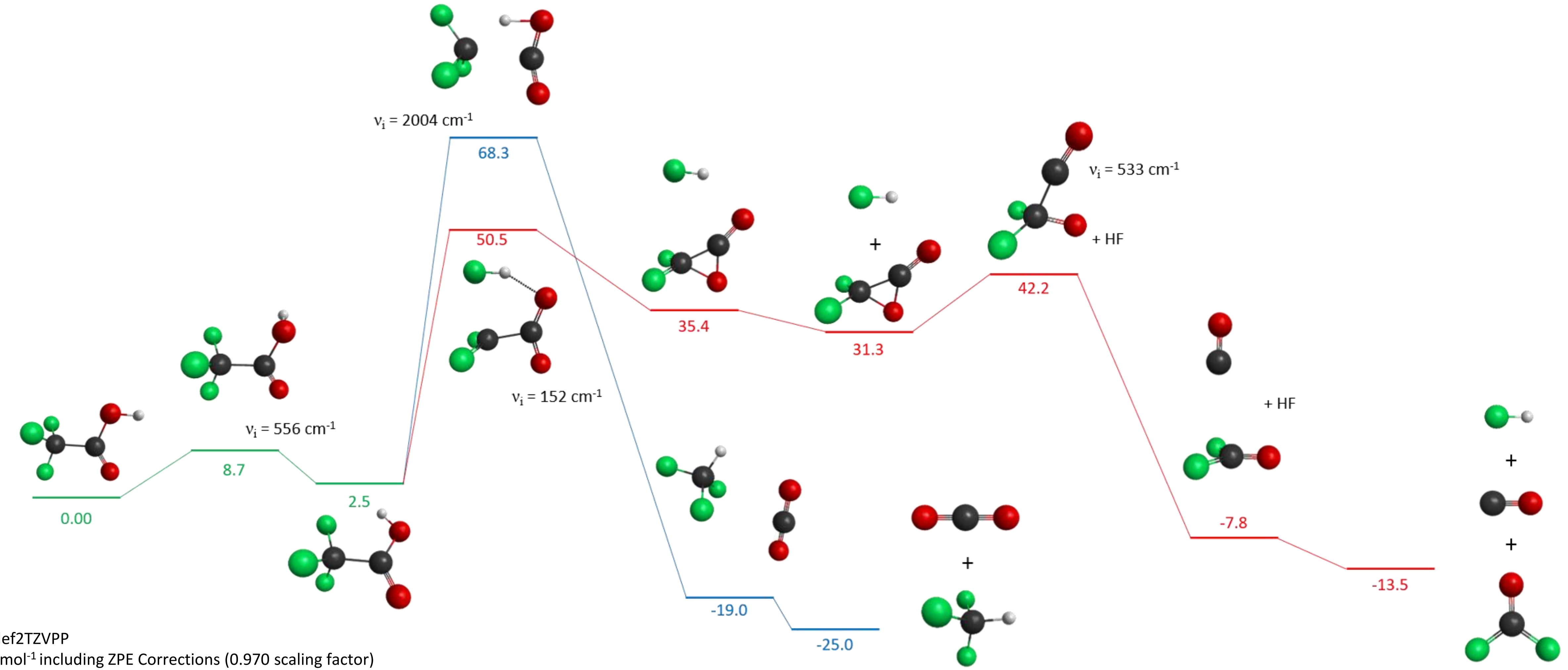
Favored Decomposition Pathways @ 298.15 K



M06-2X-D3alt/def2TZVPP

Energies in kcal mol^{-1} including ZPE Corrections (0.970 scaling factor)

Favored Decomposition Pathways @ 298.15 K



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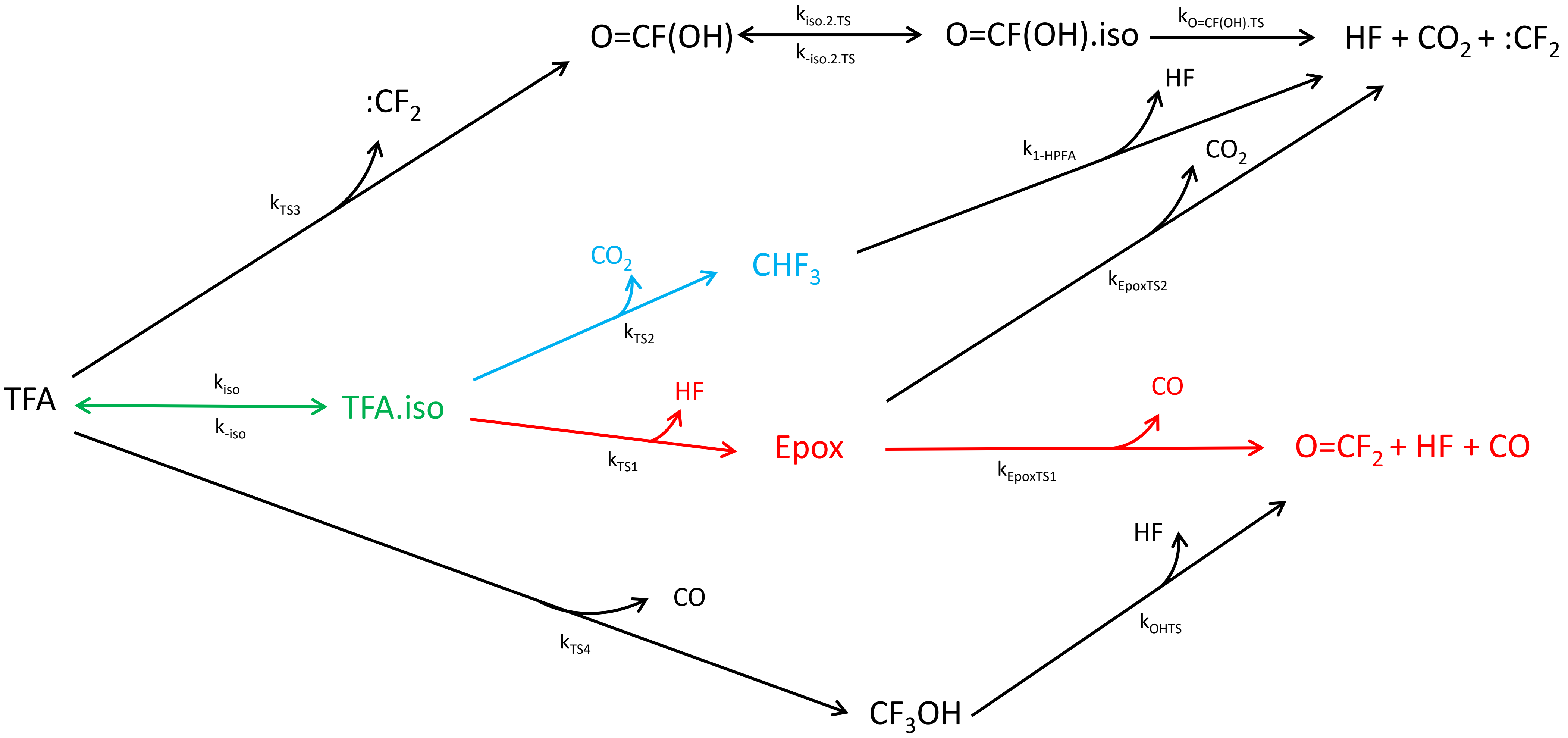
Energies in kcal mol^{-1} including ZPE Corrections (0.970 scaling factor)

TFA Decomposition Model



$O=CF(OH)$ ⇄ $O=CF(OH).iso$ ($k_{iso.2.TS}$, $k_{-iso.2.TS}$)

$O=CF(OH).iso \xrightarrow{k_{O=CF(OH).TS}} HF + CO_2 + :CF_2$

TFA ⇄ TFA.iso (k_{iso}, k_{-iso})

$TFA \xrightarrow{k_{TS3}} O=CF(OH) + :CF_2$

$TFA.iso \xrightarrow{k_{TS2}} CHF_3 + CO_2$

$CHF_3 \xrightarrow{k_{1\text{-}HPFA}} HF + CO_2 + :CF_2$ (− HF)

$TFA.iso \xrightarrow{k_{TS1}} Epox + HF$

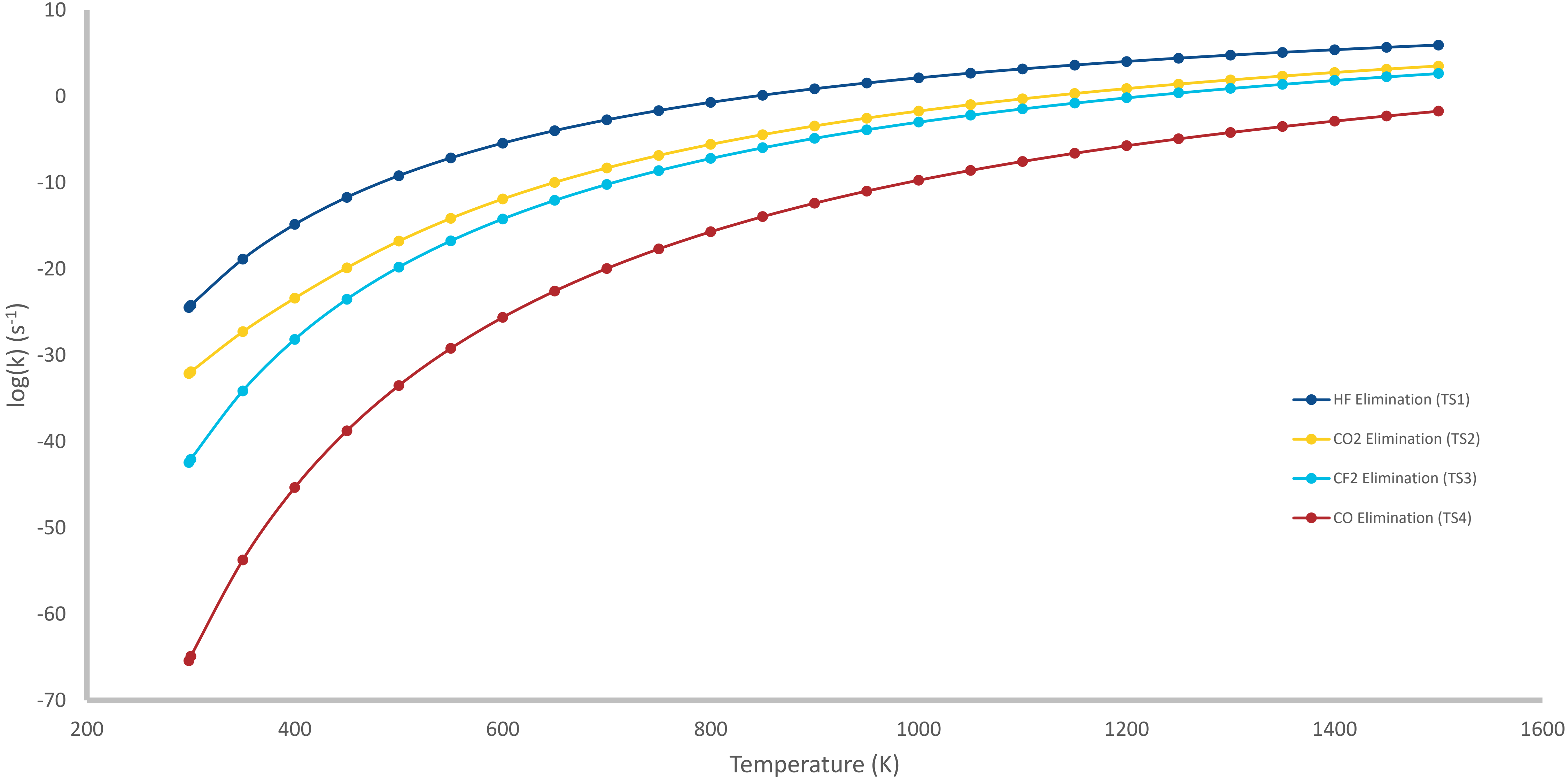
$Epox \xrightarrow{k_{EpoxTS2}} HF + CO_2 + :CF_2$ (− CO_2)

$Epox \xrightarrow{k_{EpoxTS1}} O=CF_2 + HF + CO$ (− CO)

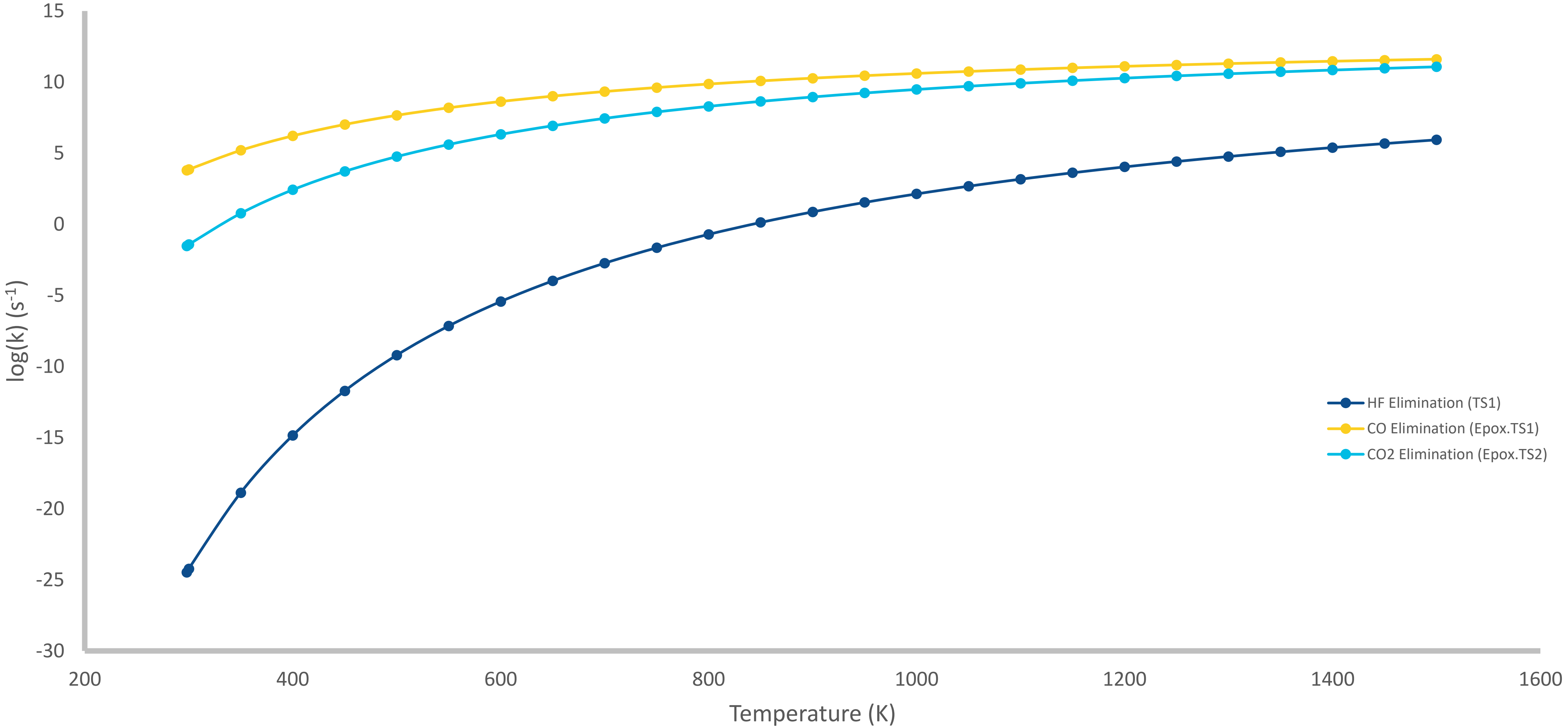
$TFA \xrightarrow{k_{TS4}} CF_3OH + CO$

$CF_3OH \xrightarrow{k_{OHTS}} O=CF_2 + HF + CO$ (− HF)

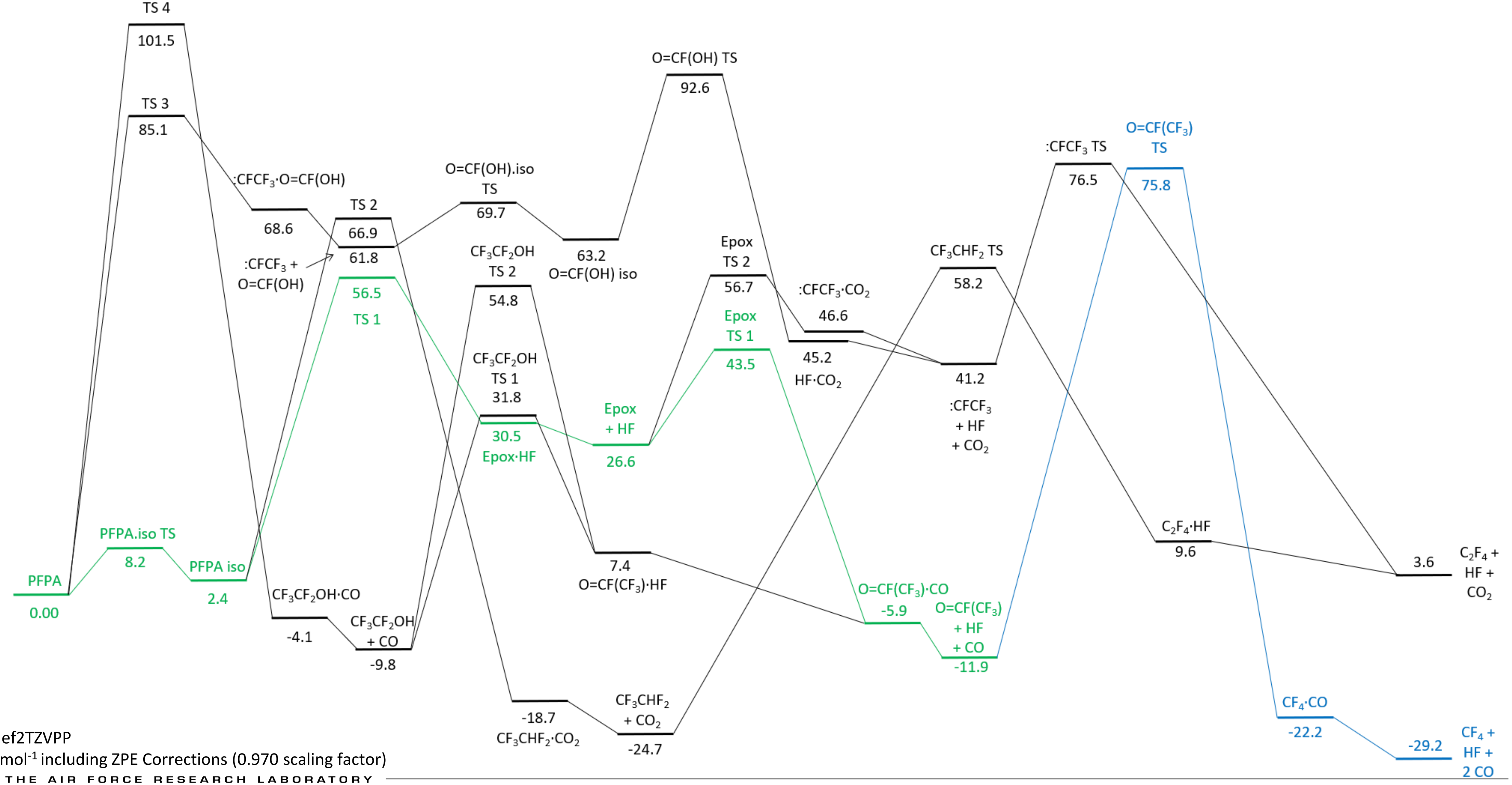
TFA Initial Decomposition Rates



Kinetically Favored TFA Decomposition Rates



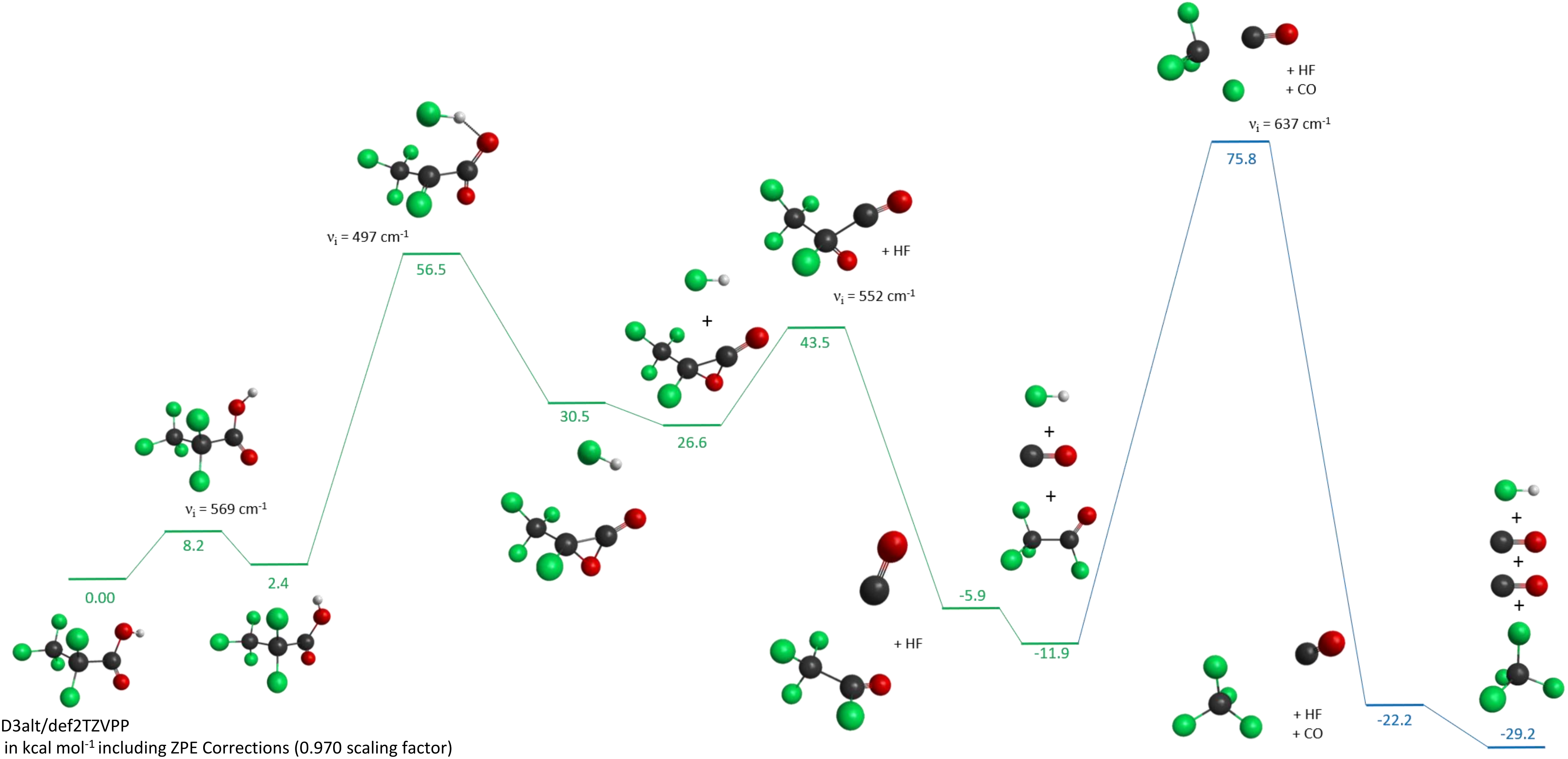
Favored Decomposition Pathways @ 298.15 K



M06-2X-D3alt/def2TZVPP

Energies in kcal mol^{-1} including ZPE Corrections (0.970 scaling factor)

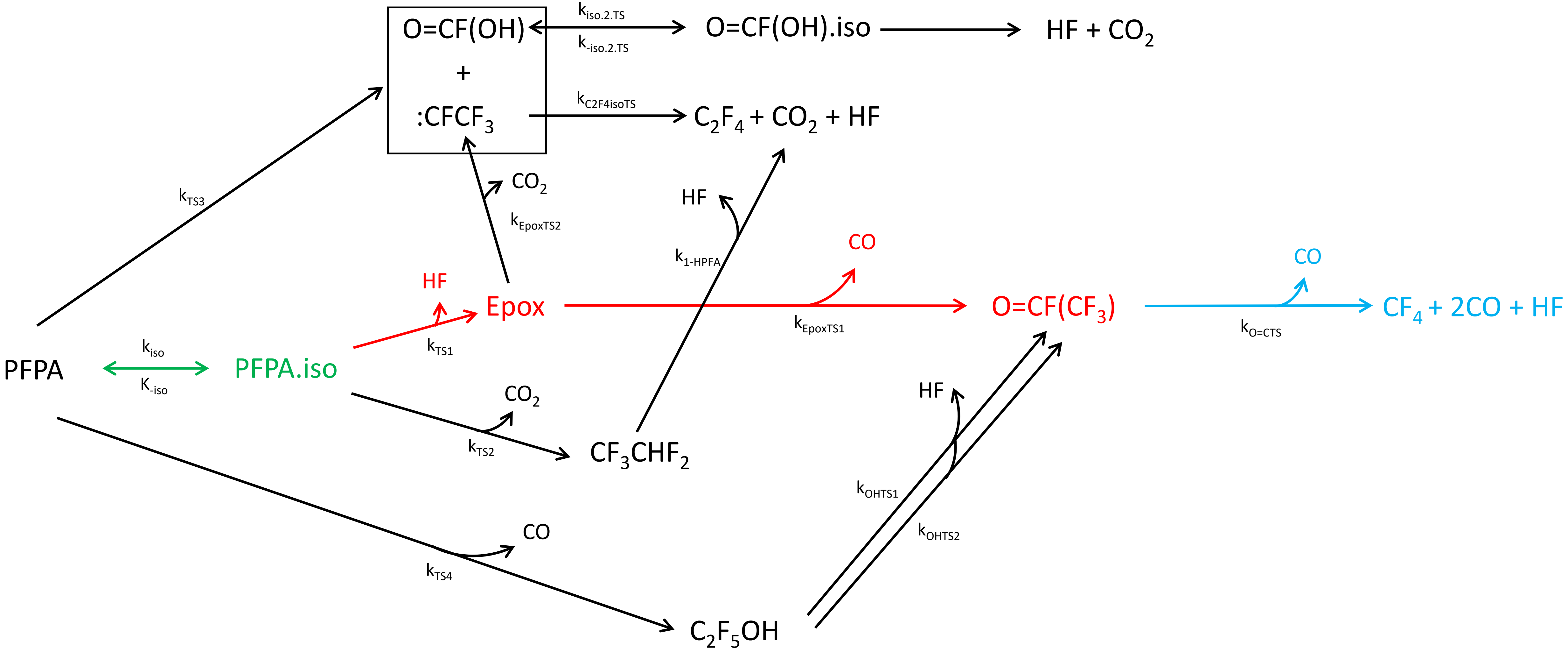
Favored Decomposition Pathways @ 298.15 K



M06-2X-D3alt/def2TZVPP

Energies in kcal mol^{-1} including ZPE Corrections (0.970 scaling factor)

PFPA Decomposition Model



$O{=}CF(OH)$ + $:CFCF_3$

$k_{iso.2.TS}$ / $k_{-iso.2.TS}$

$O{=}CF(OH).iso$

$HF + CO_2$

$k_{C2F4isoTS}$

$C_2F_4 + CO_2 + HF$

k_{TS3}

CO_2

$k_{EpoxTS2}$

HF

$k_{1\text{-}HPFA}$

CO

HF

Epox

$k_{EpoxTS1}$

$O{=}CF(CF_3)$

CO

$CF_4 + 2CO + HF$

$k_{O=CTS}$

k_{TS1}

PFPA

k_{iso} / K_{-iso}

PFPA.iso

CO_2

k_{TS2}

CF_3CHF_2

HF

k_{OHTS1}

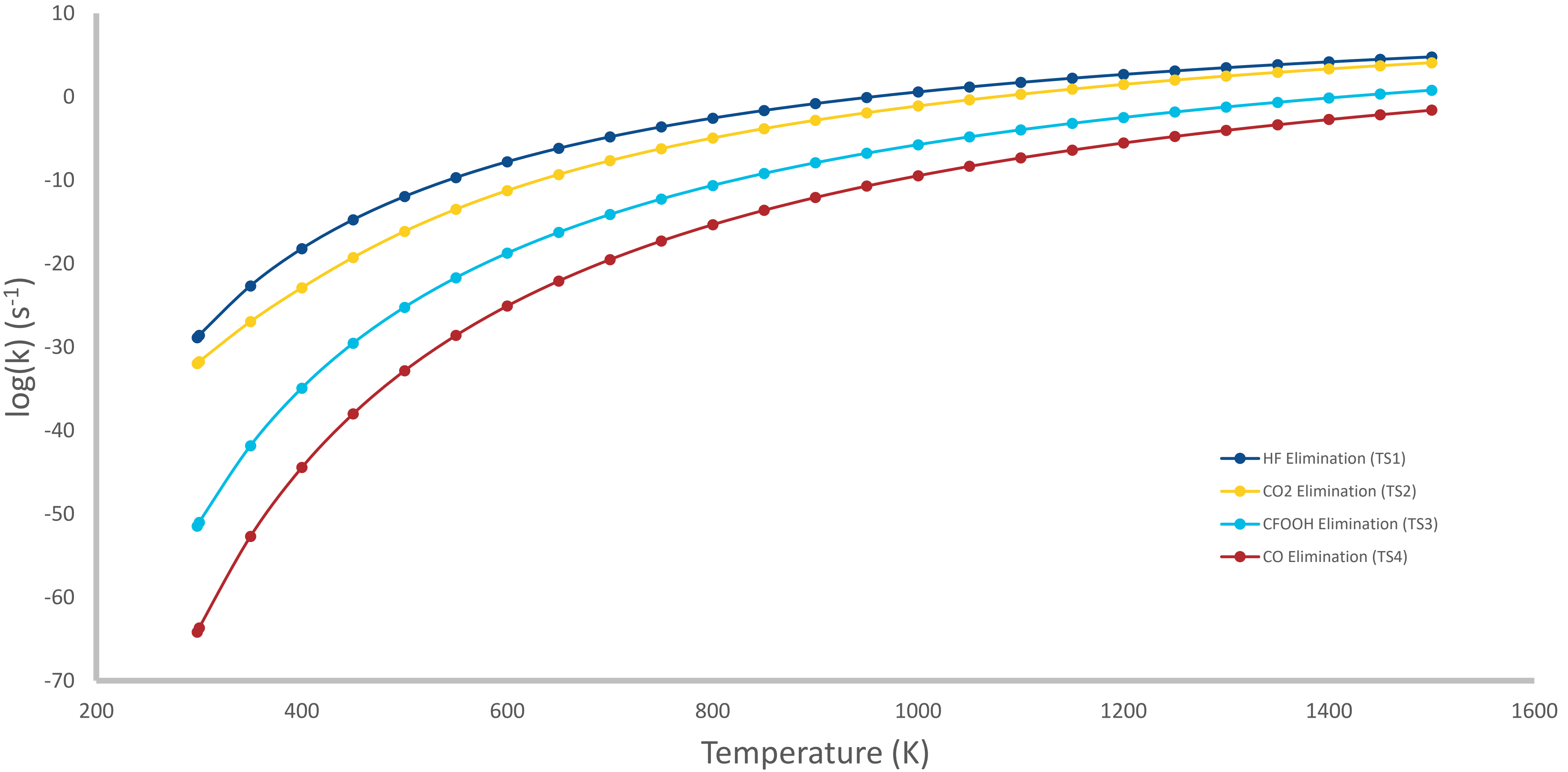
k_{OHTS2}

CO

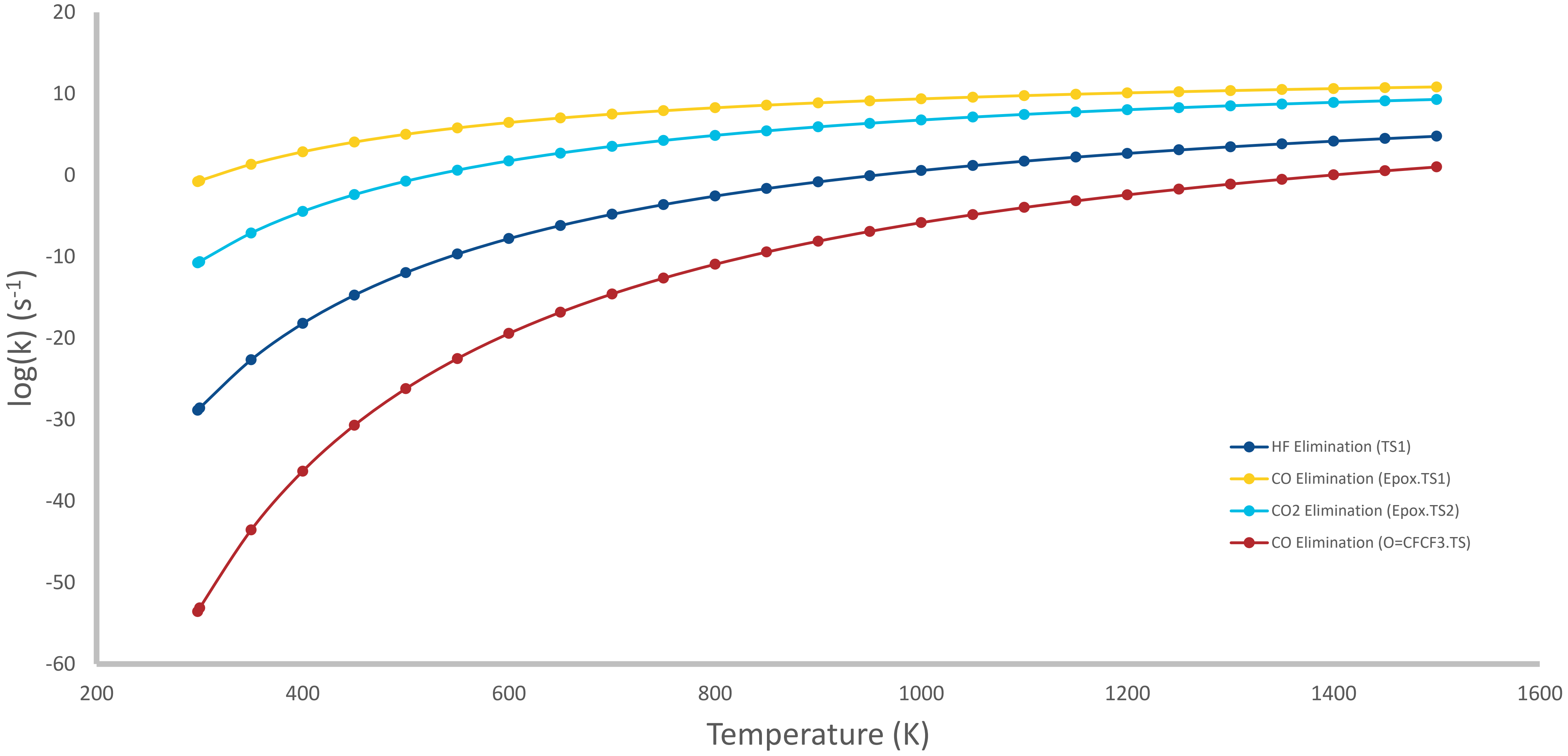
k_{TS4}

C_2F_5OH

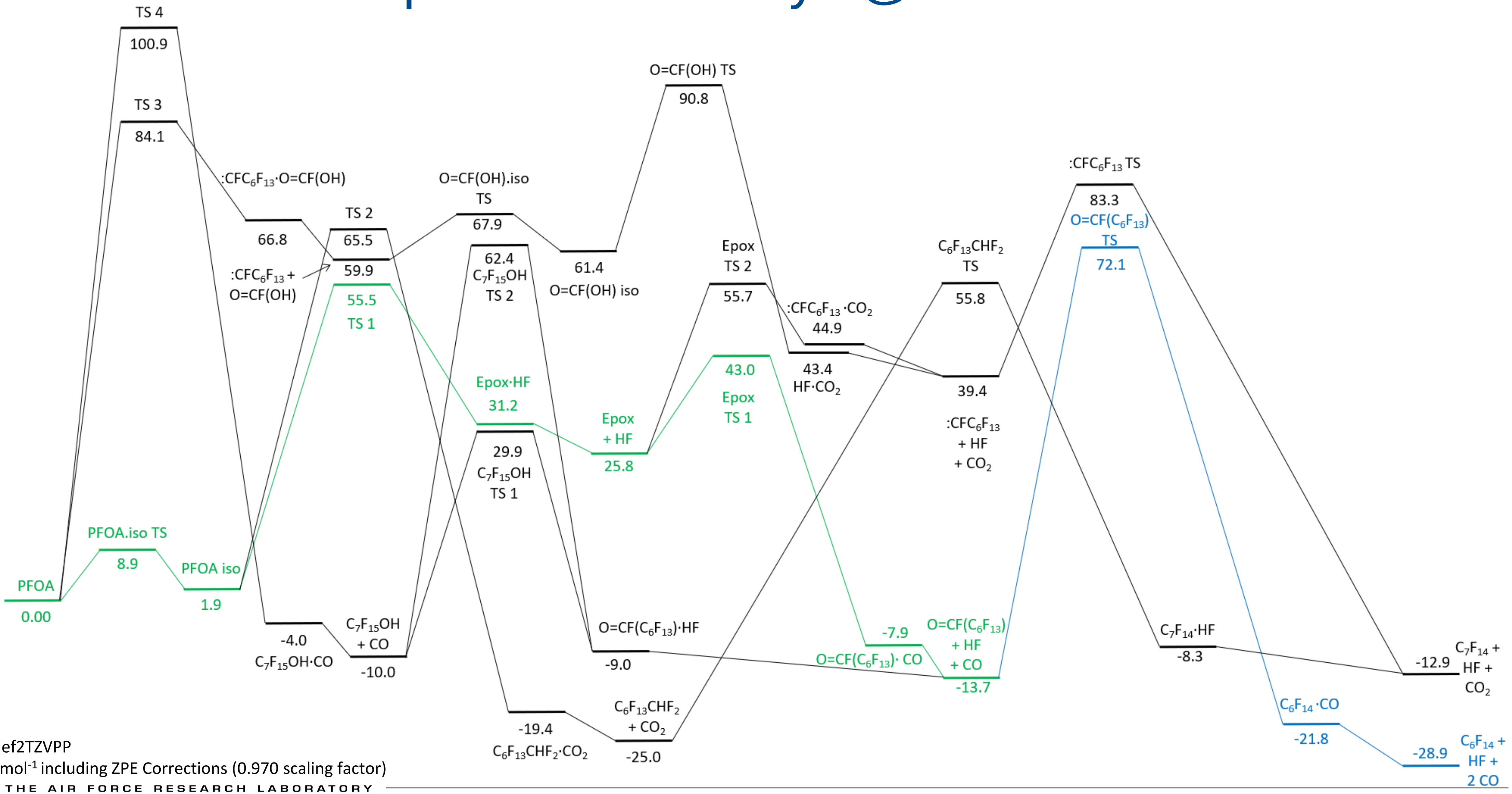
PFPA Initial Decomposition Rates



Kinetically Favored PFPA Decomposition Rates



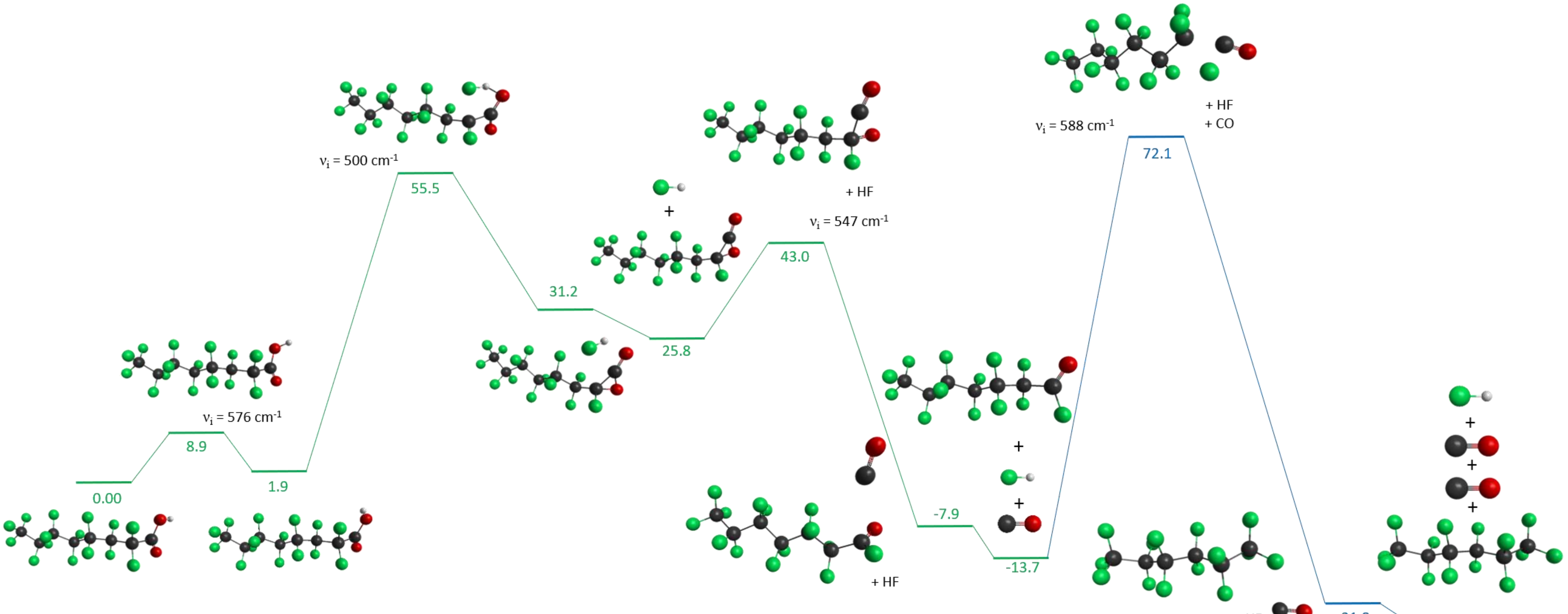
Favored Decomposition Pathways @ 298.15 K



M06-2X-D3alt/def2TZVPP

Energies in kcal mol^{-1} including ZPE Corrections (0.970 scaling factor)

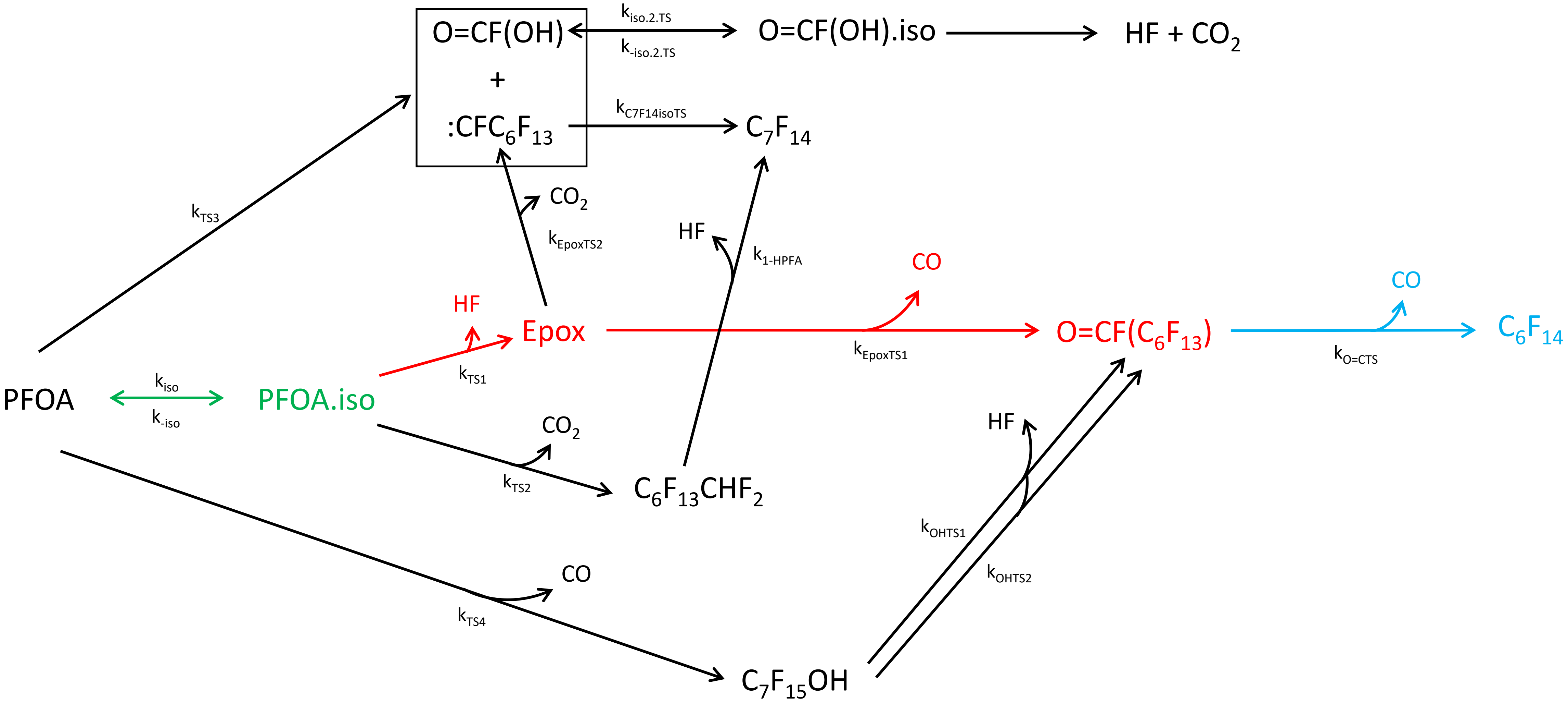
Favored Decomposition Pathways @ 298.15 K



M06-2X-D3alt/def2TZVPP

Energies in kcal mol^{-1} including ZPE Corrections (0.970 scaling factor)

PFOA Decomposition Model



O=CF(OH) + $:CFC_6F_{13}$

$k_{iso.2.TS}$

$k_{-iso.2.TS}$

O=CF(OH).iso

HF + CO_2

$k_{C7F14isoTS}$

C_7F_{14}

k_{TS3}

CO_2

$k_{EpoxTS2}$

HF

$k_{1\text{-}HPFA}$

CO

CO

HF

Epox

$O{=}CF(C_6F_{13})$

C_6F_{14}

$k_{EpoxTS1}$

$k_{O=CTS}$

k_{TS1}

PFOA

k_{iso}

k_{-iso}

PFOA.iso

CO_2

HF

k_{TS2}

$C_6F_{13}CHF_2$

k_{OHTS1}

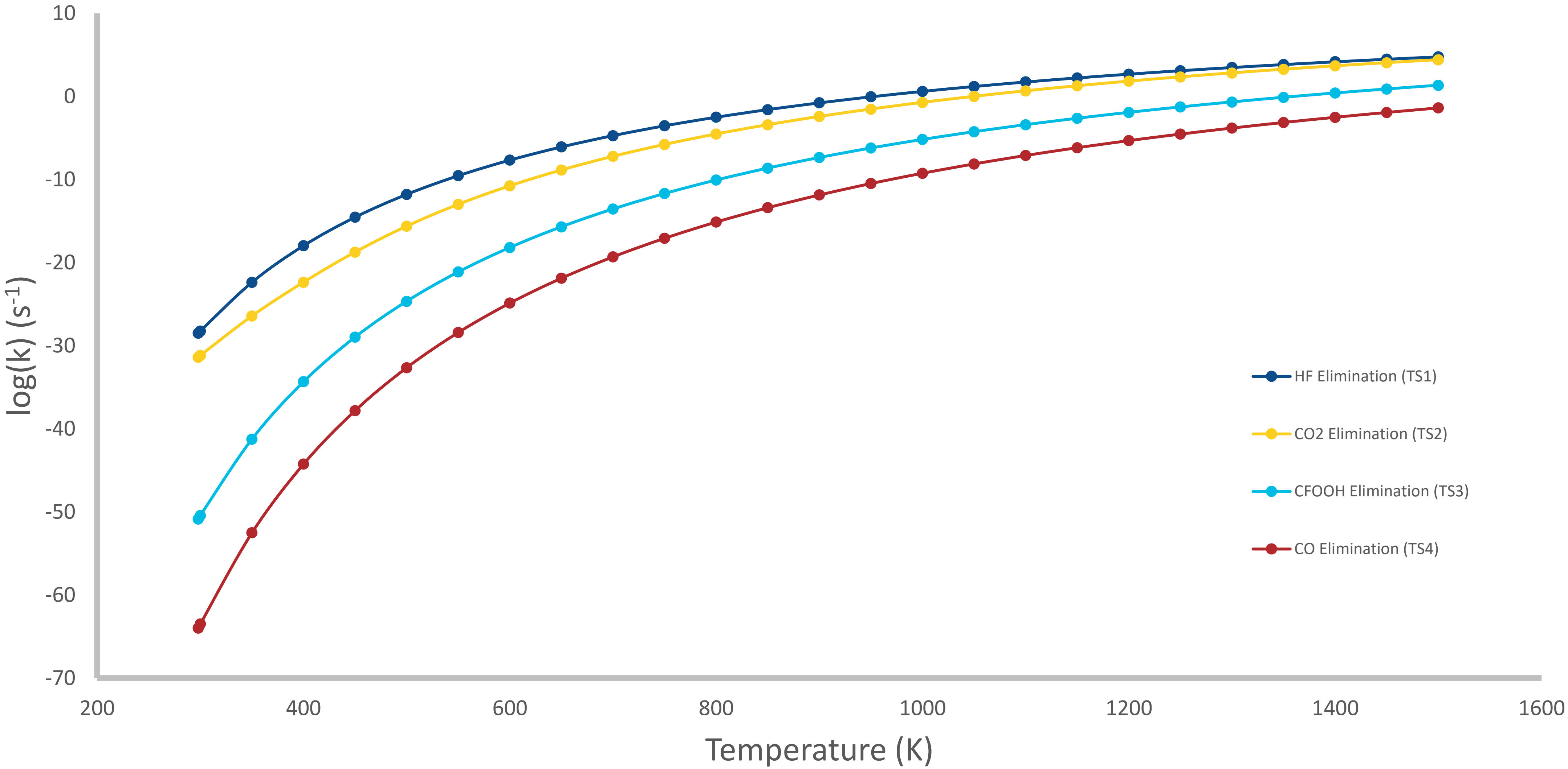
k_{OHTS2}

CO

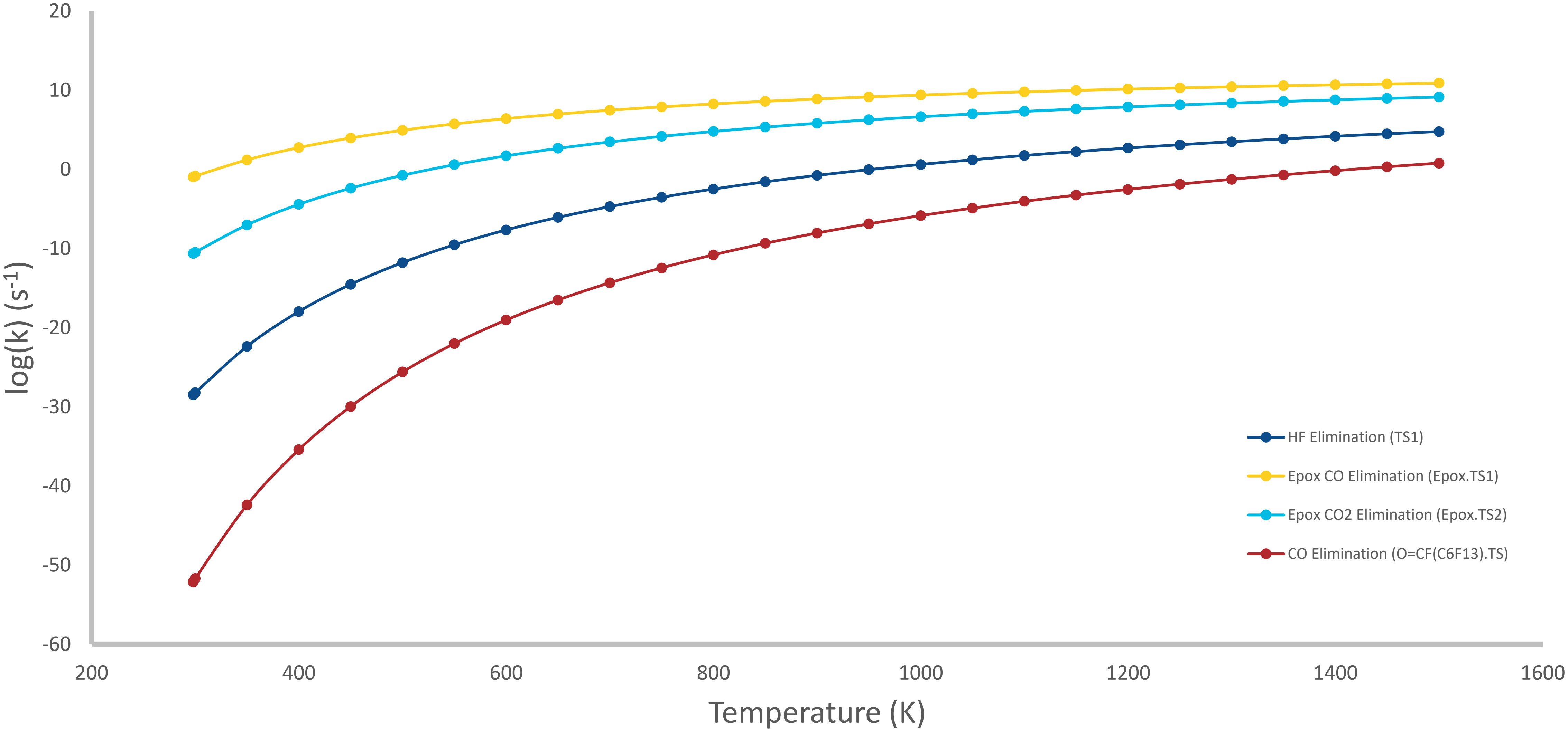
k_{TS4}

$C_7F_{15}OH$

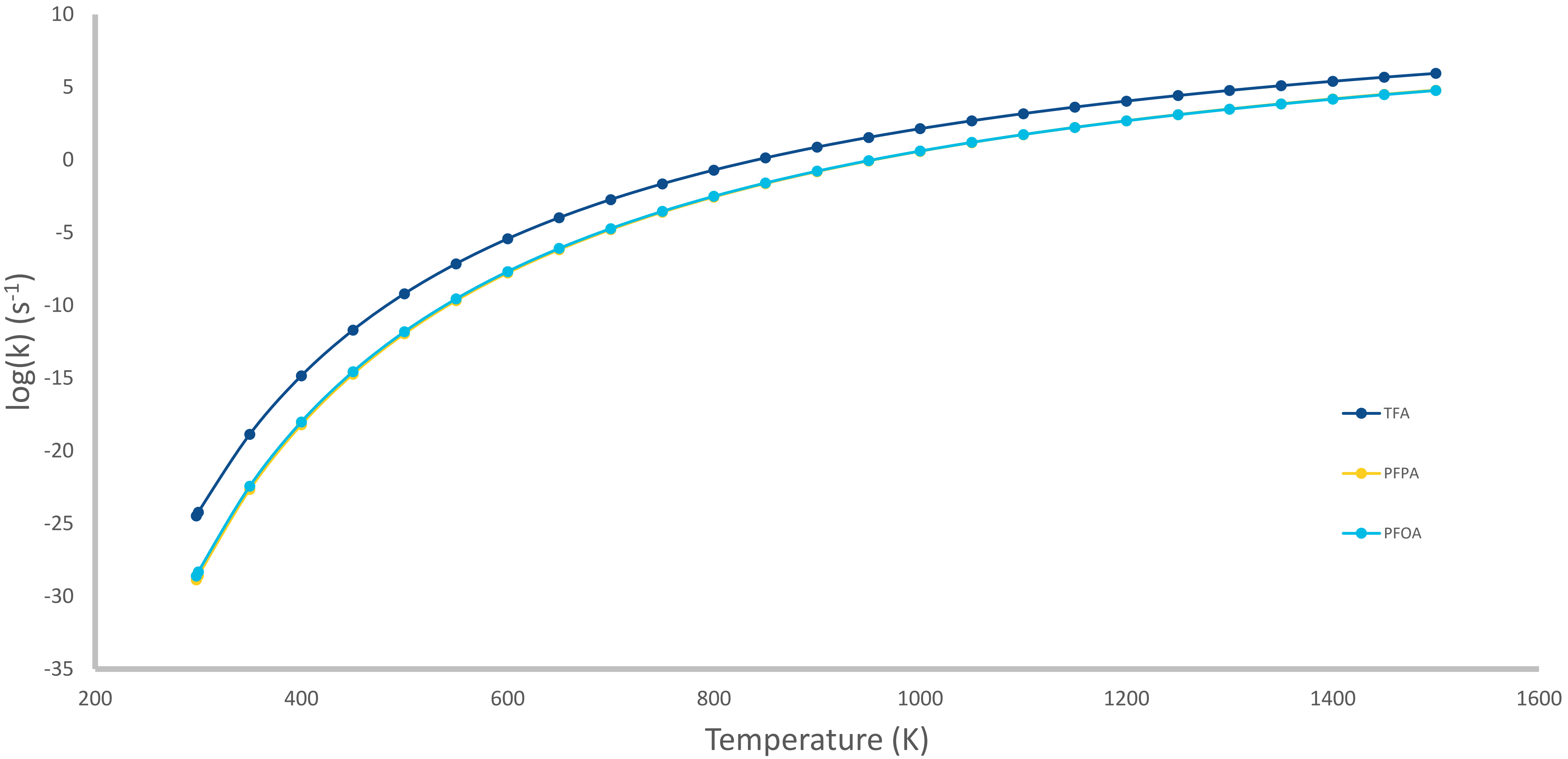
PFOA Initial Decomposition Rates



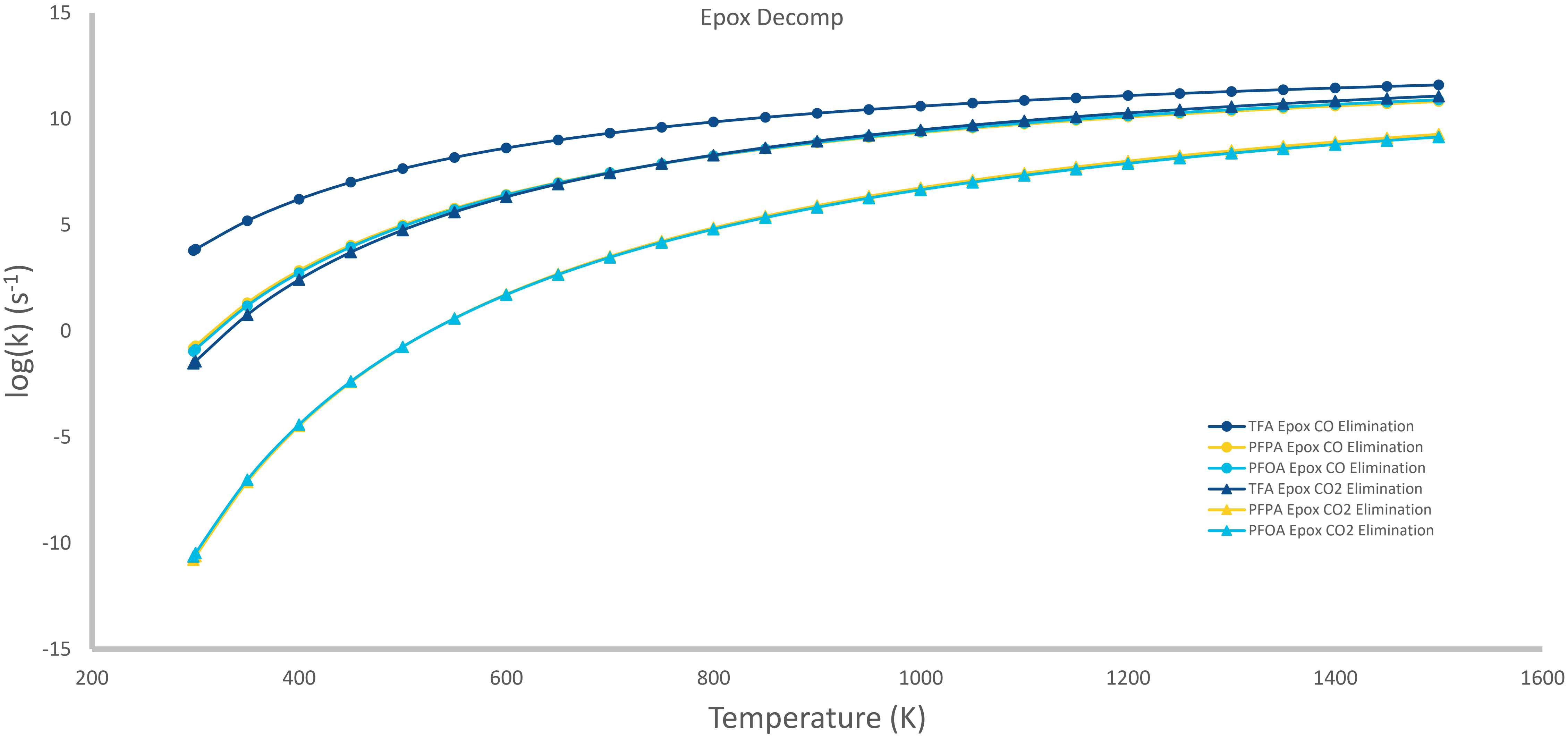
Kinetically Favored PFOA Decomposition Rates



HF Elimination Rates

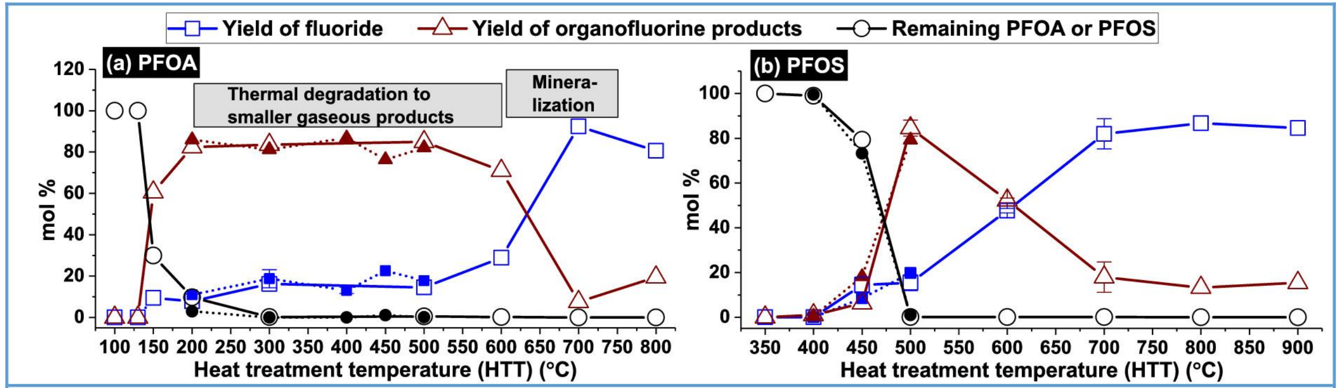


Epox Decomposition Rates



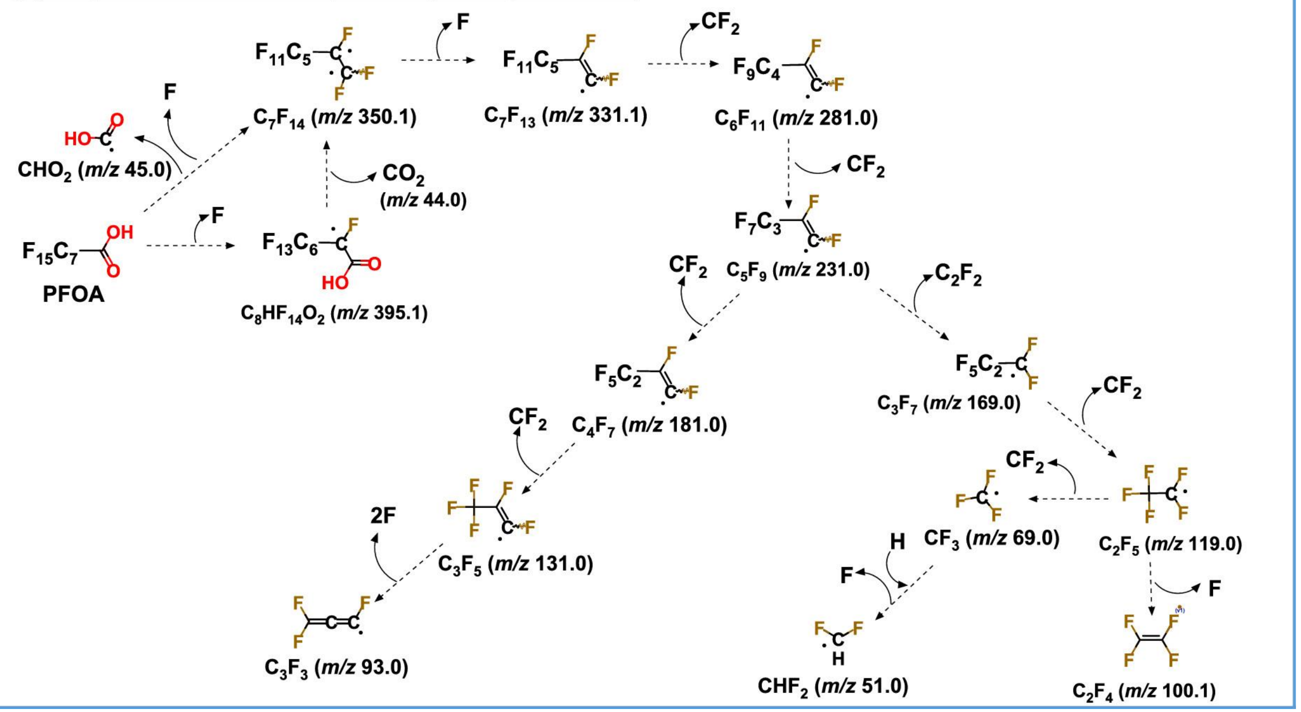
Experimental Thermal Decomposition of PFCAs

Measured yields of F from (a) PFOA and (b) PFOS during GAC thermal reactivation performed in an open system under a flow of CO_2 (open symbols) and in a closed system with air (closed symbols).



(c) Proposed thermal decomposition pathways of PFOA in an inert atmosphere on the basis of thermal decomposition products of PFOA identified by TD−Pyr−GC−MS.

(c) Proposed thermal decomposition pathways of PFOA



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PFCA Homolytic Bond Cleavage

	ΔG_{rxn} (kcal mol^{-1})				
Carbon-Carbon Bond Cleavage	298.15 K (25°C)		873.15 K (600°C)		1473.15 K (1200°C)
TFA → CF_3 + HOCO	75.1		49.8		24.6
PFPA → CF_3 + F_2C-C(O)OH	71.0		43.3		15.8
PFOA → CF_3 + $F_{12}C_6$-C(O)OH	75.4		46.8		18.4
Carbon-Fluorine Bond Cleavage					
TFA → F + F_2C-C(O)OH	106.6		85.8		64.0
PFPA → F + F_3C-CF-C(O)OH	99.5		79.3		58.1
PFOA → F + F_3C-(C_5F_{10})-CF-C(O)OH	98.4		77.6		55.8
Carbon-Oxygen Bond Cleavage					
TFA → OH + CF_3CO_2	95.0		71.7		47.6
PFPA → OH + $CF_3CF_2CO_2$	94.0		69.4		44.0
PFOA → OH + $CF_3(C_5F_{10})CO_2$	93.9		70.5		46.3
1,2 HF Elimination	ΔG_a (kcal mol^{-1})				
TFA → HF + F_2C-O-CO	50.5		49.8		49.6
PFPA → HF + F_3CCF_2-O-CO	56.5		57.7		59.6
PFOA → HF + $F_3C(C_5F_{10})$-O-CO	55.5		56.6		58.3

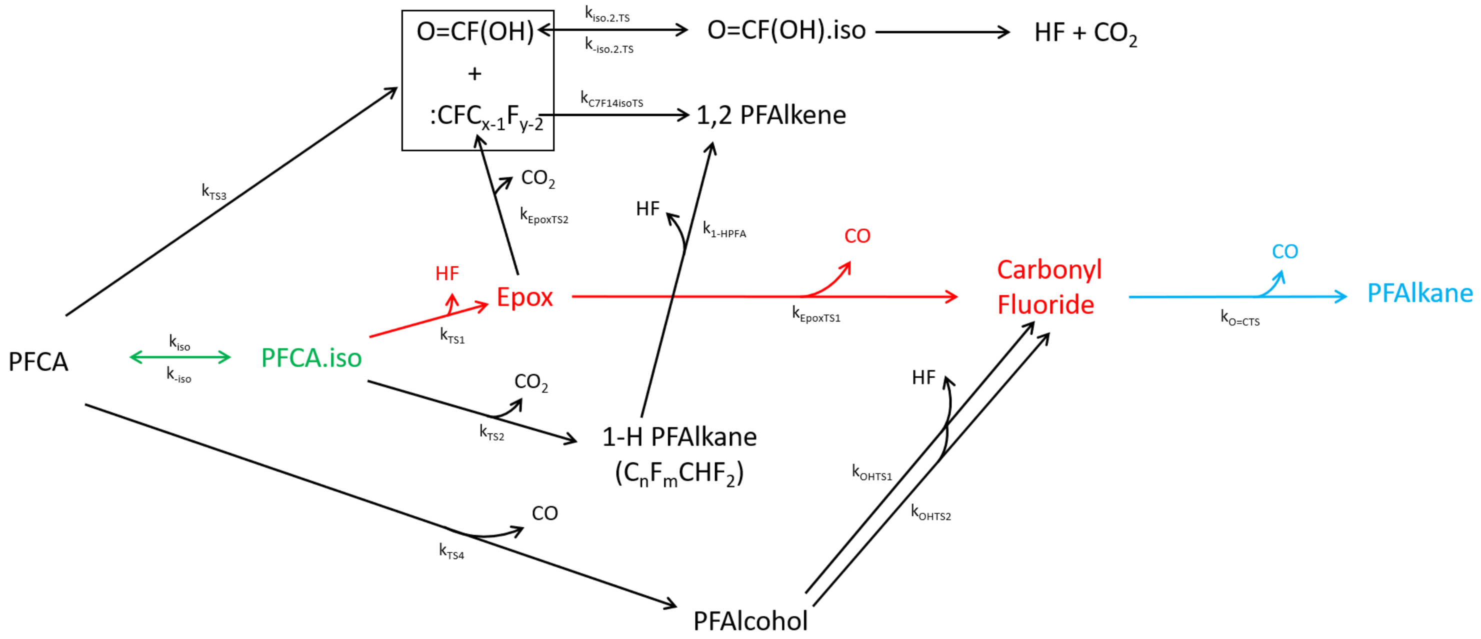
M06-2X-D3alt/def2TZVPP
Energies in kcal mol^{-1} including ZPE Corrections (0.970 scaling factor)

Objectives

- What is the Mechanism for thermal Decomposition of PFCAs?
- What byproducts can we expect to be formed?
- Does this change with respect to chain length or temperature?

Conclusions

- PFCAs Decompose similarly independent of chain length



- Entropic stabilization at high temperatures leads to favorable ΔG_{rxn} of Homolytic bond cleavages
  - TFA
    - C-C bond cleavage is competitive at 600 °C and favored at 1200 °C
  - PFPA
    - C-C bond cleavage is favored at both 600 °C and 1200 °C

Future Work

- Determine rates of bond cleavage reactions at relevant temperatures
  - Variational Transition State Theory (VTST)
- Investigate bimolecular decomposition mechanisms
- Investigate relevant radical reactions
  - Reactions with OH and H

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HIGH PERFORMANCE COMPUTING
MODERNIZATION PROGRAM

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Questions?

Back-up Slides

Functional Benchmarking – Δ H_f with Aug-cc-PVDZ Basis

Species	B3LYP	B3PW91	PBE0	M05-2X	ωB97x-D	MP2	Experiment
CF_4	-200.24	-208.35	-211.92	-215.95	-209.08	-212.59	-223.02
C_3F_8	-368.84	-388.86	-401.37	-407.52	-391.85	-398.08	-426.55
CF_3OH	-214.03	-210.47	-211.82	-217.36	-213.29	-217.55	-220.70
HF	-60.67	-60.27	-58.56	N/A	-61.07	-61.62	-65.14
2F	33.50	33.44	31.34	26.55	32.75	33.50	37.95

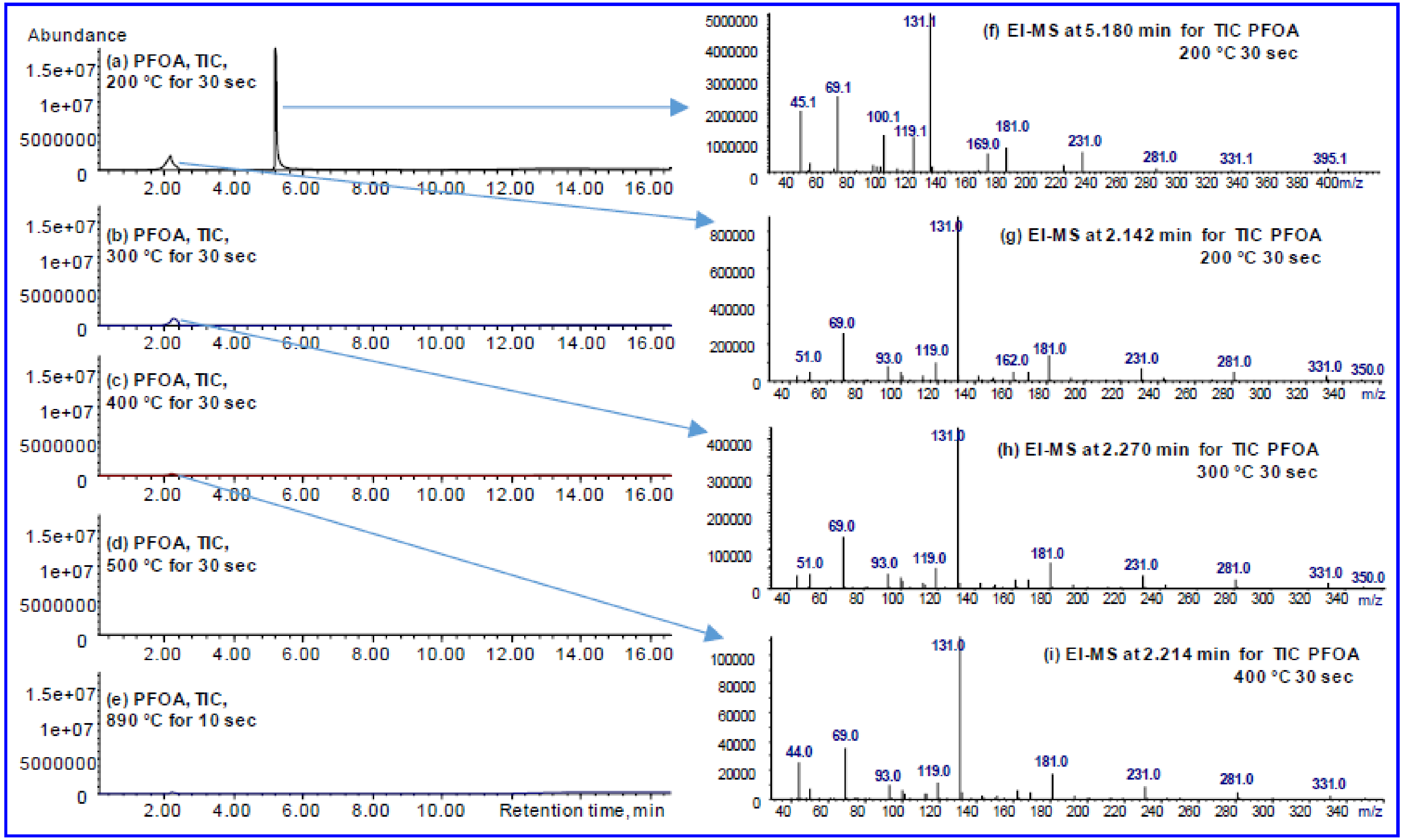
Energies in kcal mol^{-1}

Basis Set Benchmarking with M06-2X-D3 funtional

Basis Set	Mean	Max	Dev
def2TZVPP	0.77	1.68	0.45
6-311+G(d,p)	5.67	16.44	7.92
6-311+G(2df,p)	1.96	4.84	2.22
6-311+G(3df,2p)	1.27	3.07	0.87
Jun-CC-pVTZ	3.02	8.18	4.11
Aug-CC-pVTZ	3.13	8.32	4.12
Aug-CC-pVQZ	1.26	3.49	1.79
Aug-Pcseg-2	1.05	6.28	1.75
Aug-Pcseg-3	0.96	4.36	1.20
Aug-CC-pV5Z	0.00	0.00	0.00

Benchmarking done on set of 33 decomposition reactions of Perfluoromethanesulfonic Acid (PFMS) and Perfluoroethanesulfonic Acid (PFES) including activation and reaction energies. Energies in kcal mol^{-1}.

MS Data for Thermal Decomposition



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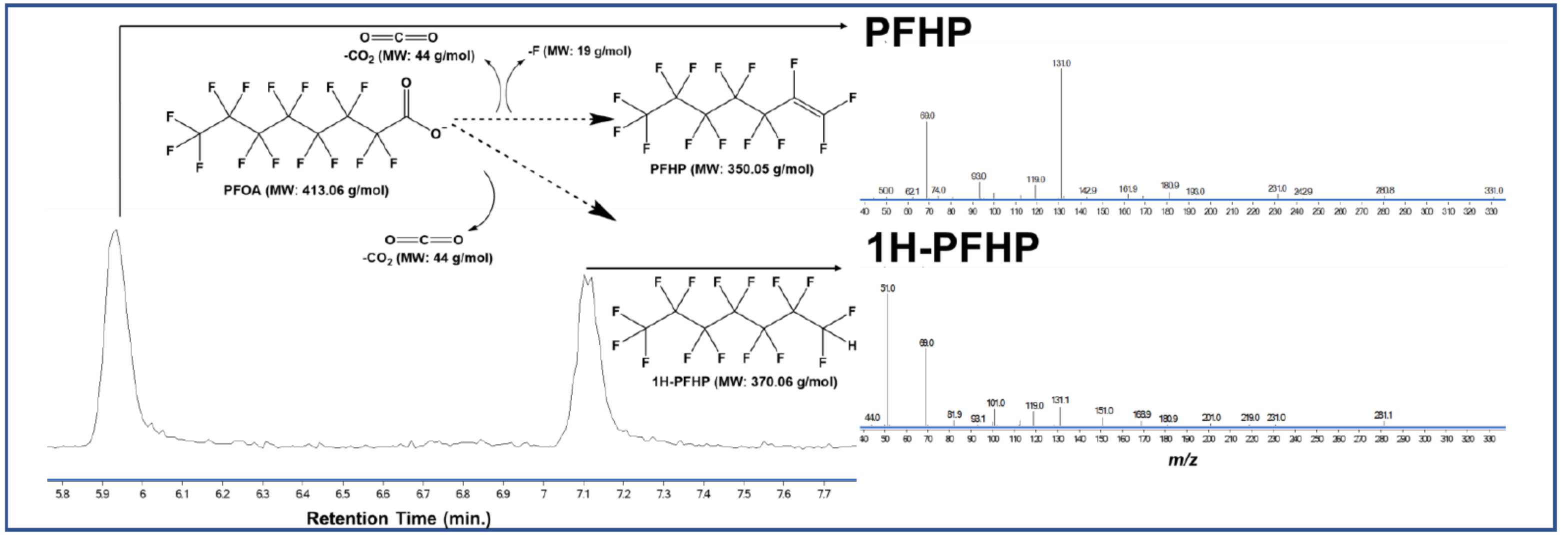
Experimental Thermal Decomposition of PFCAs

- Thermal byproducts of PFOA:
  - Perfluoroheptene (PFHP, fluoroalkene)
  - 1H-perfluoroheptane (1H-PFHP, fluoroalkane)
- PFHP is *predicted* by ECHA to be carcinogenic, mutagenic, or toxic
- Degradation of PFCAs to fluoroalkene and fluoroalkane has been previously mentioned (Kissa, 2001; Krusic *et al.*, 2005, Xiao *et al.*, 2020)

- Thermal byproducts predicted to be carcinogenic, mutagenic, or toxic by ECHA:
  - Perfluorooctene and 1H-perfluorooctane (PFNA products)
  - Perfluorohexene (PFHpA product)
  - Perfluoropentene (PFHxA product)
- Thermal byproducts of PFBA and PFPA were not observed



I. Titaley et al. *SERDP ESTCP Symposiom 2020* **(2020)**

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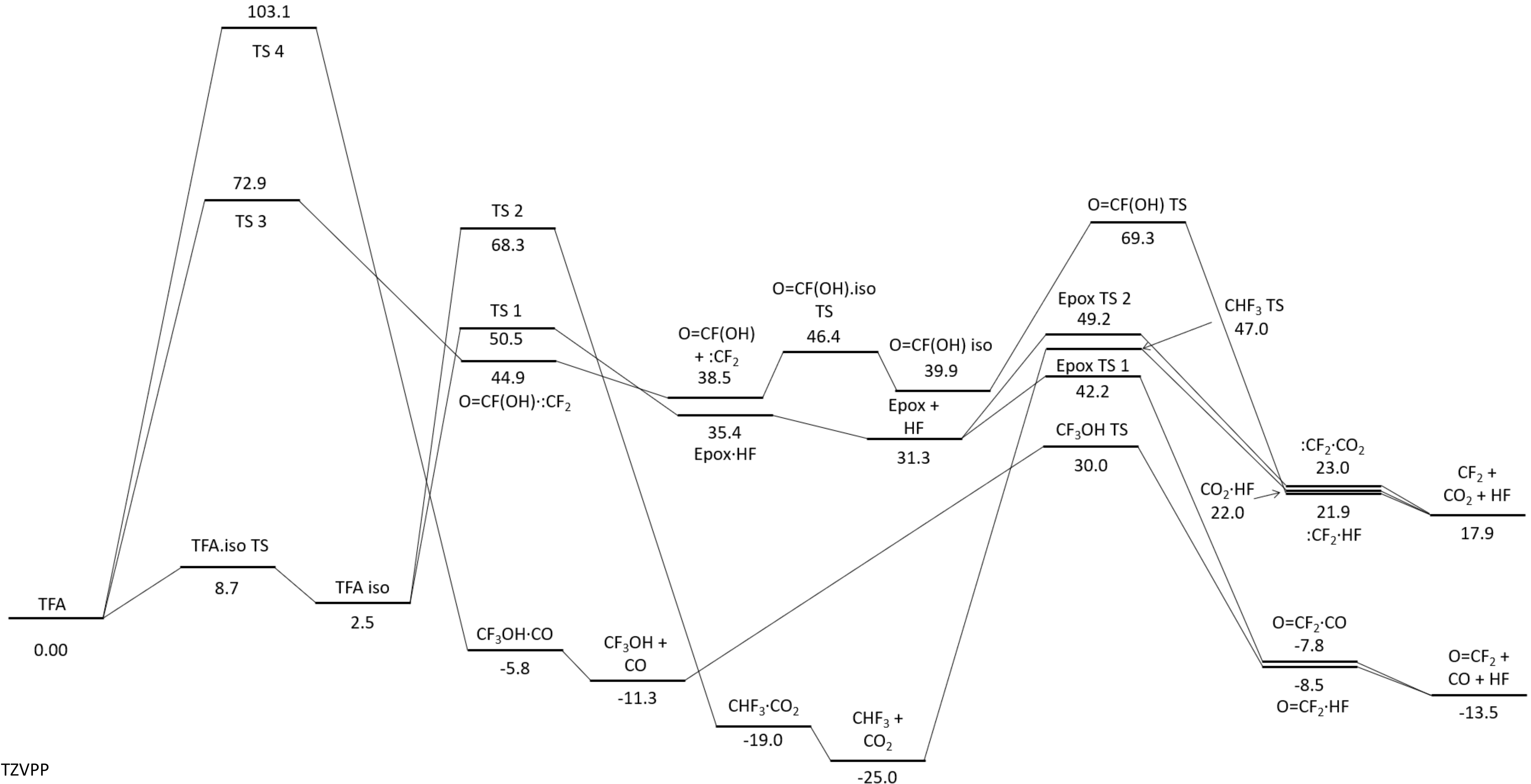
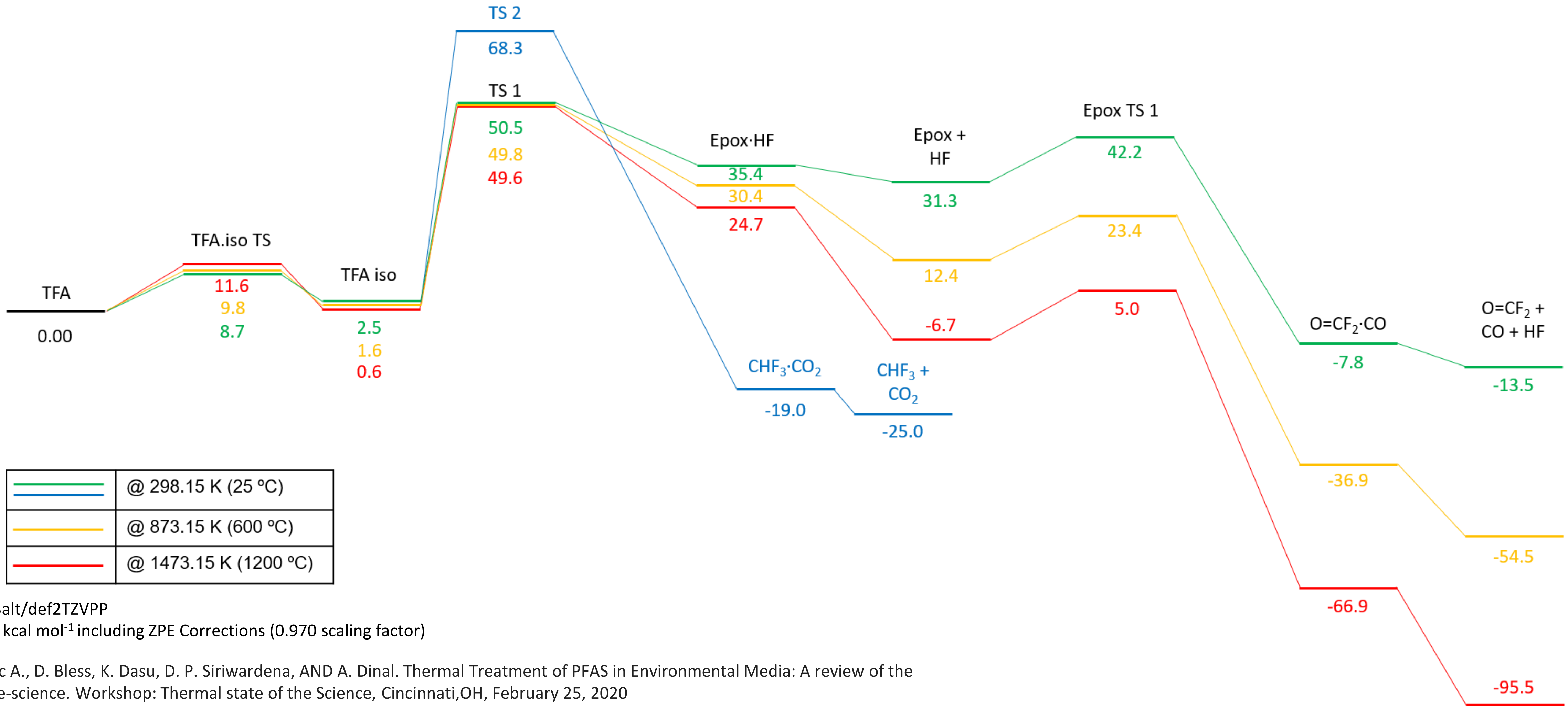
TFA Free Energy Surface @ 298.15 K



M06-2X-D3alt/def2TZVPP

Energies in kcal mol^{-1} including ZPE Corrections (0.970 scaling factor)

TFA Free Energy Surface @ Incineration Temperatures[1,2]

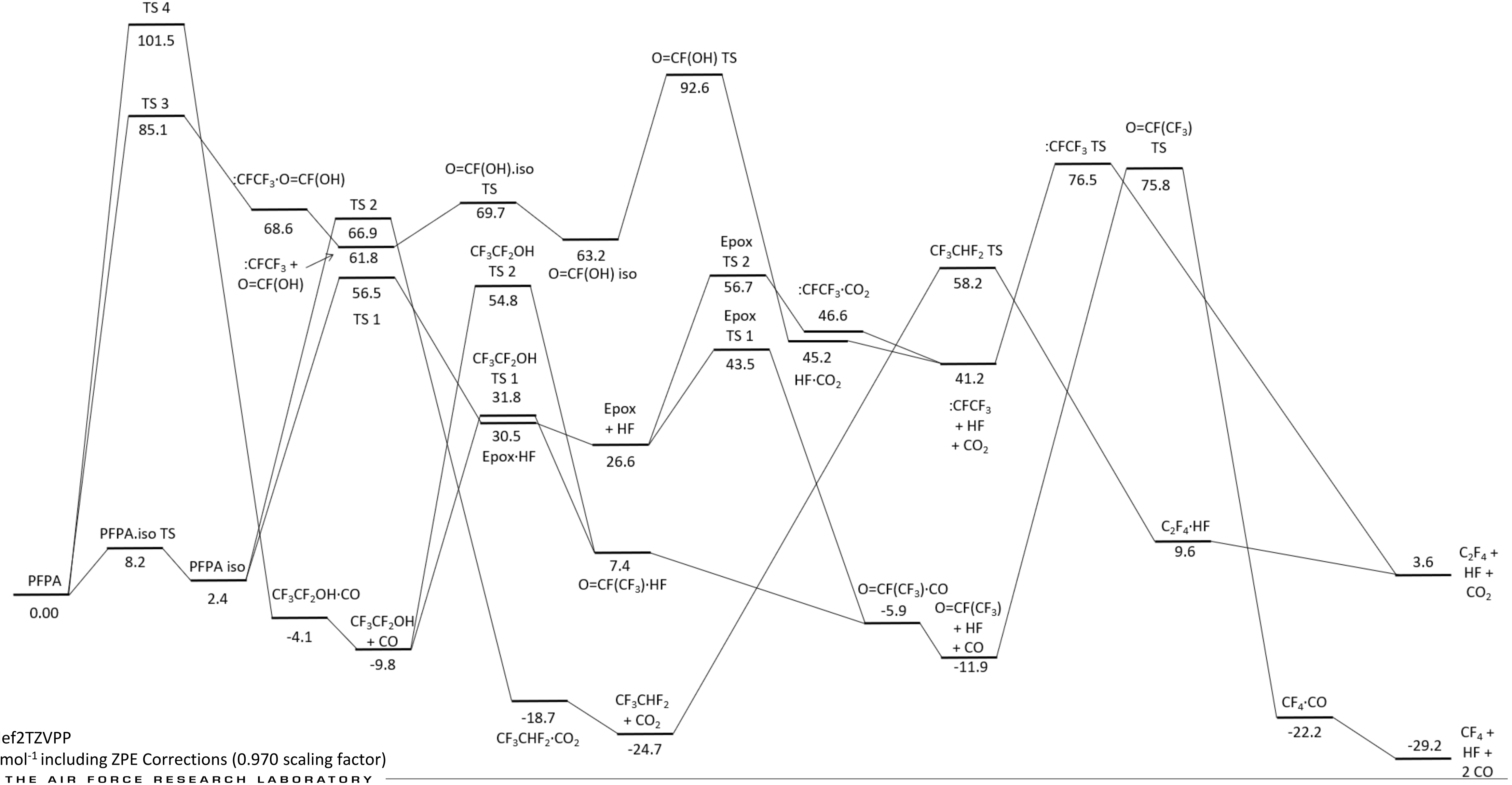


M06-2X-D3alt/def2TZVPP
Energies in kcal mol^{-1} including ZPE Corrections (0.970 scaling factor)

[1] Mills, Marc A., D. Bless, K. Dasu, D. P. Siriwardena, AND A. Dinal. Thermal Treatment of PFAS in Environmental Media: A review of the state-of-the-science. Workshop: Thermal state of the Science, Cincinnati,OH, February 25, 2020

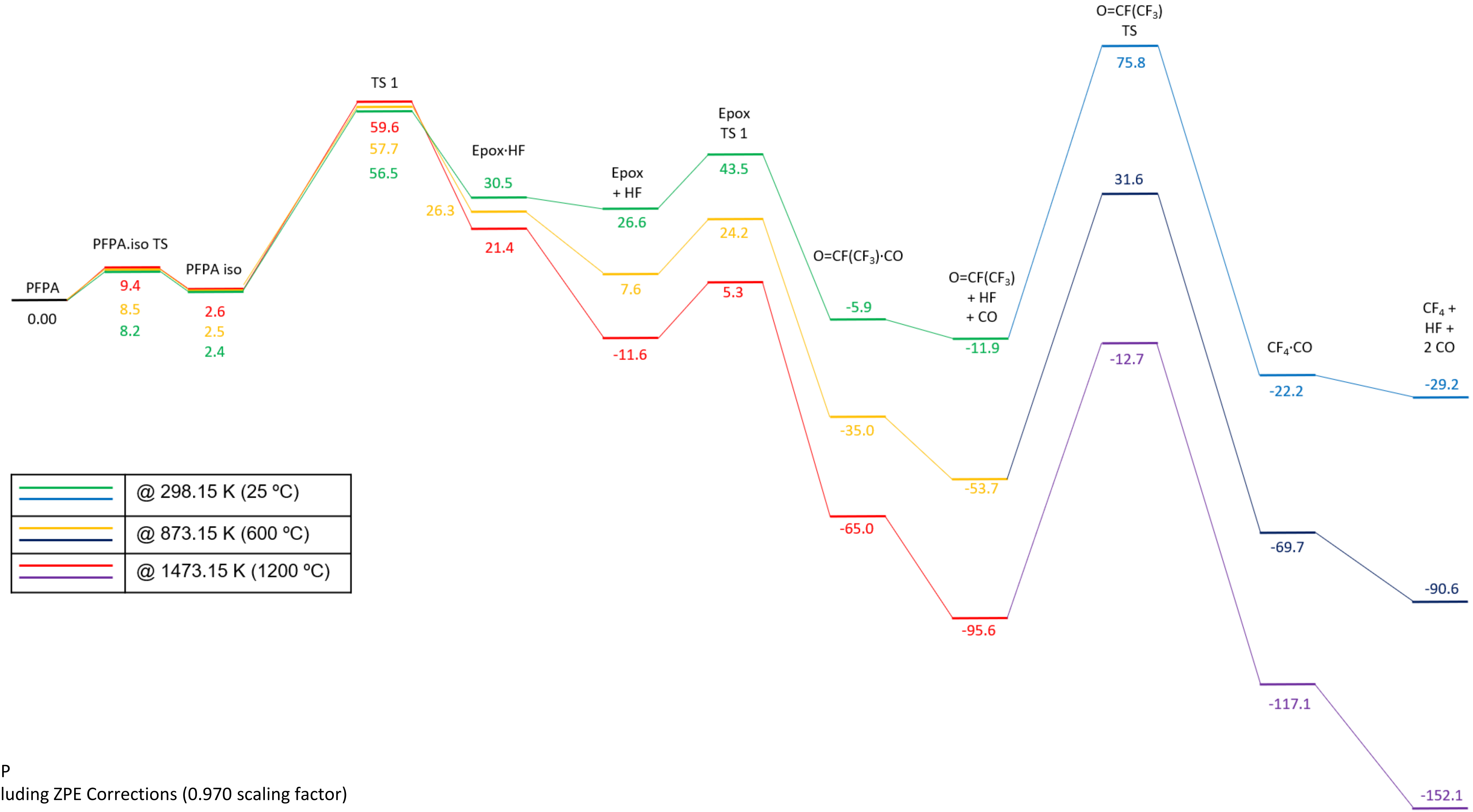
[2] Kucharzyk, K. H. et al. *Journal of Environmental Management* **2017,** *204*, 757-764.

PFPA Free Energy Surface @ 298.15 K



M06-2X-D3alt/def2TZVPP
Energies in kcal mol^{-1} including ZPE Corrections (0.970 scaling factor)

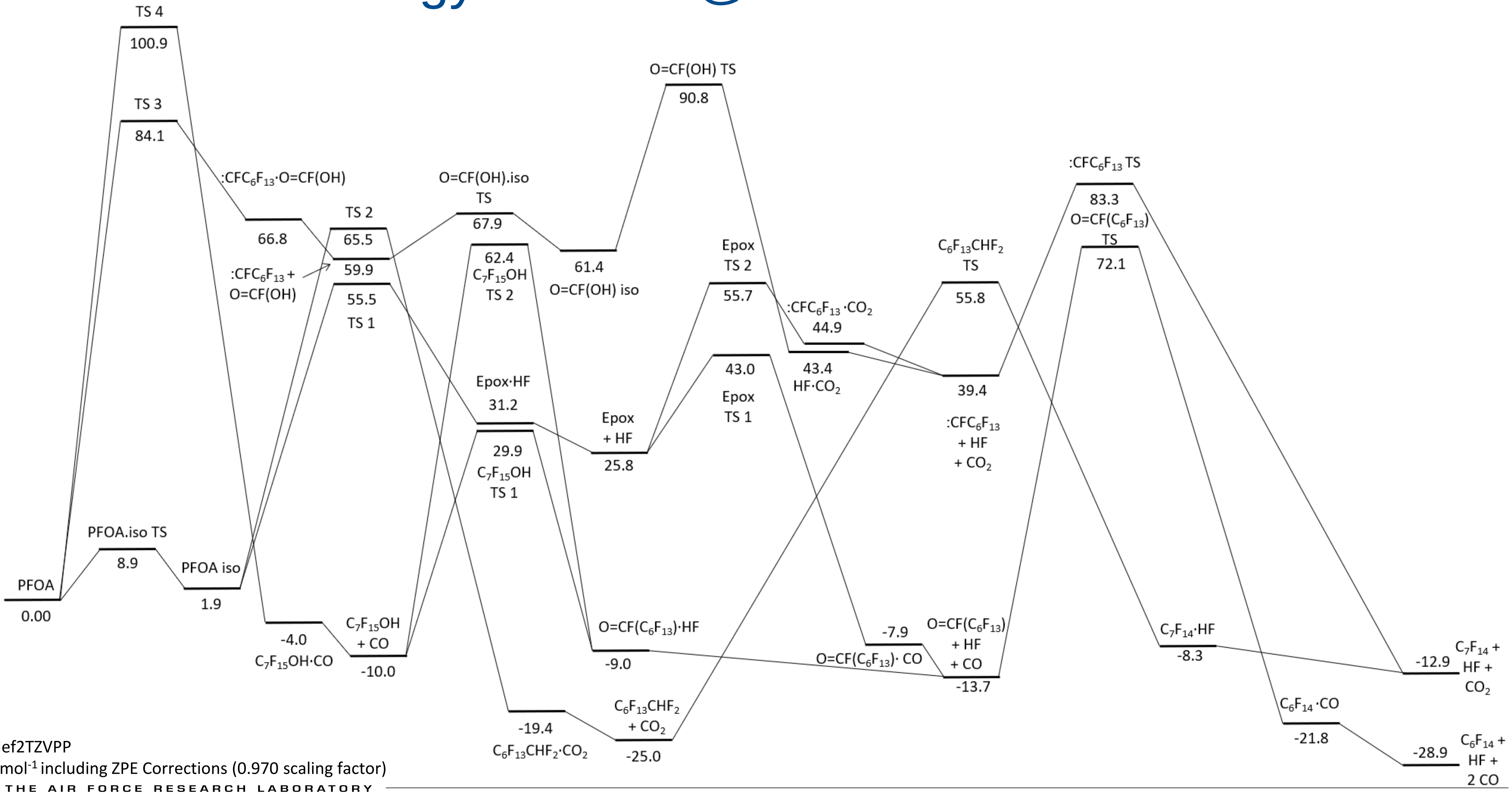
PFPA Free Energy Surface @ Incineration Temperatures



M06-2X-D3alt/def2TZVPP

Energies in kcal mol^{-1} including ZPE Corrections (0.970 scaling factor)

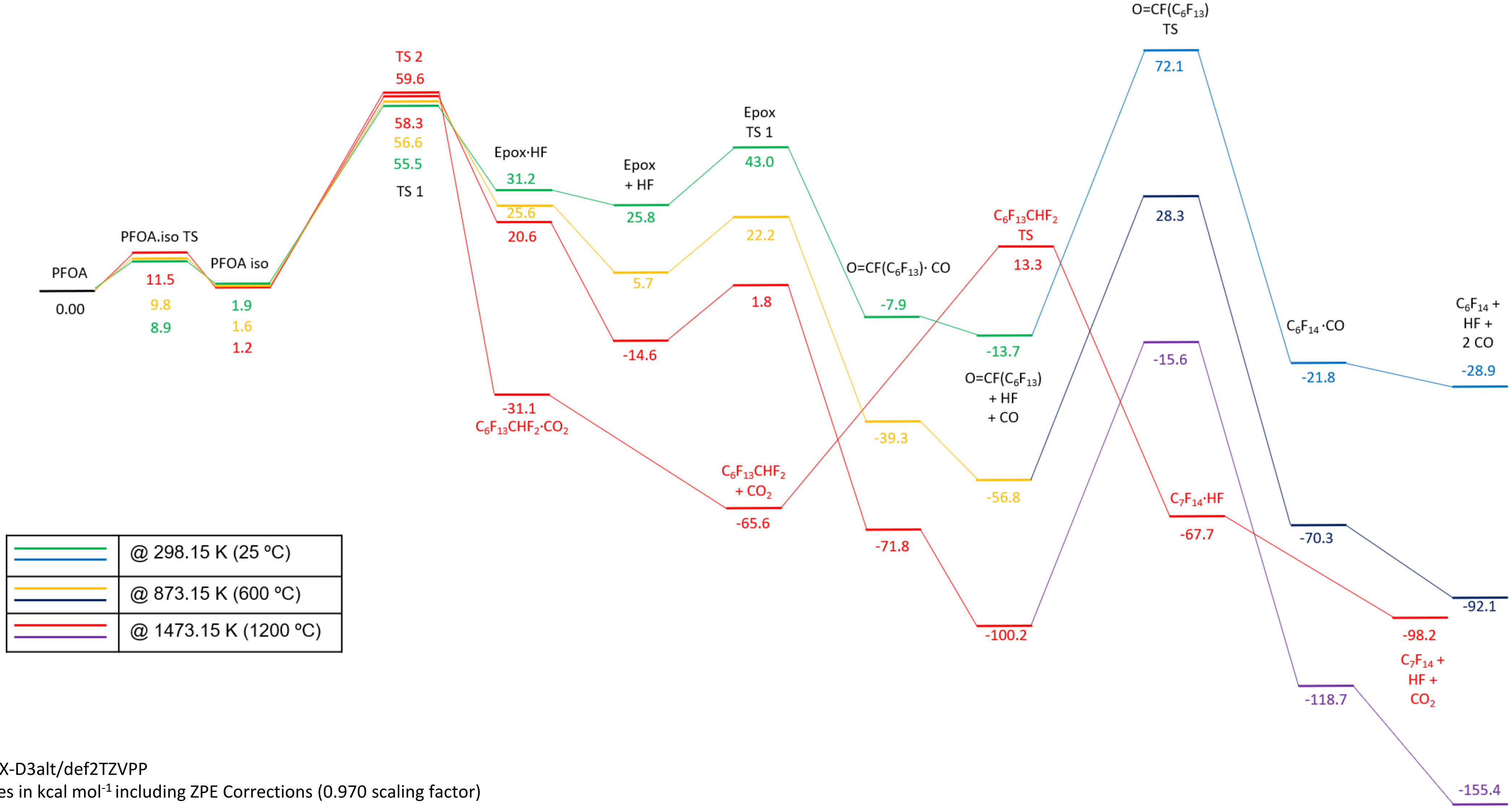
PFOA Free Energy Surface @ 298.15 K



M06-2X-D3alt/def2TZVPP

Energies in kcal mol^{-1} including ZPE Corrections (0.970 scaling factor)

PFOA Free Energy Surface @ Incineration Temperatures



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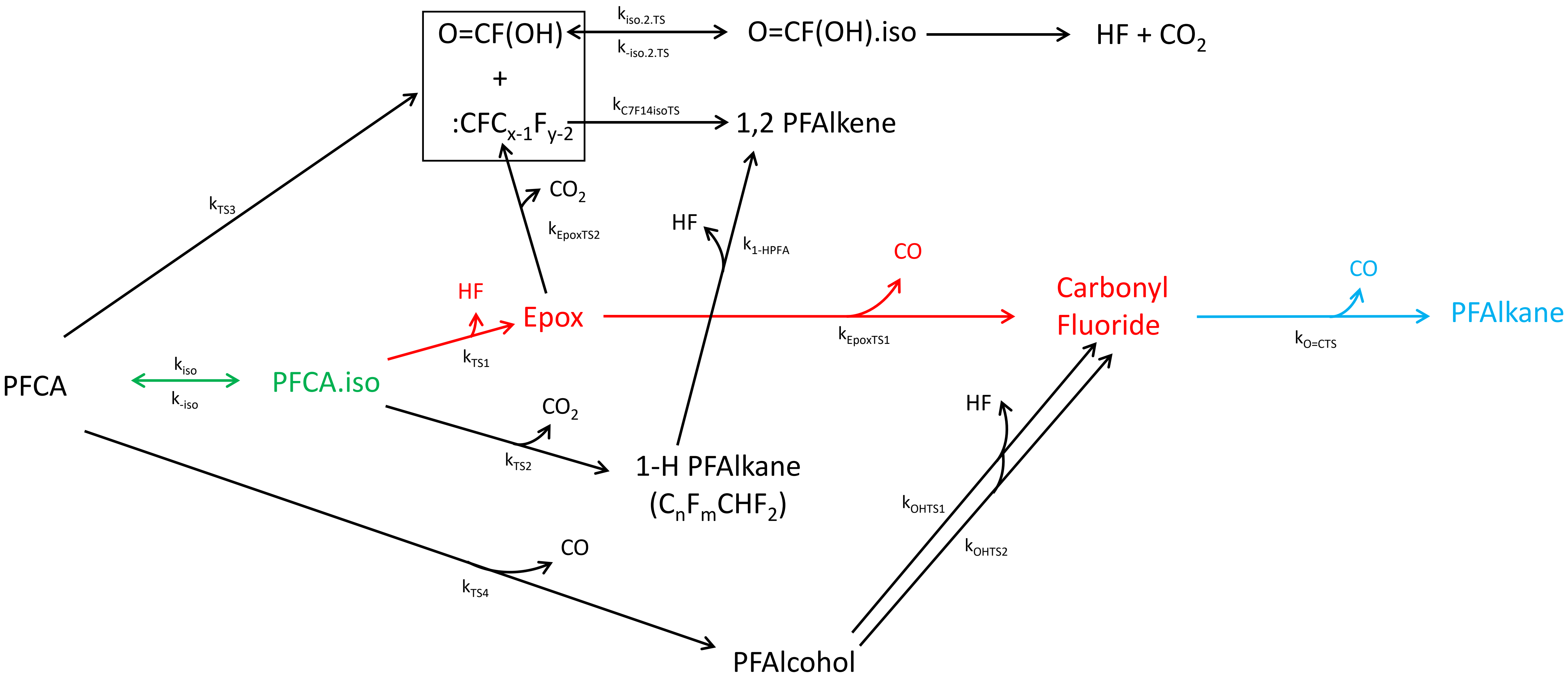
Energies in kcal mol^{-1} including ZPE Corrections (0.970 scaling factor)



O=CF(OH) + :CF$C_{x-1}F_{y-2}$

$k_{iso.2.TS}$

$k_{-iso.2.TS}$

O=CF(OH).iso

HF + CO_2

$k_{C7F14isoTS}$

1,2 PFAlkene

k_{TS3}

CO_2

$k_{EpoxTS2}$

HF

$k_{1\text{-}HPFA}$

CO

HF

Epox

Carbonyl Fluoride

CO

PFAlkane

$k_{EpoxTS1}$

$k_{O=CTS}$

PFCA

k_{iso}

k_{-iso}

PFCA.iso

k_{TS1}

CO_2

HF

k_{TS2}

1-H PFAlkane ($C_nF_mCHF_2$)

k_{OHTS1}

k_{OHTS2}

CO

k_{TS4}

PFAlcohol