Supporting Information

Atmospheric Fate of $CF_3CF_2CH_2OCH_3$ (HFE-365mcf3) Initiated by OH Radicals and Cl Atoms: Insights into the Mechanisms, Conformer-Weighted Kinetics, and Atmospheric Loss Processes

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The Supporting Information consists of four files - Supporting Information.pdf, SI2-Cartesian coordinates.pdf, SI3-Frequencies.xlsx, and SI4-Kinetics.xlsx. The Supporting Information file contains the conformational analysis, optimized energies of all the species involved in the reaction of A with OH and Cl, single point energies, *T1*-diagnostic and spin contamination values, relative energy profiles, individual rate coefficients, geometries of species involved in R1 and R5 at the M06-2X/6-311++G(d,p) level of theory, and all information on the degradation of the subsequent product radicals. The other three files include the Cartesian coordinates, vibrational frequencies of all the species involved in the reactions, and kinetics of the reactions.

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Table S1: Conformational search of HFE-365mcf3 using Conformer-Rotamer Ensemble Sampling Tool (CREST) followed by optimization at the M06-2X/6-311++G(d,p) level of theory.

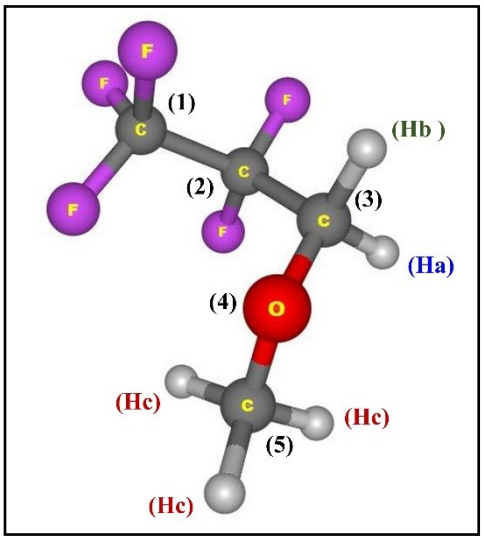
Conformers	*Structures*	*EE + ZPE (Hartree)*	*Gibbs Energy (Hartree)*	*Relative Gibbs Energy (Hartree)*	*Population*
A1	Structure-1	-729.73738	-729.77288	0.00021	0.27728
A2	Structure-2	-729.73678	-729.77309	0.00000	0.34529
A3	Structure-3	-729.73583	-729.77210	0.00099	0.12081
A4	Structure-4	-729.73589	-729.77246	0.00063	0.17673
A5	Structure-5	-729.73538	-729.77101	0.00209	0.03770
A6	Structure-6	-729.73538	-729.77100	0.00210	0.03750
A7	Structure-7	-729.73278	-729.76838	0.00472	0.00233
A8	Structure-8	-729.73278	-729.76839	0.00471	0.00236

At 298 K, we have shortlisted four conformers, **A1**, **A2**, **A3**, and **A4**. Furthermore, we have considered these four conformers to determine the Boltzmann population distribution within the 200-400 K temperature range.

Temperature	*POP-A1*	*POP-A2*	*POP-A3*	*POP-A4*
200	0.3137	0.4350	0.0910	0.1604
220	0.3112	0.4188	0.1010	0.1691
240	0.3085	0.4051	0.1100	0.1764
260	0.3060	0.3934	0.1181	0.1826
280	0.3035	0.3833	0.1253	0.1879
298	0.3014	0.3753	0.1313	0.1921
300	0.3011	0.3744	0.1319	0.1925
320	0.2989	0.3667	0.1379	0.1965
340	0.2969	0.3598	0.1433	0.2000
360	0.2949	0.3537	0.1483	0.2031
380	0.2931	0.3482	0.1528	0.2059
400	0.2915	0.3432	0.1570	0.2084

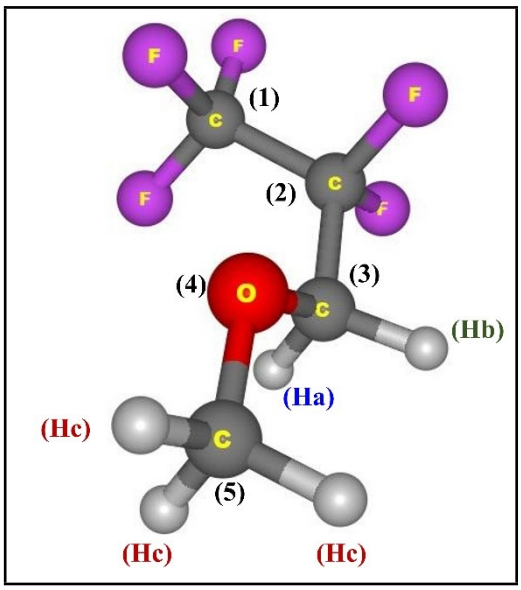
Table S2: Corrected zero-point energies (EE+ZPE), enthalpies (H), and Gibbs free energies (G) of the species computed at the M06-2X/6-311++G(d,p) level for the reaction pathways **R1, R2, R3**, and **R4**. All energies are in Hartree.

R1			
Species	***EE + ZPE***	***Enthalpy (H)***	***Gibbs Free Energy (G)***
A1	-729.7373	-729.7266	-729.7728
OH	-75.7179	-75.7146	-75.7348
CR1a	-805.4613	-805.4473	-805.5027
TS1a	-805.4549	-805.4420	-805.4941
PC1a	-805.4943	-805.4795	-805.5358
P1a	-729.0889	-729.0782	-729.1247
CR1b	-805.4630	-805.4493	-805.5030
TS1b	-805.4554	-805.4424	-805.4952
PC1b	-805.4993	-805.4846	-805.5405
P1b	-729.0914	-729.0802	-729.1289
CR1c	-805.4621	-805.4484	-805.5040
TS1c	-805.4543	-805.4414	-805.4948
PC1c	-805.4935	-805.4788	-805.5364
P1c	-729.0870	-729.0762	-729.1236
H_2O	-76.3992	-76.3955	-76.4175



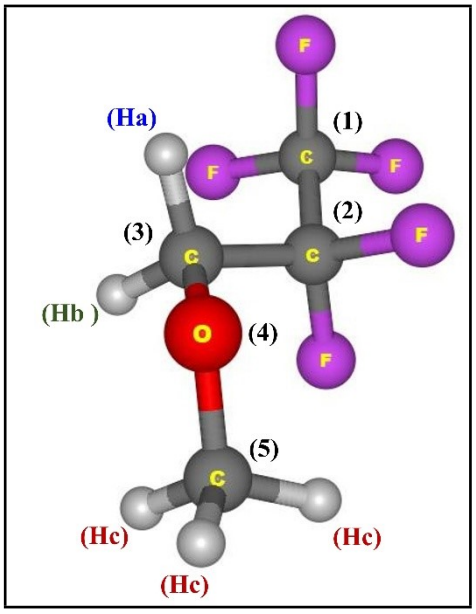
A1

R2			
Species	***EE + ZPE***	***Enthalpy (H)***	***Gibbs Free Energy (G)***
A2	-729.7367	-729.7258	-729.7730
OH	-75.7179	-75.7146	-75.7348
CR2a	-805.4631	-805.4494	-805.5033
TS2a	-805.4554	-805.4424	-805.4952
PC2a	-805.4994	-805.4846	-805.5409
P2a	-729.0914	-729.0802	-729.1289
CR2b	-805.4634	-805.4497	-805.5041
TS2b	-805.4553	-805.4422	-805.4952
PC2b	-805.4991	-805.4843	-805.5412
P2b	-729.0913	-729.0800	-729.1292
CR2c	-805.4583	-805.4437	-805.5012
TS2c	-805.4530	-805.4399	-805.4939
PC2c	-805.4933	-805.4788	-805.5348
P2c	-729.0865	-729.0755	-729.1235
H_2O	-76.3992	-76.3955	-76.4175



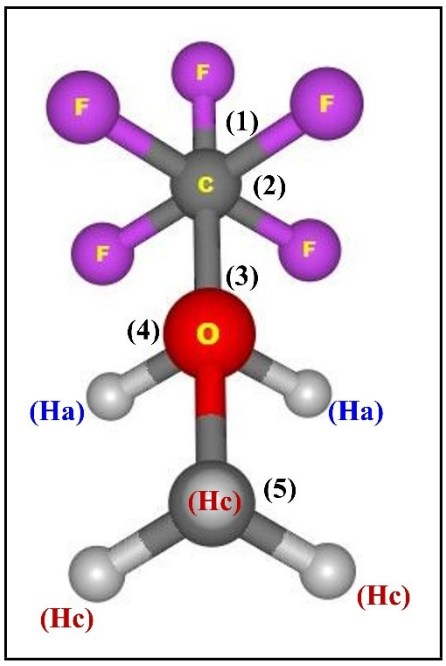
A2

R3			
Species	***EE + ZPE***	***Enthalpy (H)***	***Gibbs Free Energy (G)***
A3	-729.7358	-729.7250	-729.7721
OH	-75.7179	-75.7146	-75.7348
CR3a	-805.4632	-805.4492	-805.5042
TS3a	-805.4541	-805.4409	-805.4944
PC3a	-805.4996	-805.4846	-805.5421
P3a	-729.0912	-729.0799	-729.1289
CR3b	-805.4600	-805.4461	-805.5005
TS3b	-805.4537	-805.4408	-805.4930
PC3b	-805.4953	-805.4806	-805.5370
P3b	-729.0900	-729.0791	-729.1265
CR3c	-805.4616	-805.4476	-805.5038
TS3c	-805.4530	-805.4401	-805.4931
PC3c	-805.4931	-805.4787	-805.5338
P3c	-729.0861	-729.0752	-729.1234
H_2O	-76.3992	-76.3955	-76.4175



A3

R4			
Species	***EE + ZPE***	***Enthalpy (H)***	***Gibbs Free Energy (G)***
A4	-729.7358	-729.7248	-729.7724
OH	-75.7179	-75.7146	-75.7348
CR4a	-805.4630	-805.4492	-805.5036
TS4a	-805.4542	-805.4409	-805.4945
PC4a	-805.4994	-805.4846	-805.5415
P4a	-729.0912	-729.0799	-729.1287
CR4c	-805.4635	-805.4503	-805.5031
TS4c	-805.4537	-805.4406	-805.4951
PC4c	-805.4929	-805.4784	-805.5344
P4c	-729.0859	-729.0748	-729.1231
H_2O	-76.3992	-76.3955	-76.4175



A4

***For the conformer A4, the H-atoms attached to the central carbon atom C3 are indistinguishable, thus H_a=H_b**

Table S3: Corrected zero-point energies (EE+ZPE), enthalpies (H), and Gibbs free energies (G) of the species computed at the M06-2X/6-311++G(d,p) level for the reaction pathways **R5, R6, R7**, and **R8**. All energies are in Hartree.

R5			
Species	***EE + ZPE***	***Enthalpy (H)***	***Gibbs Free Energy (G)***
A1	-729.7373	-729.7266	-729.7728
Cl	-460.1326	-460.1303	-460.1483
CR5a	-1189.8744	-1189.8613	-1189.9163
TS5a	-1189.8773	-1189.8648	-1189.9168
PC5a	-1189.8823	-1189.8685	-1189.9242
P5a	-729.0889	-729.0782	-729.1247
CR5b	-1189.8785	-1189.8655	-1189.9190
TS5b	-1189.8776	-1189.8648	-1189.9180
PC5b	-1189.8867	-1189.8731	-1189.9282
P5b	-729.0913	-729.0800	-729.1291
CR5c	-1189.8803	-1189.8673	-1189.9211
TS5c	-1189.8798	-1189.8674	-1189.9202
PC5c	-1189.8823	-1189.8686	-1189.9247
P5c	-729.0870	-729.0762	-729.1236
HCl	-460.7896	-460.7863	-460.8075

R6			
Species	***EE + ZPE***	***Enthalpy (H)***	***Gibbs Free Energy (G)***
A2	-729.7367	-729.7258	-729.7730
Cl	-460.1326	-460.1303	-460.1483
CR6a	-1189.8784	-1189.8654	-1189.9188
TS6a	-1189.8776	-1189.8647	-1189.9180
PC6a	-1189.8873	-1189.8724	-1189.9326
P6a	-729.0914	-729.0802	-729.1289
CR6c	-1189.8786	-1189.8655	-1189.9204
TS6c	-1189.8794	-1189.8668	-1189.9208
PC6c	-1189.8810	-1189.8673	-1189.9238
P6c	-729.0865	-729.0755	-729.1235
HCl	-460.7896	-460.7863	-460.8075

***For information on reaction pathway R6b, please refer to Notes S1.**

R7			
Species	***EE + ZPE***	***Enthalpy (H)***	***Gibbs Free Energy (G)***
A3	-729.7358	-729.7250	-729.7721
Cl	-460.1326	-460.1303	-460.1483
CR7a	-1189.8779	-1189.8648	-1189.9193
TS7a	-1189.8765	-1189.8636	-1189.9179
PC7a	-1189.8878	-1189.8733	-1189.9307
P7a	-729.0912	-729.0799	-729.1288
CR7b	-1189.8733	-1189.8860	-1189.9153
TS7b	-1189.8713	-1189.8589	-1189.9116
PC7b	-1189.8851	-1189.8713	-1189.9270
P7b	-729.0900	-729.0791	-729.1265
CR7c	-1189.8789	-1189.8659	-1189.9202
TS7c	-1189.8794	-1189.8669	-1189.9200
PC7c	-1189.8821	-1189.8690	-1189.9231
P7c	-729.0862	-729.0753	-729.1230
HCl	-460.7896	-460.7863	-460.8075

R8			
Species	***EE + ZPE***	***Enthalpy (H)***	***Gibbs Free Energy (G)***
A4	-729.7358	-729.7248	-729.7724
Cl	-460.1326	-460.1303	-460.1483
CR8a	-1189.8779	-1189.8648	-1189.9193
TS8a	-1189.8764	-1189.8636	-1189.9172
PC8a	-1189.8878	-1189.8733	-1189.9308
P8a	-729.0912	-729.0799	-729.1289
CR8c	-1189.8763	-1189.8635	-1189.9177
TS8c	-1189.8790	-1189.8664	-1189.9208
PC8c	-1189.8811	-1189.8671	-1189.9245
P8c	-729.0858	-729.0748	-729.1229
HCl	-460.7896	-460.7863	-460.8075

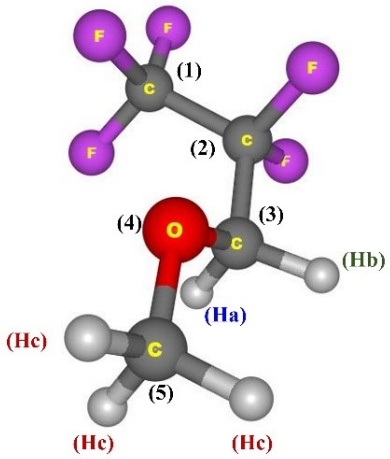


Fig: Optimized structure of the conformer A2 at the M06-2X/6-311++G(d,p) level.

Notes S1: Exception for the reaction of conformer A2 with Cl atoms.

For the conformer A2, the two hydrogens attached to C-3 are not equivalent, as also observed from the reaction of A2 with the OH radical. Thus, there should be two different transition states (TS). However, for the reaction of A2 with Cl, we were able to obtain only one TS that involves the abstraction of Ha (Pathway R6a) at the M06-2X level of theory. And despite extensive attempts, we were unable to obtain the TS corresponding to the abstraction of Hb (Pathway R6b) using any DFT-based method. Consequently, the MP2 level of theory was employed to locate the TS for Pathway R6b.

To ensure the use of the MP2 level is justified, we performed a comparative analysis between the M06-2X and MP2 level of theory for the analogous pathway R6a. We computed the total electronic energies at both levels of theory, as well as their corresponding CCSD(T) single-point energies [CCSD(T)/M06-2X and CCSD(T)/MP2], shown in Table S4. The comparison of the CCSD(T) energies obtained from both methods showed that the energy differences for all the species involved in Pathway R6a are less than 1 kcal/mol. This close agreement validates the use of MP2 for pathway R6b. The comparison data (Table S4), as well as the energies of all the species at the MP2 level of theory for pathway R6b, have been calculated below.

Table S4: Energy comparison of the species involved in Pathway R6a and corresponding single point energies at the M06-2X/6-311++G(d,p) and MP2/6-311++G(d,p) level of theory, that have been used for the preparation of energy profiles.

Species	M06-2X (Hartree)	CCSD(T)/M06-2X (Hartree)	MP2 (Hartree)	CCSD(T)/MP2 (Hartree)	Δ CCSD(T) (kcal/mol)
CR6a	-1189.878448	-1188.13956	-1187.929733	-1188.1402	**0.412**
TS6a	-1189.877621	-1188.126721	-1187.922243	-1188.1275	**0.550**
PC6a	-1189.887346	-1188.139683	-1187.93695	-1188.1406	**0.628**
P6a	-729.176822	-727.868454	727.6926	-727.8684	**0.020**

The energy difference between the CCSD(T) energies are less than 1 kcal/mol, thus for the pathway R6b, we have used the corresponding CCSD(T) energies for preparing the energy profile diagram. These energies have been included in Table S5.

Table S5: Corrected zero-point energies (EE+ZPE), enthalpies (H), and Gibbs free energies (G) of the species computed at the MP2/6-311++G(d,p) level for the reaction pathway **R6b**. All energies are in Hartree.

Species	*EE + ZPE*	*Enthalpy (H)*	*Gibbs Free Energy (G)*
CR6b	-1187.930392	-1187.917145	-1187.972535
TS6b	-1187.922401	-1187.909695	-1187.9632
PC6b	-1187.938493	-1187.94043	-1187.98239
P6b	-727.692982	-727.681862	-727.730197

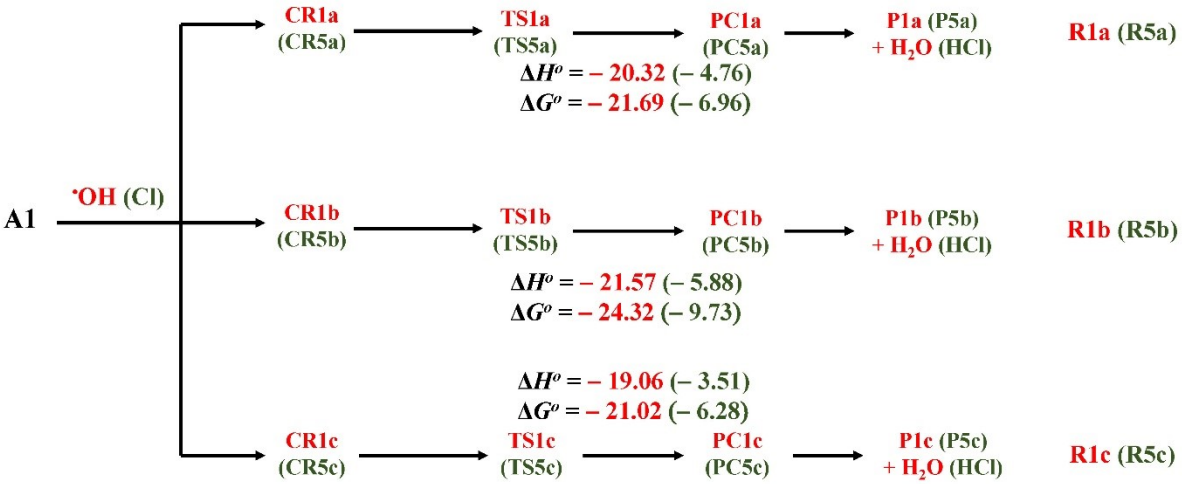
Kinetics for Pathway 6b

For the reaction of conformer A2 with •OH having pathways R2a and R2b, the corresponding rate coefficients (k_{2a} and k_{2b}) were (4.210×10^{-14}) and (4.312×10^{-14}) cm^3 $molecule^{-1}$ s^{-1}, respectively, at 298 K. This difference between the rate coefficients, k_{2a} and k_{2b}, can be considered negligible. Thus, for the reaction of A2 with Cl, we have considered the rate coefficient of k_{6a} and k_{6b} to be the same.

$k_{6a} = k_{6b} = 2.1724 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}

Table S6: The enthalpy change (ΔH) and Gibbs free energy change (ΔG) for the reaction pathways **R1-R8**.

Pathway	ΔH	ΔG
R1a	–20.32	-21.69
R1b	–21.57	–24.32
R1c	–19.06	–21.02
R2a	–22.08	–24.19
R2b	–21.95	–24.36
R2c	–19.16	–20.81
R3a	–22.45	–24.81
R3b	–21.95	–23.30
R3c	–19.49	–21.35
R4a	–22.52	–24.45
R4c	–19.36	–20.97
R5a	–4.76	–6.96
R5b	–5.88	–9.73
R5c	–3.51	–6.28
R6a	–6.53	–9.45
R6c	–3.61	–6.08
R7a	–6.89	–10.02
R7b	–6.39	–8.57
R7c	–3.99	–6.39
R8a	–6.98	–9.88
R8c	–3.78	–6.12



Scheme S1: Reaction pathways of conformer A1 with OH and Cl, including the enthalpies and Gibbs free energy changes (ΔH^0 and ΔG^0). Calculations are at the M06-2X/6-311++G(d,p) level of theory at 298 K and energies are in kcal/mol.

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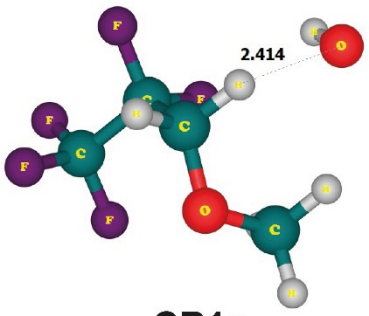
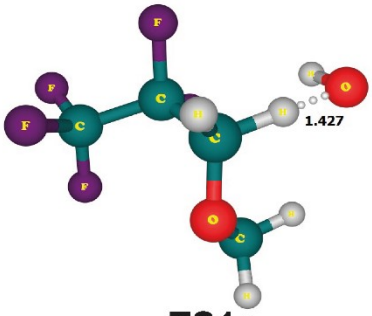
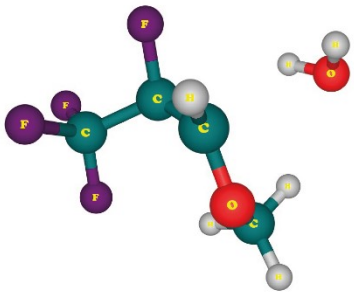


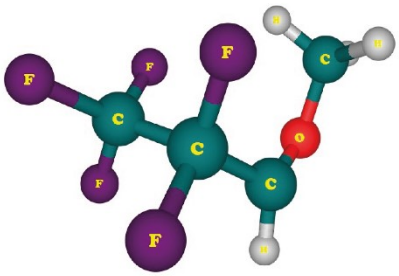
CR1a



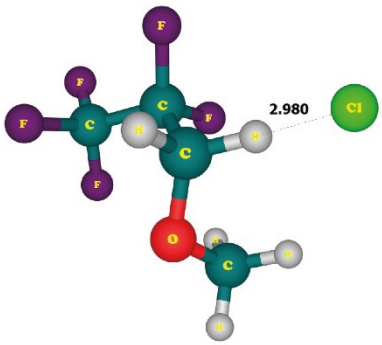
TS1a



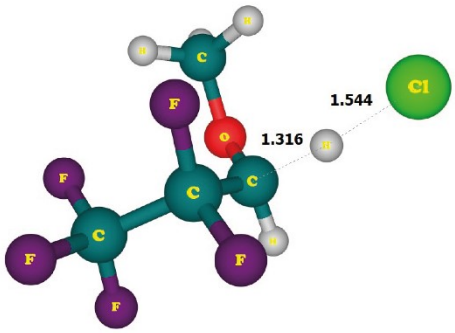
PC1a



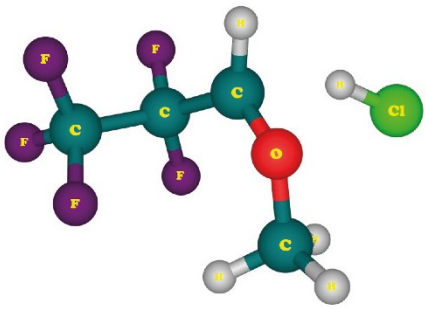
P1a



CR5a



TS5a



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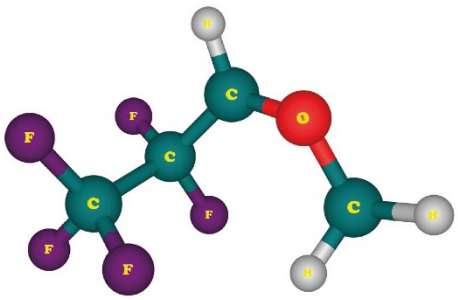

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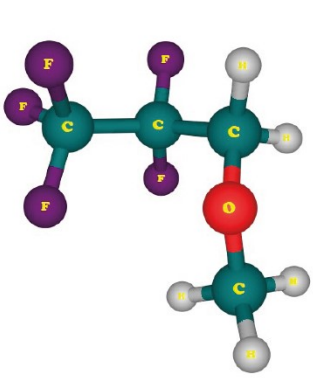
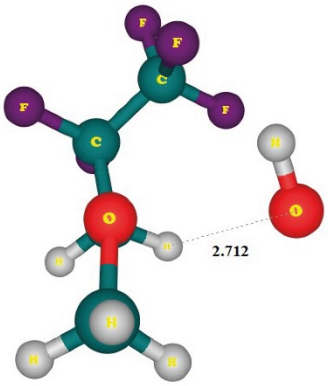
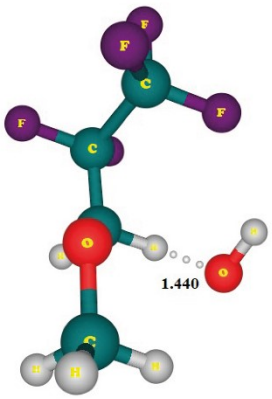


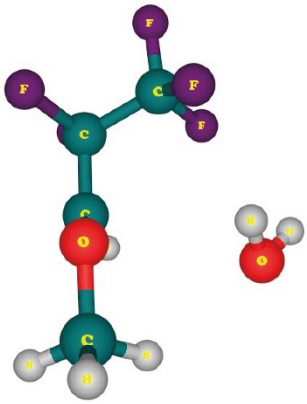
A1



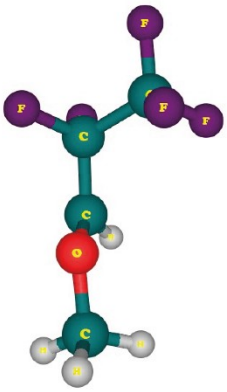
CR1b



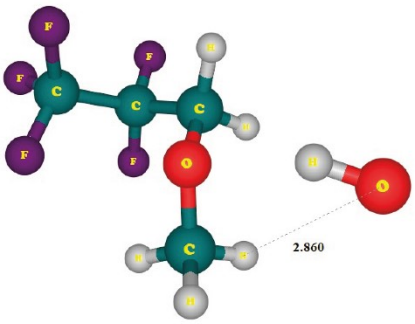
TS1b



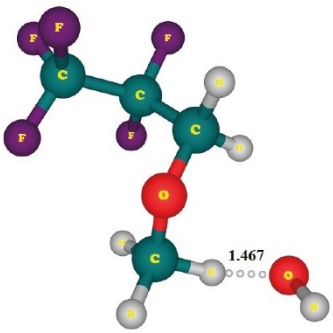
PC1b



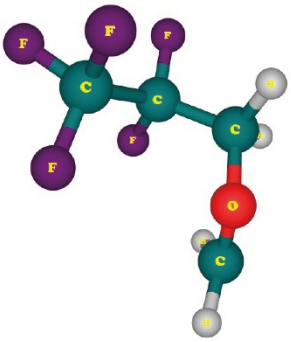
P1b



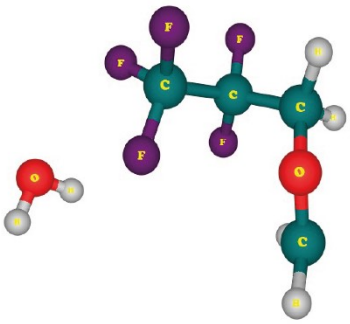
CR1c



TS1c



PC1c



P1c

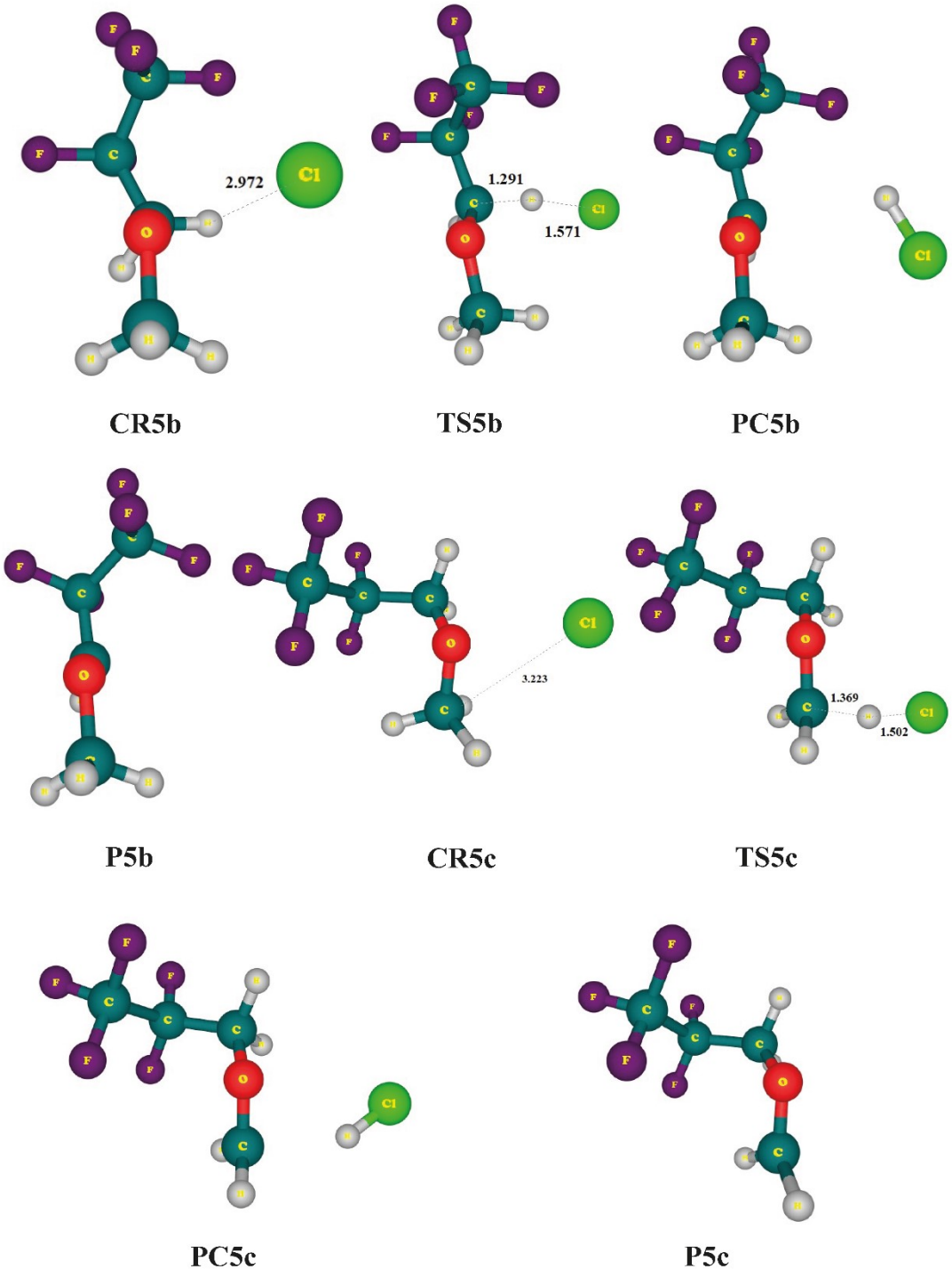


Figure S1: Optimized structure of the species involved in the reaction pathways, **R1** and **R5** at the M06-2X/6-311++G(d,p) level of theory.

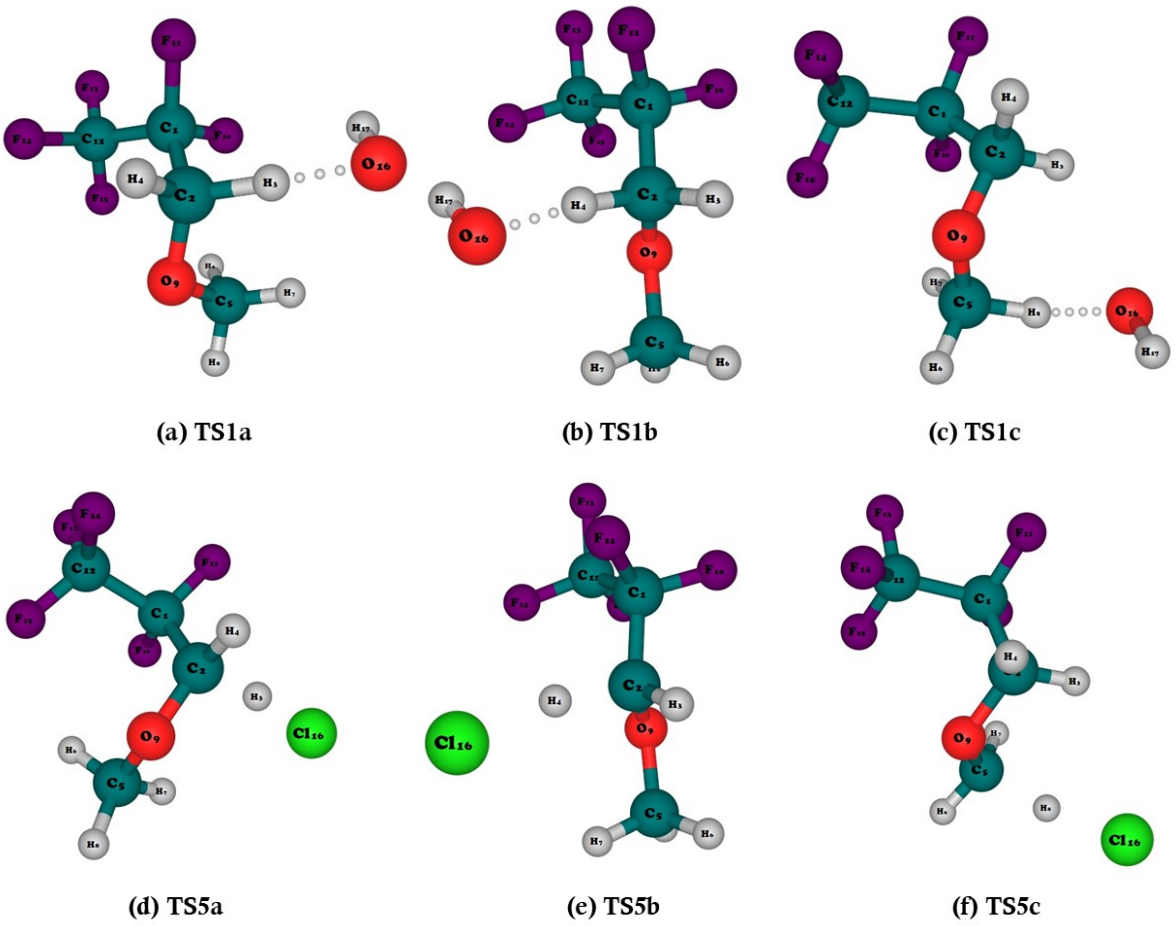
Table S7: Zero-point and SOC corrected relative energies of the species involved in the pathways R1 and R5 at the CCSD(T)//M06-2X/6-311++G(d,p) level of theory along with the relative energies (RE).

Pathways	Species	RE (kcal/mol)	Pathways	Species	RE (kcal/mol)
Reactants	**A1**	0.00	**Reactants**	**A1**	0.00
	OH†			**Cl†**	
R1a	**CR1a**	-2.3	**R5a**	**CR5a**	-4.5
	TS1a	2.2		**TS5a**	0.2
	PC1a	-21.0		**PC5a**	-4.9
	P1a	-18.3		**P5a**	-2.5
	H_2O			**HCl**	
R1b	**CR1b**	-3.3	**R5b**	**CR5b**	-4.0
	TS1b	1.0		**TS5b**	-0.6
	PC1b	-24.5		**PC5b**	-8.1
	P1b	-20.8		**P5b**	-4.7
	H_2O			**HCl**	
R1c	**CR1c**	-3.2	**R5c**	**CR5c**	-4.4
	TS1c	2.3		**TS5c**	-1.3
	PC1c	-21.5		**PC5c**	-5.4
	P1c	-18.3		**P5c**	-2.4
	H_2O			**HCl**	

† : SOC are considered for ˙OH and Cl

Figure 4 of the manuscript have been constructed using this table. More details on these energies can be found in the subsequent tables of S8.

Notes S2: Natural Bond Orbital (NBO) Analysis.



(a) TS1a (b) TS1b (c) TS1c

(d) TS5a (e) TS5b (f) TS5c

Structures of the transition states, TS1a, TS1b, TS1c, TS5a, TS5b, and TS5c of the pathways R1a, R1b, R1c, R5a, R5b, and R5c, respectively, showing the numbering of the atoms.

Details of the donor-acceptor NBO and second-order perturbation stabilization energies $E^{(2)}$ (kcal/mol) of the TS involved in the reaction pathways R1 and R5 optimized at the M06-2X/6-311++G(d,p) level of theory.

Pathway	Species	Interactions	$E^{(2)}$ (kcal/mol)
R1a	TS1a	$LP_{O16} \rightarrow \sigma^*_{C2-H3}$	33.97
R1b	TS1b	$LP_{O16} \rightarrow \sigma^*_{C2-H4}$	32.04
R1c	TS1c	$LP_{O16} \rightarrow \sigma^*_{C5-H8}$	27.29
R5a	TS5a	$LP_{Cl16} \rightarrow \sigma^*_{C2-H3}$	86.66
R5b	TS5b	$LP_{Cl16} \rightarrow \sigma^*_{C2-H4}$	75.35
R5c	TS5c	$LP_{Cl16} \rightarrow \sigma^*_{C5-H8}$	102.84

For reaction with •OH, R1a and R1b are predominant pathways, i.e., abstraction of H-atom from the methylene carbon atom, as evident from greater donor-acceptor interaction energy, $E^{(2)}$. In contrast, for the reaction with the Cl atom, R5c is the predominant pathway, i.e., abstraction of the H-atom from the methoxy carbon atom, evident from greater $E^{(2)}$.

Table S8: Single point and relative energies of all the species involved in the reaction pathways **R1-R8** at the CCSD(T)//M06-2X/6-311++G(d,p) level of theory with zero-point energy corrections (ZPE) and spin-orbit coupling corrections (SOC) for the reaction of HFE-365mcf3 with OH and Cl atoms.

R1				
Species	***Zero-point Energy Correction (ZPE) [M06-2X] (Hartree)***	***CCSD(T) (Hartree)***	***CCSD(T) + ZPE (Hartree)***	***Relative Energies (kcal/mol)***
A1	0.0998	-728.5269	-728.4271	0.00
OH	0.0086	-75.5965	-75.5878	
CR1a	0.1100	-804.1286	-804.0185	-2.3174
TS1a	0.1066	-804.1180	-804.0114	2.1837
PC1a	0.1097	-804.1581	-804.0483	-21.0056
P1a	0.0862	-727.8655	-727.7792	-18.3511
CR1b	0.1105	-804.1306	-804.0201	-3.2719
TS1b	0.1063	-804.1195	-804.0132	1.0367
PC1b	0.1097	-804.1637	-804.0540	-24.5561
P1b	0.0854	-727.8685	-727.7831	-20.7922
CR1c	0.1107	-804.1307	-804.0200	-3.2324
TS1c	0.1069	-804.1182	-804.0112	2.3155
PC1c	0.1091	-804.1583	-804.0492	-21.5277
P1c	0.0853	-727.8645	-727.7791	-18.2997
H_2O	0.0216	-76.2865	-76.2649	

R2				
Species	***Zero-point Energy Correction (ZPE) [M06-2X] (Hartree)***	***CCSD(T) (Hartree)***	***CCSD(T) + ZPE (Hartree)***	***Relative Energies (kcal/mol)***
A2	0.0994	-728.5270	-728.4275	0.0
OH	0.0086	-75.5965	-75.5878	
CR2a	0.1103	-804.1306	-804.0202	-3.1
TS2a	0.1062	-804.1195	-804.0132	1.3
PC2a	0.1096	-804.1637	-804.0540	-24.3
P2a	0.0853	-727.8684	-727.7831	-20.5
CR2b	0.1105	-804.1314	-804.0209	-3.5
TS2b	0.1066	-804.1199	-804.0133	1.2
PC2b	0.1096	-804.1639	-804.0543	-24.4
P2b	0.0852	-727.8679	-727.7827	-20.2
CR2c	0.1092	-804.1247	-804.0155	-0.1
TS2c	0.1065	-804.1174	-804.0108	2.9
PC2c	0.1094	-804.1590	-804.0496	-21.5
P2c	0.0852	-727.8647	-727.7795	-18.2
H_2O	0.0216	-76.2865	-76.2649	

R3				
Species	***Zero-point Energy Correction (ZPE) [M06-2X] (Hartree)***	***CCSD(T) (Hartree)***	***CCSD(T) + ZPE (Hartree)***	***Relative Energies (kcal/mol)***
A3	0.09973	-728.5253	-728.4256	0.00
OH	0.00863	-75.5964	-75.58783	
CR3a	0.11024	-804.1307	-804.0205	-4.4
TS3a	0.10637	-804.1181	-804.0117	1.1
PC3a	0.10948	-804.1638	-804.0543	-25.7
P3a	0.08531	-727.8676	-727.7823	-21.2
CR3b	0.11027	-804.1270	-804.0167	-2.1
TS3b	0.10668	-804.1168	-804.0101	2.1
PC3b	0.10982	-804.1583	-804.0485	-22.0
P3b	0.08591	-727.8655	-727.7796	-19.5
CR3c	0.11028	-804.1297	-804.0194	-3.8
TS3c	0.10638	-804.1160	-804.0096	2.4
PC3c	0.10981	-804.1579	-804.0480	-21.7
P3c	0.08527	-727.8635	-727.7782	-18.7
H_2O	0.02161	-76.2865	-76.2649	

R4				
Species	***Zero-point Energy Correction (ZPE) [M06-2X] (Hartree)***	***CCSD(T) (Hartree)***	***CCSD(T) + ZPE (Hartree)***	***Relative Energies (kcal/mol)***
A4	0.0993	-728.5259	-728.4266	0.00
OH	0.0086	-75.5965	-75.5878	
CR4a	0.1104	-804.1307	-804.0203	-3.7
TS4a	0.1063	-804.1182	-804.0118	1.6
PC4a	0.1096	-804.1639	-804.0542	-25.0
P4a	0.0854	-727.8677	-727.7823	-20.6
CR4c	0.1099	-804.1308	-804.0209	-4.0
TS4c	0.1067	-804.1180	-804.0113	2.0
PC4c	0.1095	-804.1585	-804.0491	-21.8
P4c	0.0851	-727.8640	-727.7789	-18.4
H_2O	0.0216	-76.2865	-76.2649	

R5				
Species	***Zero-point Energy Correction (ZPE) [M06-2X] (Hartree)***	***CCSD(T) (Hartree)***	***CCSD(T) + ZPE (Hartree)***	***Relative Energies (kcal/mol)***
A1	0.0998	-728.5269	-728.4271	0.00
Cl*	0.0013	-459.6044	-459.6058	
CR5a	0.0960	-1188.1359	-1188.0399	-4.4666
TS5a	0.0933	-1188.1258	-1188.0325	0.2284
PC5a	0.0950	-1188.1358	-1188.0452	-4.9875
P5a	0.0862	-727.8655	-727.7792	-2.4925
CR5b	0.1003	-1188.1396	-1188.0393	-4.0469
TS5b	0.0930	-1188.1267	-1188.0337	-0.5761
PC5b	0.0939	-1188.1397	-1188.0458	-8.1389
P5b	0.0853	-727.8679	-727.7827	-4.6506
HCl	0.0068	-460.2644	-460.2576	
CR5c	0.1006	-1188.1404	-1188.0398	-4.3675
TS5c	0.0933	-1188.1282	-1188.0349	-1.3176
PC5c	0.0944	-1188.1358	-1188.0415	-5.4249
P5c	0.0853	-727.8645	-727.7791	-2.4160
HCl	0.0068	-460.2644	-460.2576	

*: Spin-orbit coupling correction incorporated for Cl atoms [1].

Reference

[1] National Institute of Standards and Technology. *Computational Chemistry Comparison and Benchmark Database (CCCBDB) – Electronic Spin Splitting Corrections.* Standard Reference Database 101, Release 22 (May 2022). https://cccbdb.nist.gov/elecspinx.asp (accessed Oct 21, 2025).

R6				
Species	***Zero-point Energy Correction (ZPE) [M06-2X] (Hartree)***	***CCSD(T) (Hartree)***	***CCSD(T) + ZPE (Hartree)***	***Relative Energies (kcal/mol)***
A2	0.0994	-728.5270	-728.4275	0.00
Cl*	0.0013*	-459.6044*	-459.6058*	
CR6a	0.1004	-1188.1396	-1188.0392	-3.6
TS6a	0.0930	-1188.1267	-1188.0338	-0.3
PC6a	0.0933	-1188.1397	-1188.0464	-8.2
P6a	0.0854	-727.8685	-727.7831	-4.6
CR6b†	0.1000	-1188.1406	-1188.0405	-4.5
TS6b†	0.0940	-1188.1281	-1188.0341	-0.5
PC6b†	0.0943	-1188.1423	-1188.0480	-9.2
P6b†	0.0856	-727.8689	-727.7832	-4.7
CR6c	0.1002	-1188.1401	-1188.0398	-4.1
TS6c	0.0928	-1188.1280	-1188.0352	-1.1
PC6c	0.0945	-1188.1357	-1188.0411	-4.8
P6c	0.0852	-727.8647	-727.7795	-2.4
HCl	0.0068	-460.2644	-460.2576	

*: Spin-orbit coupling correction incorporated for Cl atoms, †: Calculation at the MP2/6-311++G(d,p) level of theory.

R7				
Species	***Zero-point Energy Correction (ZPE) [M06-2X] (Hartree)***	***CCSD(T) (Hartree)***	***CCSD(T) + ZPE (Hartree)***	***Relative Energies (kcal/mol)***
A3	0.0997	-728.5254	-728.4256	0.00
Cl*	0.0013*	-459.6044	-459.6058	
CR7a	0.10024	-1188.1389	-1188.0387	-4.6
TS7a	0.09316	-1188.1258	-1188.0327	-0.8
PC7a	0.09397	-1188.1405	-1188.0411	-9.5
P7a	0.08535	-727.8676	-727.7823	-5.3
CR7b	0.1000	-1188.1346	-1188.0346	-2.0
TS7b	0.0977	-1188.1281	-1188.0304	0.7
PC7b	0.0938	-1188.1362	-1188.0424	-6.9
P7b	0.0859	-727.8656	-727.7797	-3.7
CR7c	0.1005	-1188.1387	-1188.0382	-4.3
TS7c	0.0932	-1188.1277	-1188.0345	-1.9
PC7c	0.0940	-1188.1351	-1188.0411	-6.1
P7c	0.0853	-727.8638	-727.7785	-2.9
HCl	0.0068	-460.2644	-460.2576	

*: Spin-orbit coupling correction incorporated for Cl atoms.

R8				
Species	***Zero-point Energy Correction (ZPE) [M06-2X] (Hartree)***	***CCSD(T) (Hartree)***	***CCSD(T) + ZPE (Hartree)***	***Relative Energies (kcal/mol)***
A4	0.0993	-728.5259	-728.4266	0.0
Cl*	0.0013	-459.6044	-459.6058	
CR8a	0.1002	-1188.1390	-1188.0387	-4.0
TS8a	0.0933	-1188.1259	-1188.0326	-0.1
PC8a	0.0939	-1188.1406	-1188.0467	-9.0
P8a	0.0853	-727.8677	-727.7824	-4.8
CR8c	0.1002	-1188.1390	-1188.0387	-4.0
TS8c	0.0927	-1188.1276	-1188.0349	-1.6
PC8c	0.0939	-1188.1353	-1188.0414	-5.6
P8c	0.0852	-727.8640	-727.7788	-2.5
HCl	0.0068	-460.2644	-460.2576	

*: Spin-orbit coupling correction incorporated for Cl atoms.

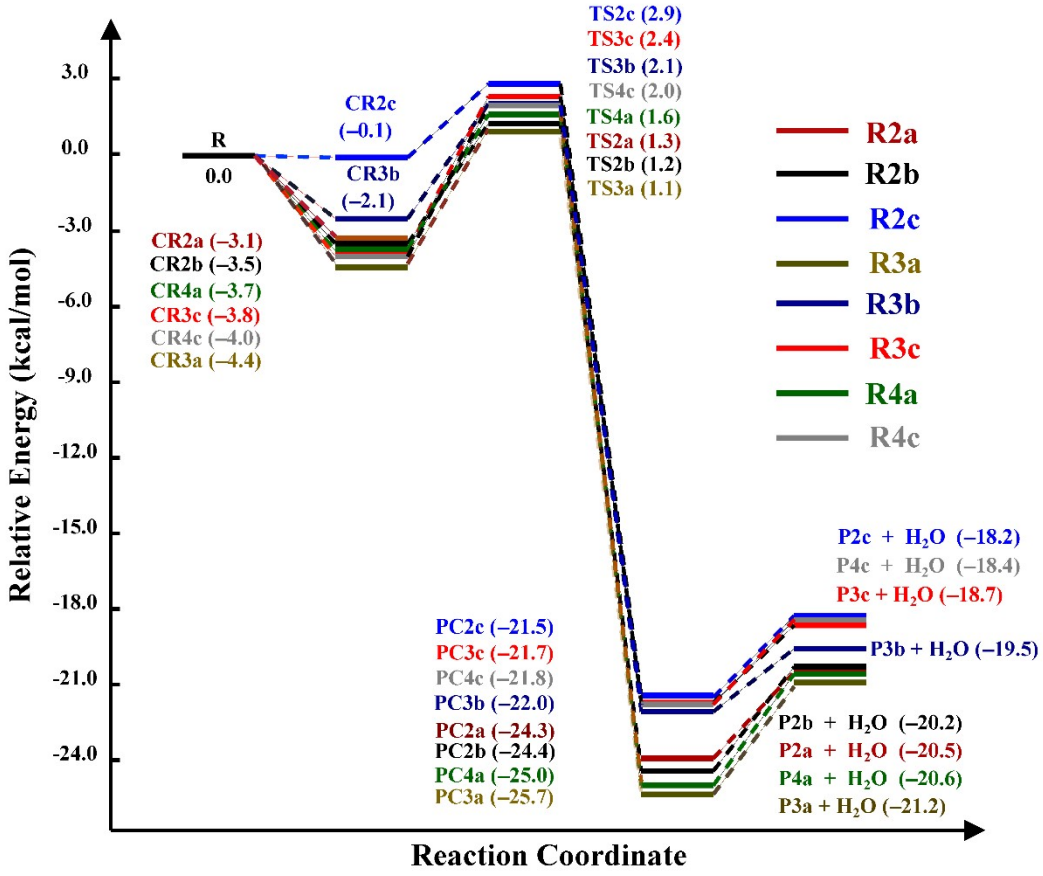


Figure S2: Relative energy profile diagram for the reaction pathways **R2-R4** at the CCSD(T)/6-311++G(d,p)//M06-2X/6-311++G(d,p) level of theory with zero-point energy corrections and spin-orbit coupling corrections. Energies are in kcal/mol.

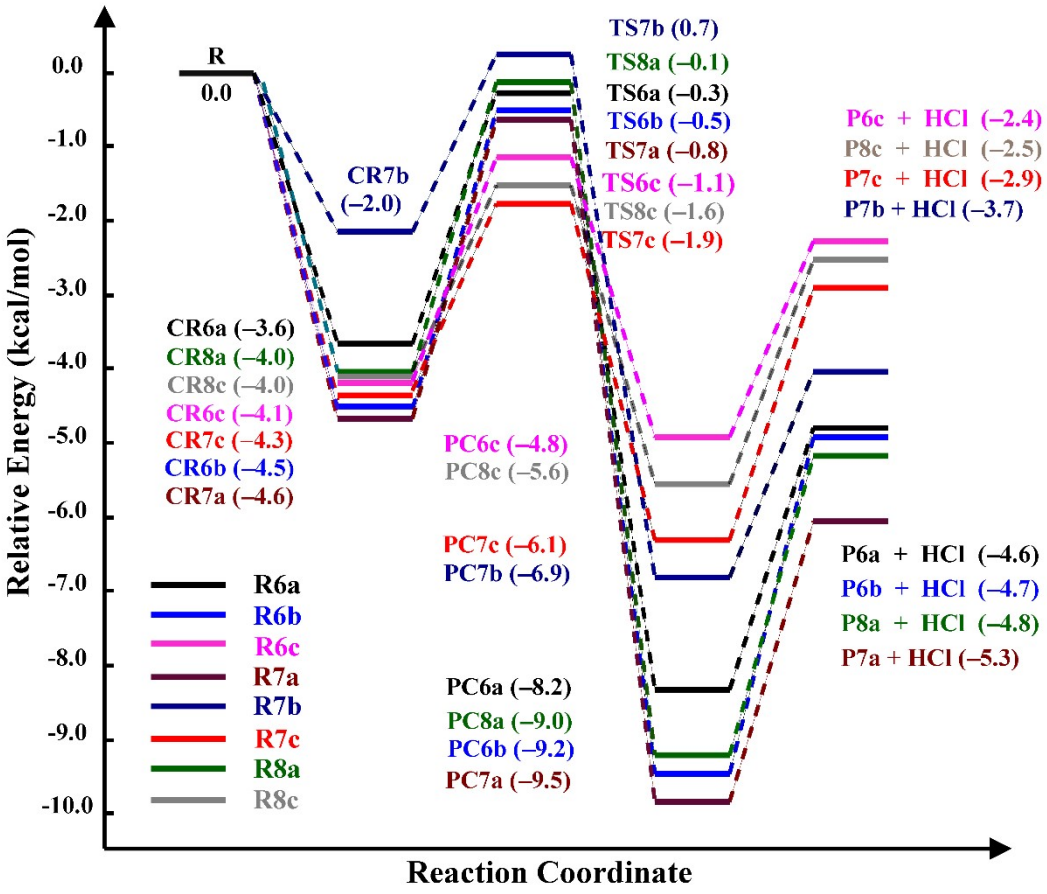


Figure S3: Relative energy profile diagram for the reaction pathways **R6-R8** at the CCSD(T)/6-311++G(d,p)//M06-2X/6-311++G(d,p) level of theory with zero-point energy corrections and spin-orbit coupling corrections. Energies are in kcal/mol.

Table S9: *T1*-diagnostic and spin-contamination $\langle S^2 \rangle$ values of all the stationary points that are involved in the reaction of HFE-365mcf3 with •OH and Cl atoms (reaction pathways **R1**-**R8**), calculated at the CCSD(T)/6-311++G(d,p) level of theory.

R1		
Species	***T1-Diagnostics***	$\langle S^2 \rangle$
A1	0.0126	0.0000
OH	0.0101	0.7500
CR1a	0.01317	0.7500
TS1a	0.0177	0.7502
PC1a	0.01494	0.7501
P1a	0.01509	0.7501
CR1b	0.0132	0.7500
TS1b	0.0176	0.7502
PC1b	0.0147	0.7501
P1b	0.0150	0.7501
CR1c	0.0125	0.7500
TS1c	0.0172	0.7502
PC1c	0.0143	0.7501
P1c	0.0144	0.7501

H_2O	0.0104	0.0000

R2		
Species	***T1-Diagnostics***	**$<S^2>$**
A2	0.0125	0.0000
OH	0.0101	0.7500
CR2a	0.01319	0.7500
TS2a	0.0175	0.7502
PC2a	0.0147	0.7501
P2a	0.01498	0.7501
CR2b	0.0194	0.7500
TS2b	0.0174	0.7502
PC2b	0.0148	0.7501
P2b	0.0150	0.7501
CR2c	0.0125	0.7500
TS2c	0.0174	0.7502
PC2c	0.0143	0.7501
P2c	0.0145	0.7501
H_2O	0.0104	0.0000

R3		
Species	***T1-Diagnostics***	**$\langle S^2 \rangle$**
A3	0.0125	0.0000
OH	0.0101	0.7500
CR3a	0.01292	0.7500
TS3a	0.01753	0.7502
PC3a	0.01485	0.7501
P3a	0.01503	0.7501
CR3b	0.0133	0.7500
TS3b	0.0178	0.7502
PC3b	0.0150	0.7501
P3b	0.0152	0.7500
CR3c	0.0124	0.7500
TS3c	0.0171	0.7502
PC3c	0.0141	0.7501
P3c	0.0143	0.7501
H_2O	0.0104	0.0000

R4		
Species	***T1-Diagnostics***	***<S²>***
A4	0.0124	0.0000
OH	0.0101	0.7500
CR4a	0.0129	0.7500
TS4a	0.0175	0.7502
PC4a	0.0148	0.7501
P4a	0.0150	0.7501
CR4c	0.0129	0.7500
TS4c	0.0172	0.7502
PC4c	0.0143	0.7501
P4c	0.0144	0.7501
H_2O	0.0104	0.0000

R5		
Species	***T1-Diagnostics***	***<S²>***
A1	0.0126	0.0000
Cl	0.0057	0.7500
CR5a	0.0122	0.7500
TS5a	0.0157	0.7505
PC5a	0.0146	0.7501
P5a	0.0150	07501
CR5b	0.0143	0.7500
TS5b	0.0158	0.7505
PC5b	0.0143	0.7501
P5b	0.0149	0.7501
CR5c	0.0145	0.7502
TS5c	0.0149	0.7504
PC5c	0.0141	0.7501
P5c	0.0144	0.7501
HCl	0.0056	0

R6		
Species	***T1-Diagnostics***	**$<S^2>$**
A2	0.0125	0.0000
Cl	0.0057	0.7500
CR6a	0.0143	0.75
TS6a	0.0158	0.7505
PC6a	0.0143	0.7501
P6a	0.0149	0.7501
CR6b†	0.0133	0.7500
TS6b†	0.0162	0.7503
PC6b†	0.0143	0.7501
P6b†	0.0151	0.7501
CR6c	0.0140	0.75
TS6c	0.0149	0.7504
PC6c	0.0141	0.7501
P6c	0.0144	0.7501
HCl	0.0056	0

†: Calculations at the CCSD(T)//MP2/6-311++G(d,p) level of theory.

R7		
Species	***T1-Diagnostics***	**<S^2>**
A3	0.0125	0.0000
Cl	0.0057	0.7500
CR7a	0.0141	0.7500
TS7a	0.0161	0.7504
PC7a	0.0144	0.7501
P7a	0.0150	0.7501
CR7b	0.0123	0.7500
TS7b	0.0154	0.7501
PC7b	0.0146	0.7500
P7b	0.0152	0.7501
CR7c	0.0146	0.7500
TS7c	0.0149	0.7500
PC7c	0.0140	0.7501
P7c	0.0144	0.7500
HCl	0.0056	0

R8		
Species	***T1-Diagnostics***	***<S²>***
A4	0.0124	0.0000
Cl	0.0057	0.7500
CR8a	0.0141	0.7501
TS8a	0.0161	0.7504
PC8a	0.0144	0.7501
P8a	0.0150	0.7501
CR8c	0.0141	0.7501
TS8c	0.0148	0.7504
PC8c	0.0140	0.7501
P8c	0.0144	0.7501
HCl	0.0056	0

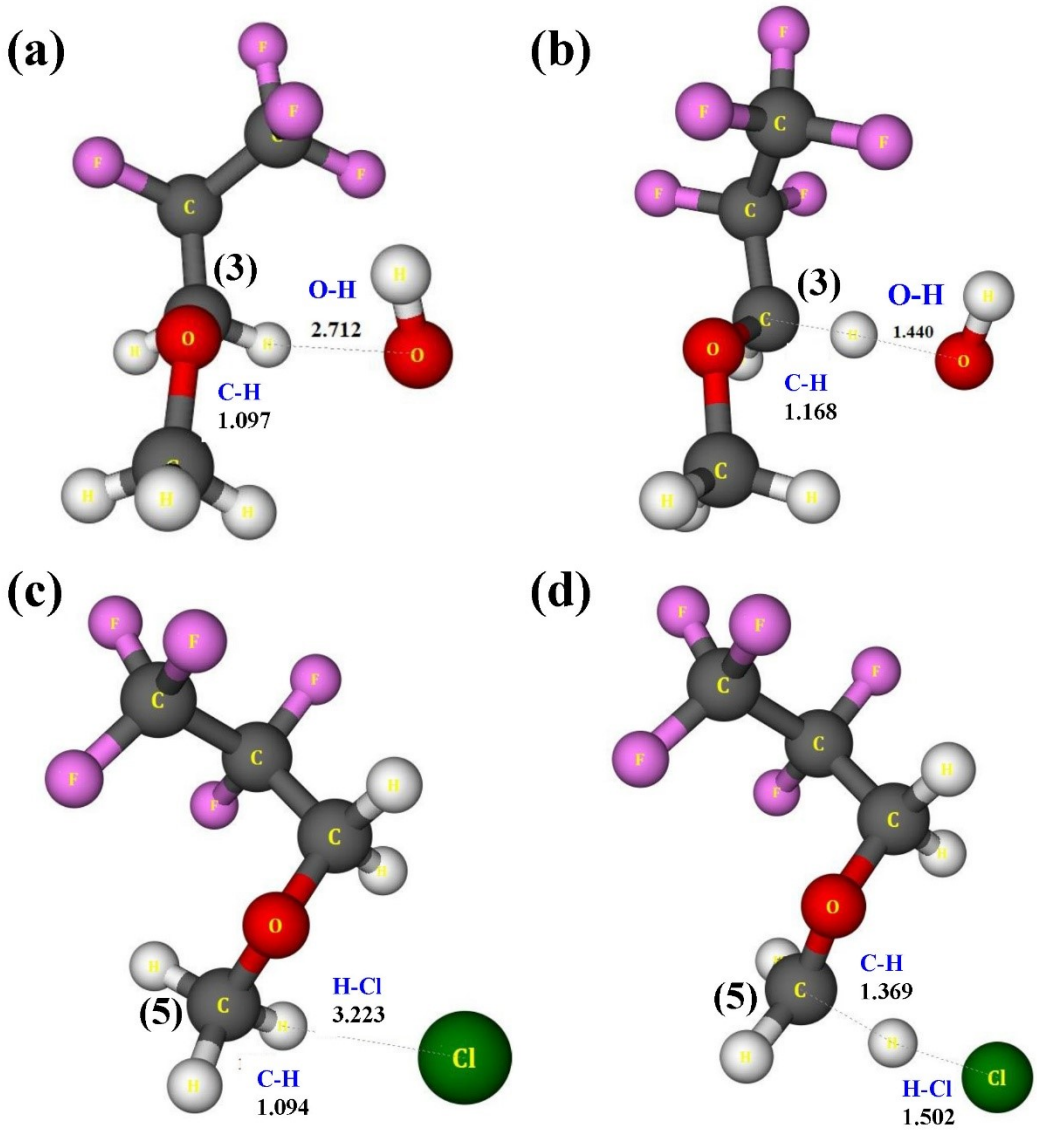


Figure S4: Optimized geometries of (a) CR1b and (b) TS1b for the OH-initiated pathway R1b, and (c) CR5c and (d) TS5c for the Cl-initiated pathway R5c, calculated at the M06-2X/6-311++G(d,p) level of theory. Bond lengths (in Å) corresponding to the breaking of the C–H bond and the forming of O–H or Cl–H bonds are shown.

Notes S3: Kinetic Model Derivation.

For the reaction

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CR \xrightarrow{k_{uni}} PC \qquad \text{(N3.1)}$$

Where A and B are the reactant and atmospheric oxidant, respectively. k_1 and k_{-1} are the forward and backward rate coefficients, respectively. k_{uni} is the unimolecular rate coefficient.

Applying steady-state approximation to the CR, we get

$$\frac{d[CR]}{dt} = k_1[A][B] - k_{-1}[CR] - k_{uni}[CR] \approx 0 \qquad \text{(N3.2)}$$

$$[CR] = \frac{k_1[A][B]}{k_{-1} + k_{uni}} \qquad \text{(N3.3)}$$

Thus, the expression for the formation of the product, PC is

$$\frac{d[PC]}{dt} = k_{uni}[CR] \qquad \text{(N3.4)}$$

Substituting the value of [CR] in the above equation, we get

$$\frac{d[PC]}{dt} = k_{uni}\frac{k_1}{k_{-1} + k_{uni}}[A][B] \qquad \text{(N3.5)}$$

Therefore, the composite rate coefficient is given by

$$k_o = \frac{k_1 \times k_{uni}}{k_{-1} + k_{uni}} \qquad \text{(N3.6)}$$

Reverse rate concept

The reverse rate (k_{-1}) becomes relevant in the pre-reactive complex when the energy barrier of the back-dissociation step to the individual reactant is greater or similar to the energy barrier of the transition state.

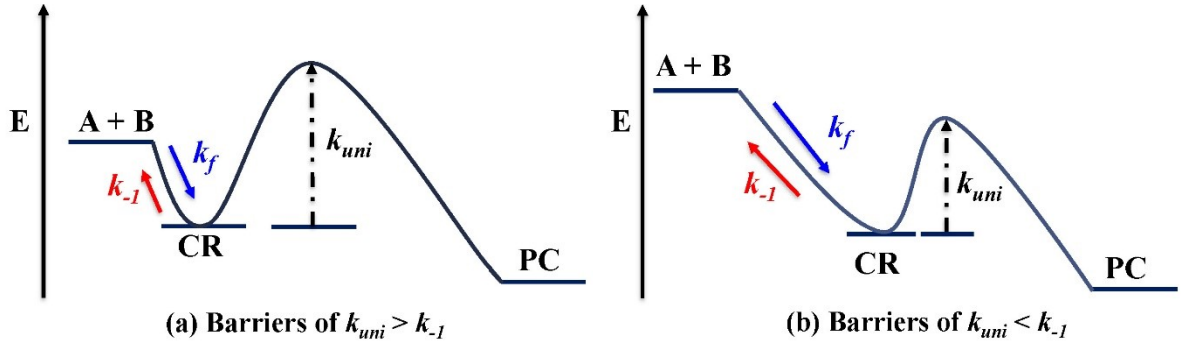


Figure S5: Schematic representation of the reaction pathways (a) forward energy barrier is greater than reverse energy barrier, and (b) reverse energy barrier is greater than forward energy barrier, with respect to pre-reactive complex CR.

In the case of $^{\bullet}$OH, the reaction pathway Fig. S5 (a) is followed where the energy barrier of k_{uni} is greater than k_{-1}. Thus, the reverse energy barrier does not influence the kinetics here.

Again, for the Cl-initiated reactions, the consideration of reverse barrier is important and the pathway Fig. S5 (b) is mostly followed (also evident from energy profile diagrams shown in Fig. 4 of manuscript and Figs. S2 and S3 of the SI).

However, for specific pathways R5a and R7b, the reaction pathway Fig. S5 (a) is followed and similar to the reaction with $^{\bullet}$OH, the reverse energy barrier does not influence the kinetics. But, for the other pathways, R5b, R5c, R6a, R6c, R7a, R7c, R8a, and R8c, the reverse energy barrier plays a more significant role. In these cases, k_{-1} were calculated variationally using the KiSThelP software, The forward rate constant k_f was then derived from the equilibrium constant relation $K_{eq} = (k_f/k_{-1})$. Using the calculated k_f, k_{uni}, and k_{-1}, the overall rate coefficient was evaluated from the expression below.

$$k_o = \frac{k_1 \times k_{uni}}{k_{-1} + k_{uni}}$$

To improve the clarity, we have now revised the Supporting Information to explicitly describe the rate coefficient calculations involving high reverse energy barriers. Additionally, detailed excel sheets have been added to SI4-Kinetics.xlsx file providing data for these pathways (R5b, R5c, R6a, R6c, R7a, R7c, R8a, and R8c).

Table S10: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (k_{1a}) for the reaction pathway **R1a** in the temperature range 200-400 K at the M06-2X level.

R1a			
Temperature (K)	K_{eq} ***(cm³ molecule⁻¹)***	k_{uni} ***(s⁻¹)***	k_{1a} ***(cm³ molecule⁻¹ s⁻¹)***
200	1.358×10^{-22}	5.300×10^{7}	7.200×10^{-15}
220	5.559×10^{-23}	1.000×10^{8}	5.559×10^{-15}
240	2.637×10^{-23}	1.800×10^{8}	4.746×10^{-15}
260	1.401×10^{-23}	3.000×10^{8}	4.204×10^{-15}
280	8.147×10^{-24}	4.700×10^{8}	3.829×10^{-15}
298	5.318×10^{-24}	6.800×10^{8}	3.616×10^{-15}
300	5.088×10^{-24}	7.100×10^{8}	3.613×10^{-15}
320	3.369×10^{-24}	1.000×10^{9}	3.369×10^{-15}
340	2.341×10^{-24}	1.400×10^{9}	3.277×10^{-15}
360	1.693×10^{-24}	1.900×10^{9}	3.217×10^{-15}
380	1.267×10^{-24}	2.400×10^{9}	3.041×10^{-15}
400	9.757×10^{-25}	3.100×10^{9}	3.025×10^{-15}

Table S11: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (k_{1b}) for the reaction pathway **R1b** in the temperature range 200-400 K at the M06-2X level.

R1b			
Temperature (K)	K_{eq} ***(cm^3 molecule^{-1})***	k_{uni} ***(s^{-1})***	k_{1b} ***(cm^3 molecule^{-1} s^{-1})***
200	4.496×10^{-22}	4.800×10^{8}	2.158×10^{-13}
220	1.443×10^{-22}	9.600×10^{8}	1.385×10^{-13}
240	5.590×10^{-23}	1.800×10^{9}	1.006×10^{-13}
260	2.503×10^{-23}	3.100×10^{9}	7.759×10^{-14}
280	1.256×10^{-23}	5.000×10^{9}	6.281×10^{-14}
298	7.308×10^{-24}	7.300×10^{9}	5.335×10^{-14}
300	6.908×10^{-24}	7.600×10^{9}	5.250×10^{-14}
320	4.092×10^{-24}	1.100×10^{10}	4.501×10^{-14}
340	2.577×10^{-24}	1.600×10^{10}	4.123×10^{-14}
360	1.708×10^{-24}	2.100×10^{10}	3.587×10^{-14}
380	1.182×10^{-24}	2.800×10^{10}	3.310×10^{-14}
400	8.485×10^{-25}	3.600×10^{10}	3.054×10^{-14}

Table S12: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (***Total*** k_{1c}) for the reaction pathway **R1c** in the temperature range 200-400 K at the M06-2X level.

R1c				
Temperature (K)	K_{eq} ***(cm^3 molecule^{-1})***	k_{uni} ***(s^{-1})***	k_{1c} ***(cm^3 molecule^{-1} s^{-1})***	***Total*** k_{1c} **(3 *** k_{1c}**)** ***(cm^3 molecule^{-1} s^{-1})***
200	7.948×10^{-22}	5.400×10^{6}	4.292×10^{-15}	1.288×10^{-14}
220	2.917×10^{-22}	1.400×10^{7}	4.083×10^{-15}	1.225×10^{-14}
240	1.263×10^{-22}	3.300×10^{7}	4.169×10^{-15}	1.251×10^{-14}
260	6.218×10^{-23}	7.000×10^{7}	4.353×10^{-15}	1.306×10^{-14}
280	3.384×10^{-23}	1.300×10^{8}	4.400×10^{-15}	1.320×10^{-14}
298	2.098×10^{-23}	2.300×10^{8}	4.826×10^{-15}	1.448×10^{-14}
300	1.997×10^{-23}	2.400×10^{8}	4.792×10^{-15}	1.437×10^{-14}
320	1.258×10^{-23}	4.000×10^{8}	5.030×10^{-15}	1.509×10^{-14}
340	8.361×10^{-24}	6.300×10^{8}	5.268×10^{-15}	1.580×10^{-14}
360	5.815×10^{-24}	9.400×10^{8}	5.466×10^{-15}	1.640×10^{-14}
380	4.202×10^{-24}	1.400×10^{9}	5.882×10^{-15}	1.765×10^{-14}
400	3.135×10^{-24}	1.900×10^{9}	5.957×10^{-15}	1.787×10^{-14}

Table S13: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (k_{2a}) for the reaction pathway **R2a** in the temperature range 200-400 K at the M06-2X level.

R2a			
Temperature (K)	K_{eq} ***(cm^3 molecule^{-1})***	k_{uni} ***(s^{-1})***	k_{2a} ***(cm^3 molecule^{-1} s^{-1})***
200	6.91×10^{-22}	3.5000×10^{8}	2.418×10^{-13}
220	2.005×10^{-22}	7.000×10^{8}	1.403×10^{-13}
240	7.140×10^{-23}	1.300×10^{9}	9.282×10^{-14}
260	2.977×10^{-23}	2.300×10^{9}	6.848×10^{-14}
280	1.406×10^{-23}	3.700×10^{9}	5.202×10^{-14}
298	7.796×10^{-24}	5.400×10^{9}	4.210×10^{-14}
300	7.333×10^{-24}	5.600×10^{9}	4.107×10^{-14}
320	4.148×10^{-24}	8.300×10^{9}	3.442×10^{-14}
340	2.508×10^{-24}	1.200×10^{10}	3.009×10^{-14}
360	1.603×10^{-24}	1.600×10^{10}	2.564×10^{-14}
380	1.074×10^{-24}	2.100×10^{10}	2.255×10^{-14}
400	7.485×10^{-25}	2.700×10^{10}	2.021×10^{-14}

Table S14: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (k_{2b}) for the reaction pathway **R2b** in the temperature range 200-400 K at the M06-2X level.

R2b			
Temperature (K)	K_{eq} (cm^3 $molecule^{-1}$)	k_{uni} (s^{-1})	k_{2b} (cm^3 $molecule^{-1}$ s^{-1})
200	2.037×10^{-21}	1.200×10^{8}	2.444×10^{-13}
220	5.663×10^{-22}	2.500×10^{8}	1.416×10^{-13}
240	1.946×10^{-22}	4.700×10^{8}	9.146×10^{-14}
260	7.874×10^{-23}	8.400×10^{8}	6.614×10^{-14}
280	3.623×10^{-23}	1.400×10^{9}	5.073×10^{-14}
298	1.969×10^{-23}	2.190×10^{9}	4.312×10^{-14}
300	1.848×10^{-23}	2.200×10^{9}	4.066×10^{-14}
320	1.025×10^{-23}	3.300×10^{9}	3.382×10^{-14}
340	6.090×10^{-24}	4.800×10^{9}	2.923×10^{-14}
360	3.833×10^{-24}	6.700×10^{9}	2.568×10^{-14}
380	2.533×10^{-24}	9.000×10^{9}	2.280×10^{-14}
400	1.744×10^{-24}	1.200×10^{10}	2.093×10^{-14}

Table S15: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (***Total*** k_{2c}) for the reaction pathway **R2c** in the temperature range 200-400 K at the M06-2X level.

R2c				
Temperature (K)	K_{eq} (cm^3 $molecule^{-1}$)	k_{uni} (s^{-1})	k_{2c} (cm^3 $molecule^{-1}$ s^{-1})	***Total*** k_{2c} ($3 * k_{2c}$) (cm^3 $molecule^{-1}$ s^{-1})
200	6.620×10^{-24}	1.800×10^{9}	1.192×10^{-14}	3.575×10^{-14}
220	3.849×10^{-24}	2.700×10^{9}	1.039×10^{-14}	3.118×10^{-14}
240	2.447×10^{-24}	3.800×10^{9}	9.299×10^{-15}	2.790×10^{-14}
260	1.666×10^{-24}	5.200×10^{9}	8.665×10^{-15}	2.599×10^{-14}
280	1.198×10^{-24}	6.800×10^{9}	8.145×10^{-15}	2.444×10^{-14}
298	9.239×10^{-25}	8.500×10^{9}	7.853×10^{-15}	2.356×10^{-14}
300	8.993×10^{-25}	8.700×10^{9}	7.824×10^{-15}	2.347×10^{-14}
320	6.995×10^{-25}	1.100×10^{10}	7.695×10^{-15}	2.308×10^{-14}
340	5.602×10^{-25}	1.300×10^{10}	7.283×10^{-15}	2.185×10^{-14}
360	4.598×10^{-25}	1.500×10^{10}	6.897×10^{-15}	2.069×10^{-14}
380	3.852×10^{-25}	1.800×10^{10}	6.934×10^{-15}	2.080×10^{-14}
400	3.284×10^{-25}	2.100×10^{10}	6.897×10^{-15}	2.069×10^{-14}

Table S16: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (k_{3a}) for the reaction pathway **R3a** in the temperature range 200-400 K at the M06-2X level.

R3a			
Temperature (K)	K_{eq} ***(cm^3 molecule^{-1})***	k_{uni} ***(s^{-1})***	k_{3a} ***(cm^3 molecule^{-1} s^{-1})***
200	8.546×10^{-21}	3.100×10^{7}	2.649×10^{-13}
220	2.159×10^{-21}	6.900×10^{7}	1.490×10^{-13}
240	6.852×10^{-22}	1.400×10^{8}	9.592×10^{-14}
260	2.592×10^{-22}	2.600×10^{8}	6.738×10^{-14}
280	1.126×10^{-22}	4.700×10^{8}	5.290×10^{-14}
298	5.845×10^{-23}	7.400×10^{8}	4.325×10^{-14}
300	5.461×10^{-23}	7.800×10^{8}	4.259×10^{-14}
320	2.899×10^{-23}	1.200×10^{9}	3.478×10^{-14}
340	1.657×10^{-23}	1.900×10^{9}	3.148×10^{-14}
360	1.008×10^{-23}	2.700×10^{9}	2.721×10^{-14}
380	6.457×10^{-24}	3.800×10^{9}	2.454×10^{-14}
400	4.325×10^{-24}	5.200×10^{9}	2.249×10^{-14}

Table S17: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (k_{3b}) for the reaction pathway **R3b** in the temperature range 200-400 K at the M06-2X level.

R3b			
Temperature (K)	K_{eq} ***(cm³ molecule⁻¹)***	k_{uni} ***(s⁻¹)***	k_{3b} ***(cm³ molecule⁻¹ s⁻¹)***
200	7.211×10^{-26}	3.300×10^{8}	2.380×10^{-17}
220	5.024×10^{-26}	6.100×10^{8}	3.064×10^{-17}
240	3.713×10^{-26}	1.100×10^{9}	4.084×10^{-17}
260	2.872×10^{-26}	1.700×10^{9}	4.882×10^{-17}
280	2.303×10^{-26}	2.600×10^{9}	5.987×10^{-17}
298	1.935×10^{-26}	3.700×10^{9}	7.159×10^{-17}
300	1.900×10^{-26}	3.800×10^{9}	7.221×10^{-17}
320	1.606×10^{-26}	5.300×10^{9}	8.511×10^{-17}
340	1.384×10^{-26}	7.200×10^{9}	9.962×10^{-17}
360	1.212×10^{-26}	9.400×10^{9}	1.139×10^{-16}
380	1.076×10^{-26}	1.200×10^{10}	1.291×10^{-16}
400	9.666×10^{-27}	1.500×10^{10}	1.450×10^{-16}

Table S18: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (***Total*** k_{3c}) for the reaction pathway R3c in the temperature range 200-400 K at the M06-2X level.

R3c				
Temperature (K)	K_{eq} (cm^3 $molecule^{-1}$)	k_{uni} (s^{-1})	k_{3c} (cm^3 $molecule^{-1}$ s^{-1})	***Total*** k_{3c} ($3 * k_{3c}$) (cm^3 $molecule^{-1}$ s^{-1})
200	2.532×10^{-21}	7.800×10^{5}	1.975×10^{-15}	5.924×10^{-15}
220	8.033×10^{-22}	2.200×10^{6}	1.767×10^{-15}	5.302×10^{-15}
240	3.083×10^{-22}	5.500×10^{6}	1.695×10^{-15}	5.086×10^{-15}
260	1.369×10^{-22}	1.200×10^{7}	1.643×10^{-15}	4.930×10^{-15}
280	6.826×10^{-23}	2.400×10^{7}	1.638×10^{-15}	4.914×10^{-15}
298	3.949×10^{-23}	4.300×10^{7}	1.698×10^{-15}	5.094×10^{-15}
300	3.731×10^{-23}	4.500×10^{7}	1.679×10^{-15}	5.037×10^{-15}
320	2.199×10^{-23}	7.800×10^{7}	1.715×10^{-15}	5.145×10^{-15}
340	1.378×10^{-23}	1.300×10^{8}	1.792×10^{-15}	5.376×10^{-15}
360	9.099×10^{-24}	2.000×10^{8}	1.820×10^{-15}	5.459×10^{-15}
380	6.273×10^{-24}	2.900×10^{8}	1.819×10^{-15}	5.458×10^{-15}
400	4.488×10^{-24}	4.200×10^{8}	1.885×10^{-15}	5.655×10^{-15}

Table S19: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (***Total*** k_{4a}) for the reaction pathway **R4a** in the temperature range 200-400 K at the M06-2X level.

R4a				
Temperature (K)	K_{eq} (cm^3 $molecule^{-1}$)	k_{uni} (s^{-1})	k_{4a} (cm^3 $molecule^{-1}$ s^{-1})	***Total*** k_{4a} ($2 * k_{4a}$) (cm^3 $molecule^{-1}$ s^{-1})
200	3.460×10^{-21}	5.800×10^{7}	2.007×10^{-13}	4.013×10^{-13}
220	8.997×10^{-22}	1.300×10^{8}	1.170×10^{-13}	2.339×10^{-13}
240	2.925×10^{-22}	2.600×10^{8}	7.604×10^{-14}	1.521×10^{-13}
260	1.129×10^{-22}	5.000×10^{8}	5.645×10^{-14}	1.129×10^{-13}
280	4.990×10^{-23}	8.800×10^{8}	4.391×10^{-14}	8.782×10^{-14}
298	2.627×10^{-23}	1.400×10^{9}	3.677×10^{-14}	7.354×10^{-14}
300	2.457×10^{-23}	1.500×10^{9}	3.686×10^{-14}	7.372×10^{-14}
320	1.322×10^{-23}	2.300×10^{9}	3.040×10^{-14}	6.080×10^{-14}
340	7.645×10^{-24}	3.500×10^{9}	2.676×10^{-14}	5.352×10^{-14}
360	4.698×10^{-24}	5.100×10^{9}	2.396×10^{-14}	4.792×10^{-14}
380	3.038×10^{-24}	7.100×10^{9}	2.157×10^{-14}	4.314×10^{-14}
400	2.052×10^{-24}	9.700×10^{9}	1.990×10^{-14}	3.981×10^{-14}

Table S20: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (***Total*** k_{4c}) for the reaction pathway **R4c** in the temperature range 200-400 K at the M06-2X level.

R4c				
Temperature (K)	K_{eq} (cm^3 $molecule^{-1}$)	k_{uni} (s^{-1})	k_{4b} (cm^3 $molecule^{-1}$ s^{-1})	***Total*** k_{4b} ***(3 * k*** $_{4c}$***)*** (cm^3 $molecule^{-1}$ s^{-1})
200	5.71×10^{-21}	5.10×10^{7}	2.91×10^{-13}	8.74×10^{-13}
220	1.45×10^{-21}	1.50×10^{8}	2.17×10^{-13}	6.53×10^{-13}
240	4.62×10^{-22}	3.90×10^{8}	1.80×10^{-13}	5.41×10^{-13}
260	1.75×10^{-22}	9.10×10^{8}	1.59×10^{-13}	4.79×10^{-13}
280	7.65×10^{-23}	1.90×10^{9}	1.45×10^{-13}	4.36×10^{-13}
298	3.98×10^{-23}	3.50×10^{9}	1.39×10^{-13}	4.18×10^{-13}
300	3.72×10^{-23}	3.70×10^{9}	1.37×10^{-13}	4.13×10^{-13}
320	1.98×10^{-23}	6.60×10^{9}	1.30×10^{-13}	3.92×10^{-13}
340	1.13×10^{-23}	1.10×10^{10}	1.24×10^{-13}	3.74×10^{-13}
360	6.91×10^{-24}	1.80×10^{10}	1.24×10^{-13}	3.73×10^{-13}
380	4.44×10^{-24}	2.80×10^{10}	1.24×10^{-13}	3.73×10^{-13}
400	2.97×10^{-24}	4.10×10^{10}	1.22×10^{-14}	3.66×10^{-13}

Table S21: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (k_{5a}) for the reaction pathway **R5a** in the temperature range 200-400 K at the M06-2X level.

R5a			
Temperature (K)	K_{eq} ***(cm^3 molecule^{-1})***	k_{uni} ***(s^{-1})***	k_{5a} ***(cm^3 molecule^{-1} s^{-1})***
200	5.60×10^{-24}	7.10×10^{9}	3.98×10^{-14}
220	3.60×10^{-24}	9.80×10^{9}	3.53×10^{-14}
240	2.49×10^{-24}	1.30×10^{10}	3.24×10^{-14}
260	1.82×10^{-24}	1.70×10^{10}	3.10×10^{-14}
280	1.39×10^{-24}	2.10×10^{10}	2.92×10^{-14}
298	1.13×10^{-24}	2.50×10^{10}	2.82×10^{-14}
300	1.10×10^{-24}	2.60×10^{10}	2.87×10^{-14}
320	8.99×10^{-25}	3.10×10^{10}	2.79×10^{-14}
340	7.50×10^{-25}	3.70×10^{10}	2.78×10^{-14}
360	6.38×10^{-25}	4.30×10^{10}	2.74×10^{-14}
380	5.52×10^{-25}	5.00×10^{10}	2.76×10^{-14}
400	4.84×10^{-25}	5.70×10^{10}	2.76×10^{-14}

Table S22: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), reverse reaction rate coefficient (k_r), forward reaction rate coefficient (k_f) and total rate coefficients (k_{5b}) for the reaction pathway **R5b** in the temperature range 200-400 K at the M06-2X level.

R5b					
***Temperature* (K)**	K_{eq} ***(cm³ molecule⁻¹)***	k_{uni} **(s^{-1})**	k_r **(VTST) (s^{-1})**	k_f **(s^{-1})**	***Total*** k_{5b} ***(cm³ molecule⁻¹ s⁻¹)***
200	7.91×10^{-22}	1.40×10^{9}	2.62×10^{11}	2.07×10^{-11}	1.05×10^{-12}
220	2.85×10^{-22}	2.80×10^{9}	4.30×10^{11}	1.23×10^{-11}	7.49×10^{-13}
240	1.22×10^{-22}	5.30×10^{9}	6.42×10^{11}	7.82×10^{-12}	5.96×10^{-13}
260	5.92×10^{-23}	9.10×10^{9}	9.09×10^{11}	5.38×10^{-12}	4.90×10^{-13}
280	3.19×10^{-23}	1.50×10^{10}	1.20×10^{12}	3.84×10^{-12}	4.25×10^{-13}
298	1.96×10^{-23}	2.10×10^{10}	1.49×10^{12}	2.93×10^{-12}	3.61×10^{-13}
300	1.87×10^{-23}	2.20×10^{10}	1.53×10^{12}	2.85×10^{-12}	3.59×10^{-13}
320	1.17×10^{-23}	3.20×10^{10}	1.89×10^{12}	2.21×10^{-12}	3.19×10^{-13}
340	7.70×10^{-24}	4.50×10^{10}	2.28×10^{12}	1.75×10^{-12}	2.89×10^{-13}
360	5.32×10^{-24}	6.10×10^{10}	2.67×10^{12}	1.42×10^{-12}	2.64×10^{-13}
380	3.82×10^{-24}	8.10×10^{10}	3.04×10^{12}	1.16×10^{-12}	2.45×10^{-13}
400	2.84×10^{-24}	1.00×10^{11}	3.50×10^{12}	9.94×10^{-13}	2.21×10^{-13}

Table S23: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), reverse reaction rate coefficient (k_r), forward reaction rate coefficient (k_f) and total rate coefficients (***Total*** k_{5c}) for the reaction pathway **R5c** in the temperature range 200-400 K at the M06-2X level.

R5c					
Temperature **(K)**	K_{eq} ***(cm³ molecule⁻¹)***	k_{uni} **(s^{-1})**	k_r **(VTST)** **(s^{-1})**	k_f **(s^{-1})**	***Total*** k_{5c} ***(cm³ molecule⁻¹ s⁻¹)***
200	1.82×10^{-20}	5.40×10^{9}	1.51×10^{10}	2.74×10^{-10}	2.17×10^{-10}
220	5.06×10^{-21}	9.10×10^{9}	2.55×10^{10}	1.29×10^{-10}	1.02×10^{-10}
240	1.74×10^{-21}	1.40×10^{10}	3.97×10^{10}	6.91×10^{-11}	5.41×10^{-11}
260	7.06×10^{-22}	2.20×10^{10}	5.76×10^{10}	4.07×10^{-11}	3.37×10^{-11}
280	3.26×10^{-22}	3.10×10^{10}	7.94×10^{10}	2.59×10^{-11}	2.18×10^{-11}
298	1.77×10^{-22}	4.10×10^{10}	1.02×10^{11}	1.81×10^{-11}	1.56×10^{-11}
300	1.66×10^{-22}	4.20×10^{10}	1.05×10^{11}	1.74×10^{-11}	1.50×10^{-11}
320	9.24×10^{-23}	5.60×10^{10}	1.34×10^{11}	1.24×10^{-11}	1.09×10^{-11}
340	5.50×10^{-23}	7.20×10^{10}	1.66×10^{11}	9.12×10^{-12}	8.28×10^{-12}
360	3.46×10^{-23}	9.10×10^{10}	2.01×10^{11}	6.95×10^{-12}	6.51×10^{-12}
380	2.29×10^{-23}	1.10×10^{11}	2.38×10^{11}	5.45×10^{-12}	5.17×10^{-12}
400	1.58×10^{-23}	1.40×10^{11}	2.78×10^{11}	4.38×10^{-12}	4.40×10^{-12}

Table S24: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), reverse reaction rate coefficient (k_r), forward reaction rate coefficient (k_f) and total rate coefficients (k_{6a}) for the reaction pathway **R6a** in the temperature range 200-400 K at the M06-2X level.

R6a					
***Temperature* (K)**	K_{eq} (cm^3 $molecule^{-1}$)	k_{uni} (s^{-1})	k_r (VTST) (s^{-1})	k_f (s^{-1})	***Total k6a*** (cm^3 $molecule^{-1}$ s^{-1})
200	6.59×10^{-22}	1.60×10^{9}	3.54×10^{9}	2.34×10^{-12}	7.27×10^{-13}
220	2.20×10^{-22}	3.40×10^{9}	7.48×10^{9}	1.65×10^{-12}	5.15×10^{-13}
240	8.83×10^{-23}	6.40×10^{9}	1.40×10^{10}	1.23×10^{-12}	3.88×10^{-13}
260	4.07×10^{-23}	1.10×10^{10}	2.37×10^{10}	9.66×10^{-13}	3.06×10^{-13}
280	2.10×10^{-23}	1.80×10^{10}	3.73×10^{10}	7.82×10^{-13}	2.55×10^{-13}
298	1.25×10^{-23}	2.60×10^{10}	5.30×10^{10}	6.60×10^{-13}	2.17×10^{-13}
300	1.18×10^{-23}	2.70×10^{10}	5.51×10^{10}	6.49×10^{-13}	2.14×10^{-13}
320	7.12×10^{-24}	4.00×10^{10}	7.83×10^{10}	5.57×10^{-13}	1.89×10^{-13}
340	4.56×10^{-24}	5.60×10^{10}	1.06×10^{11}	4.83×10^{-13}	1.67×10^{-13}
360	3.07×10^{-24}	7.60×10^{10}	1.39×10^{11}	4.26×10^{-13}	1.51×10^{-13}
380	2.15×10^{-24}	1.00×10^{11}	1.77×10^{11}	3.81×10^{-13}	1.37×10^{-13}
400	1.56×10^{-24}	1.30×10^{11}	2.20×10^{11}	3.44×10^{-13}	1.28×10^{-13}

Table S25: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), reverse reaction rate coefficient (k_r), forward reaction rate coefficient (k_f) and total rate coefficients (***Total*** k_{6c}) for the reaction pathway **R6c** in the temperature range 200-400 K at the M06-2X level.

R6c					
***Temperature* (K)**	K_{eq} (cm^3 $molecule^{-1}$)	k_{uni} (s^{-1})	k_r (VTST) (s^{-1})	k_f (s^{-1})	***Total k6c*** (cm^3 $molecule^{-1}$ s^{-1})
200	4.02×10^{-21}	7.40×10^{9}	3.42×10^{8}	1.38×10^{-12}	3.95×10^{-12}
220	1.31×10^{-21}	1.20×10^{10}	7.73×10^{8}	1.01×10^{-12}	2.85×10^{-12}
240	5.12×10^{-22}	1.90×10^{10}	1.52×10^{9}	7.78×10^{-13}	2.16×10^{-12}
260	2.31×10^{-22}	2.80×10^{10}	2.70×10^{9}	6.25×10^{-13}	1.71×10^{-12}
280	1.17×10^{-22}	4.00×10^{10}	4.42×10^{9}	5.18×10^{-13}	1.40×10^{-12}
298	6.86×10^{-23}	5.30×10^{10}	6.53×10^{9}	4.48×10^{-13}	1.20×10^{-12}
300	6.49×10^{-23}	5.40×10^{10}	6.79×10^{9}	4.41×10^{-13}	1.17×10^{-12}
320	3.87×10^{-23}	7.10×10^{10}	9.90×10^{9}	3.83×10^{-13}	1.01×10^{-12}
340	2.45×10^{-23}	9.10×10^{10}	1.38×10^{10}	3.38×10^{-13}	8.80×10^{-13}
360	1.63×10^{-23}	1.10×10^{11}	1.85×10^{10}	3.02×10^{-13}	7.74×10^{-13}
380	1.13×10^{-23}	1.40×10^{11}	2.40×10^{10}	2.72×10^{-13}	6.97×10^{-13}
400	8.16×10^{-24}	1.70×10^{11}	3.06×10^{10}	2.50×10^{-13}	6.35×10^{-13}

Table S26: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (k_{7a}) for the reaction pathway **R7a** in the temperature range 200-400 K at the M06-2X level.

R7a					
***Temperature* (K)**	K_{eq} ***(cm³ molecule⁻¹)***	k_{uni} **(s^{-1})**	k_r **(VTST) (s^{-1})**	k_f **(s^{-1})**	***Total*** k_{7a} ***(cm³ molecule⁻¹ s⁻¹)***
200	3.81×10^{-21}	4.50×10^{8}	1.85×10^{11}	7.04×10^{-10}	1.71×10^{-12}
220	1.20×10^{-21}	1.10×10^{9}	2.29×10^{11}	2.75×10^{-10}	1.31×10^{-12}
240	4.59×10^{-22}	2.30×10^{9}	2.74×10^{11}	1.26×10^{-10}	1.05×10^{-12}
260	2.03×10^{-22}	4.40×10^{9}	3.26×10^{11}	6.62×10^{-11}	8.81×10^{-13}
280	1.01×10^{-22}	7.60×10^{9}	3.71×10^{11}	3.75×10^{-11}	7.52×10^{-13}
298	5.83×10^{-23}	1.20×10^{10}	4.12×10^{11}	2.40×10^{-11}	6.79×10^{-13}
300	5.50×10^{-23}	1.90×10^{10}	4.17×10^{11}	2.30×10^{-11}	1.00×10^{-12}
320	3.24×10^{-23}	1.90×10^{10}	4.63×10^{11}	1.50×10^{-11}	5.91×10^{-13}
340	2.02×10^{-23}	2.80×10^{10}	5.06×10^{11}	1.02×10^{-11}	5.37×10^{-13}
360	1.33×10^{-23}	4.00×10^{10}	5.42×10^{11}	7.22×10^{-12}	4.97×10^{-13}
380	9.17×10^{-24}	5.40×10^{10}	5.71×10^{11}	5.23×10^{-12}	4.52×10^{-13}
400	6.55×10^{-24}	7.20×10^{10}	6.10×10^{11}	3.99×10^{-12}	4.22×10^{-13}

Table S27: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), and total rate coefficients (k_{7b}) for the reaction pathway **R7b** in the temperature range 200-400 K at the M06-2X level.

R7b			
Temperature (K)	K_{eq} ***(cm³ molecule⁻¹)***	k_{uni} ***(s⁻¹)***	k_{7b} ***(cm³ molecule⁻¹ s⁻¹)***
200	5.20×10^{-24}	1.50×10^{9}	7.80×10^{-15}
220	3.14×10^{-24}	2.70×10^{9}	8.48×10^{-15}
240	2.06×10^{-24}	4.40×10^{9}	9.08×10^{-15}
260	1.44×10^{-24}	6.70×10^{9}	9.68×10^{-15}
280	1.06×10^{-24}	9.60×10^{9}	1.02×10^{-14}
298	8.37×10^{-25}	1.30×10^{10}	1.09×10^{-14}
300	8.16×10^{-25}	1.30×10^{10}	1.06×10^{-14}
320	6.46×10^{-25}	1.70×10^{10}	1.10×10^{-14}
340	5.26×10^{-25}	2.20×10^{10}	1.16×10^{-14}
360	4.38×10^{-25}	2.70×10^{10}	1.18×10^{-14}
380	3.71×10^{-25}	3.30×10^{10}	1.23×10^{-14}
400	3.20×10^{-25}	3.90×10^{10}	1.25×10^{-14}

Table S28: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), reverse reaction rate coefficient (k_r), forward reaction rate coefficient (k_f) and total rate coefficients (***Total*** k_{7c}) for the reaction pathway **R7c** in the temperature range 200-400 K at the M06-2X level.

R7c					
Temperature **(K)**	K_{eq} ***(cm³ molecule⁻¹)***	k_{uni} **(s^{-1})**	k_r **(VTST)** **(s^{-1})**	k_f **(s^{-1})**	***Total*** k_{7c} ***(cm³ molecule⁻¹ s⁻¹)***
200	1.81×10^{-20}	2.30×10^{10}	3.41×10^{5}	6.17×10^{-15}	1.85×10^{-14}
220	4.91×10^{-21}	3.40×10^{10}	1.59×10^{6}	7.78×10^{-15}	2.33×10^{-14}
240	1.65×10^{-21}	4.80×10^{10}	5.74×10^{6}	9.49×10^{-15}	2.85×10^{-14}
260	6.58×10^{-22}	6.40×10^{10}	1.71×10^{7}	1.13×10^{-14}	3.38×10^{-14}
280	2.99×10^{-22}	8.40×10^{10}	4.38×10^{7}	1.31×10^{-14}	3.92×10^{-14}
298	1.61×10^{-22}	1.00×10^{11}	9.19×10^{7}	1.48×10^{-14}	4.39×10^{-14}
300	1.51×10^{-22}	1.10×10^{11}	9.92×10^{7}	1.49×10^{-14}	4.48×10^{-14}
320	8.26×10^{-23}	1.30×10^{11}	2.03×10^{8}	1.68×10^{-14}	5.03×10^{-14}
340	4.86×10^{-23}	1.60×10^{11}	3.84×10^{8}	1.87×10^{-14}	5.59×10^{-14}
360	3.03×10^{-23}	1.90×10^{11}	6.76×10^{8}	2.05×10^{-14}	6.13×10^{-14}
380	1.99×10^{-23}	2.20×10^{11}	1.12×10^{9}	2.24×10^{-14}	6.67×10^{-14}
400	1.36×10^{-23}	2.60×10^{11}	1.77×10^{9}	2.41×10^{-14}	7.18×10^{-14}

Table S29: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), reverse reaction rate coefficient (k_r), forward reaction rate coefficient (k_f) and total rate coefficients (*Total* k_{8a}) for the reaction pathway **R8a** in the temperature range 200-400 K at the M06-2X level.

R8a					
***Temperature* (K)**	K_{eq} (cm^3 $molecule^{-1}$)	k_{uni} (s^{-1})	k_r (VTST) (s^{-1})	k_f (s^{-1})	*Total* k_{8a} (cm^3 $molecule^{-1}$ s^{-1})
200	2.73×10^{-21}	1.90×10^{8}	2.22×10^{8}	6.07×10^{-13}	5.60×10^{-13}
220	8.67×10^{-22}	4.70×10^{8}	5.88×10^{8}	5.10×10^{-13}	4.53×10^{-13}
240	3.33×10^{-22}	1.00×10^{9}	1.33×10^{9}	4.41×10^{-13}	3.79×10^{-13}
260	1.48×10^{-22}	1.90×10^{9}	2.64×10^{9}	3.91×10^{-13}	3.27×10^{-13}
280	7.39×10^{-23}	3.40×10^{9}	4.76×10^{9}	3.52×10^{-13}	2.93×10^{-13}
298	4.28×10^{-23}	5.30×10^{9}	7.58×10^{9}	3.24×10^{-13}	2.67×10^{-13}
300	4.04×10^{-23}	5.50×10^{9}	7.96×10^{9}	3.22×10^{-13}	2.63×10^{-13}
320	2.38×10^{-23}	8.50×10^{9}	1.24×10^{10}	2.96×10^{-13}	2.41×10^{-13}
340	1.50×10^{-23}	1.30×10^{10}	1.85×10^{10}	2.76×10^{-13}	2.28×10^{-13}
360	9.88×10^{-24}	1.80×10^{10}	2.62×10^{10}	2.59×10^{-13}	2.11×10^{-13}
380	6.81×10^{-24}	2.40×10^{10}	3.60×10^{10}	2.45×10^{-13}	1.96×10^{-13}
400	4.87×10^{-24}	3.20×10^{10}	4.74×10^{10}	2.31×10^{-13}	1.86×10^{-13}

Table S30: Calculated equilibrium constant (K_{eq}), unimolecular rate coefficient (k_{uni}), reverse reaction rate coefficient (k_r), forward reaction rate coefficient (k_f) and total rate coefficients (***Total*** k_{8c}) for the reaction pathway **R8c** in the temperature range 200-400 K at the M06-2X level.

R8c					
***Temperature* (K)**	K_{eq} (cm^3 $molecule^{-1}$)	k_{uni} (s^{-1})	k_r (VTST) (s^{-1})	k_f (s^{-1})	***Total*** k_{8c} (cm^3 $molecule^{-1}$ s^{-1})
200	2.21×10^{-22}	4.80×10^{10}	2.98×10^{9}	6.60×10^{-13}	1.86×10^{-12}
220	8.84×10^{-23}	7.30×10^{10}	6.53×10^{9}	5.77×10^{-13}	1.59×10^{-12}
240	4.11×10^{-23}	1.10×10^{11}	1.26×10^{10}	5.18×10^{-13}	1.40×10^{-12}
260	2.15×10^{-23}	1.50×10^{11}	2.21×10^{10}	4.75×10^{-13}	1.24×10^{-12}
280	1.23×10^{-23}	1.90×10^{11}	3.59×10^{10}	4.42×10^{-13}	1.12×10^{-12}
298	7.95×10^{-24}	2.40×10^{11}	5.27×10^{10}	4.19×10^{-13}	1.03×10^{-12}
300	7.60×10^{-24}	2.50×10^{11}	5.48×10^{10}	4.17×10^{-13}	1.03×10^{-12}
320	4.98×10^{-24}	3.10×10^{11}	7.95×10^{10}	3.96×10^{-13}	9.45×10^{-13}
340	3.43×10^{-24}	3.90×10^{11}	1.11×10^{11}	3.79×10^{-13}	8.86×10^{-13}
360	2.46×10^{-24}	4.70×10^{11}	1.49×10^{11}	3.65×10^{-13}	8.32×10^{-13}
380	1.82×10^{-24}	5.60×10^{11}	1.94×10^{11}	3.53×10^{-13}	7.88×10^{-13}
400	1.39×10^{-24}	6.60×10^{11}	2.47×10^{11}	3.43×10^{-13}	7.50×10^{-13}

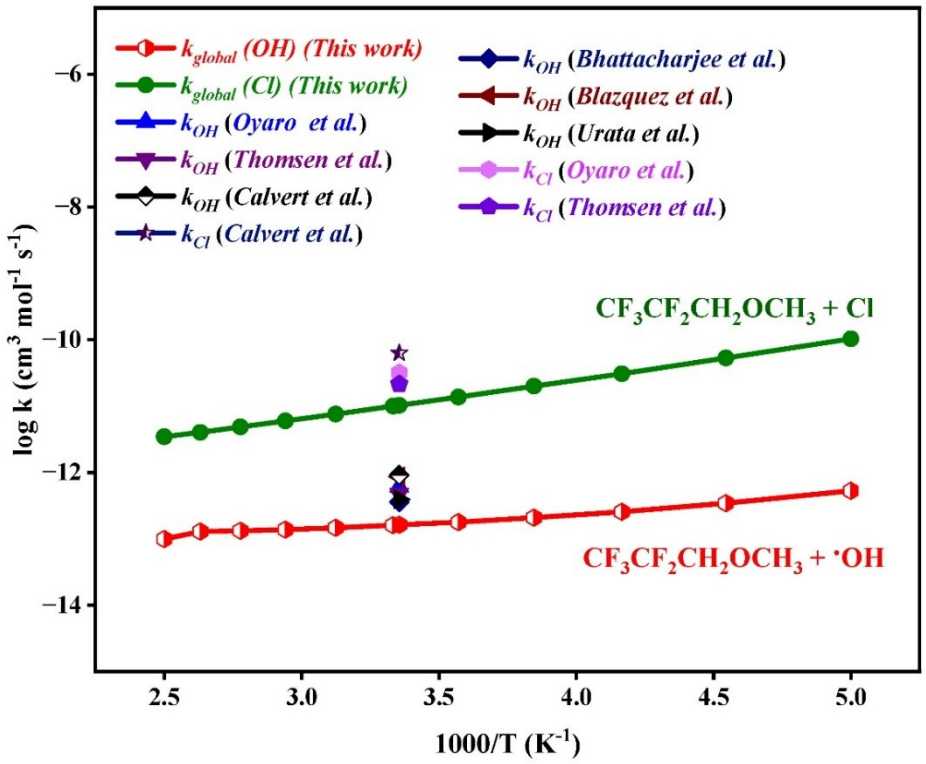


Figure S6: Comparison of the previously reported rate coefficients (cm^3 $molecule^{-1}$ s^{-1} from the works of Oyaro *et al.*[1], Thomsen *et al.*[2], Urata *et al.*[3], Blazquez *et al.*[4], Calvert *et al.*[5], and Bhattacharjee *et al.*[6] for the reaction of HFE-365mcf3 with •OH and Cl atoms obtained at the M06-2X level in the 200–400 K temperature range, with the computed rate coefficients as a function of 1000/T (K^{-1}).

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Notes S4: Radiative efficiency (RE) calculations

Frequencies and their Intensities

The radiative efficiency (RE) was calculated using the vibrational frequencies in the atmospheric window of 600-1600 cm^{-1} with respect to their corresponding intensities. The reactant is more effective if it absorbs in this range [1,2,3]. Studies have revealed that even if this compound absorbs at another wavelength with strong absorption, the additional absorption will not contribute significantly to radiative forcing. All the frequencies are in cm^{-1}.

Table S31: Frequencies and intensities of HFE-365mcf3 calculated at the M06-2X/6-311++G(d,p) level of theory.

Frequencies	*Adjusted*	*Intensity*	*(σ) Intensity × 1.66 × 10^{-19}*	*(Total) Adjusted × σ*
57.66	9.34×10^{-3}	0.122	2.025×10^{-20}	1.892×10^{-22}
87.36	2.29×10^{-2}	1.244	2.065×10^{-19}	4.729×10^{-21}
124.56	1.41×10^{-1}	4.066	6.750×10^{-19}	9.517×10^{-20}
180.38	2.78×10^{-1}	0.948	1.574×10^{-19}	4.375×10^{-20}
221.08	8.47×10^{-2}	1.443	2.395×10^{-19}	2.029×10^{-20}
233.03	3.96×10^{-1}	1.148	1.906×10^{-19}	7.546×10^{-20}
275.63	4.31×10^{-1}	11.422	1.896×10^{-18}	8.172×10^{-19}
303.8	2.89×10^{-1}	0.512	8.499×10^{-20}	2.456×10^{-20}
353.79	7.39×10^{-1}	1.413	2.346×10^{-19}	1.733×10^{-19}
391.7	1.29	2.139	3.551×10^{-19}	4.580×10^{-19}
434.23	1.51	2.474	4.107×10^{-19}	6.201×10^{-19}
478.31	1.98	5.934	9.850×10^{-19}	1.950×10^{-18}
534.87	2.29	13.069	2.169×10^{-18}	4.968×10^{-18}
598.78	1.17	2.185	3.627×10^{-19}	4.244×10^{-19}
629.14	4.35×10^{-1}	41.275	6.852×10^{-18}	2.980×10^{-18}
671.53	4.81×10^{-3}	17.467	2.900×10^{-18}	1.395×10^{-20}
793.23	2.77	3.711	6.160×10^{-19}	1.706×10^{-18}
953.2	2.82	2.988	4.960×10^{-19}	1.399×10^{-18}
998.11	2.36	60.170	9.988×10^{-18}	2.357×10^{-17}
1125.22	2.20	112.303	1.864×10^{-17}	4.101×10^{-17}
1178	1.75	137.600	2.284×10^{-17}	3.997×10^{-17}
1188.6	1.69	14.525	2.411×10^{-18}	4.075×10^{-18}
1227.34	1.62	27.208	4.517×10^{-18}	7.317×10^{-18}
1240.55	1.20	195.608	3.247×10^{-17}	3.897×10^{-17}
1259.54	3.79×10^{-1}	161.594	2.682×10^{-17}	1.017×10^{-17}
1272.44	3.59×10^{-1}	261.476	4.341×10^{-17}	1.558×10^{-17}
1284.18	5.53×10^{-1}	151.220	2.510×10^{-17}	1.388×10^{-17}
1330.78	6.45×10^{-1}	106.991	1.776×10^{-17}	1.146×10^{-17}
1409.8	2.51×10^{-1}	19.951	3.312×10^{-18}	8.313×10^{-19}
1451.43	1.18×10^{-1}	11.236	1.865×10^{-18}	2.201×10^{-19}

1480.39	1.07×10^{-1}	5.129	8.514×10^{-19}	9.110×10^{-20}
1493.58	8.81×10^{-2}	13.996	2.323×10^{-18}	2.047×10^{-19}
1506.03	1.57×10^{-2}	4.410	7.321×10^{-19}	1.149×10^{-20}
1521.69	1.51×10^{-2}	11.192	1.858×10^{-18}	2.805×10^{-20}

Total $= 2.232 \times 10^{-16} \times 10^{-3} \times 10^{18}$

$= 0.2232$ Wm^{-2} ppb^{-1}

$f = 0.277564$

Corrected RE $= 0.2232 \times f = 0.061896$ Wm^{-2} ppb^{-1}

Again, 10% temperature adjustment $= (0.0618 + 0.00618)$ Wm^{-2} ppb^{-1}

$= 0.068$ Wm^{-2} ppb^{-1}

The $AGWP_{CO2}$ (H) values for THs 20 and 100 years are 2.434×10^{-14} and 8.947×10^{-14} W m^{-2} year kg^{-1}, respectively [1].

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Table S32: Corrected zero-point energies (EE+ZPE), enthalpies (H), and Gibbs free energies (G) of the species involved in the loss processes of product radical P1A, in the presence and absence of O_2. Energies are in Hartree and all the calculations are in M06-2X/6-311++G(d,p) level of theory.

P1A						
Pathways	***Species***	***EE+ZPE***	***H***	***G***	***ΔH***	***ΔG***
	P1a	-729.0915	-729.0802	-729.1290		
	AIM1a	-1189.3474	-1189.3355	-1189.3853	-78.4400	-67.7546
	AIM2a	-879.4398	-879.4270	-879.4795	-28.5622	-16.3249
	AIM3a	-1084.5151	-1084.4999	-1084.5584	-22.1176	-8.4552
	AIM4a	-804.2930	-804.2813	-804.3308	-12.3960	-13.3298
C-C	**AIM4a-TS1**	-804.2832	-804.2715	-804.3213	***6.1326***	
	AIM4a-PC1	-804.3057	-804.2923	-804.3480		
	AIM5a	-575.3237	-575.3167	-575.3553	-3.6409	-17.0058
	AIM6a	-228.9759	-228.9705	-229.0025		
C-H	**AIM4a-TS2**	-804.2697	-804.2580	-804.3072	14.5949	
	AIM4a-PC2	-804.2836	-804.2709	-804.3224		
	AIM7a	-803.7874	-803.7759	-803.8251	6.0499	-2.0325
C-O	**AIM4a-TS3**	-804.2578	-804.2461	-804.2954	***22.0636***	
	AIM4a-PC3	-804.2766	-804.2631	-804.3179		
	AIM8a	-689.2749	-689.2658	-689.3088	16.5019	3.6622
	AIM9a	-114.9932	-114.9893	-115.0161		
	O_2 (Triplet)	-150.3046	-150.3013	-150.3245		
	Cl	-460.1327	-460.1303	-460.1483		
	NO	-129.8755	-129.8722	-129.8955		
	NO_2	-205.0415	-205.0376	-205.0655		
	H	-0.4982	-0.4958	-0.5088		

*Values in both **Bold** and *Italics* are the Barrier heights.

Table S33: Corrected zero-point energies (EE+ZPE), enthalpies (H), and Gibbs free energies (G) of the species involved in the loss processes of product radical AIM5, in the presence and absence of O_2. Energies are in Hartree and all the calculations are in M06-2X/6-311++G(d,p) level of theory.

AIM5						
Pathways	***Species***	***EE+ZPE***	***H***	***G***	***ΔH***	***ΔG***
	AIM5a	-575.3237	-575.3167	-575.3553		
	SIM1	-725.6825	-725.6737	-725.7167	-34.9842	-23.0990
NO_2 addition	**SIM2**	-930.7627	-930.7514	-930.8007	-25.1341	-11.6850
NO addition NO_2 removal	**SIM3**	-650.5349	-650.5271	-650.5673	-11.8212	-12.9049
C-F	**SIM3-TS1**	-650.4839	-650.4759	-650.5168	***31.9747***	
	SIM4	-550.7676	-550.7607	-550.7986	26.9752	17.6151
	F	-99.7258	-99.7234	-99.7406		
C-C	**SIM3-TS2**	-650.5211	-650.5142	-650.5523	***8.6416***	
	SIM5	-337.5447	-337.5404	-337.5714	-3.1156	-16.2358
	CF2O	-312.9960	-312.9917	-313.0217		
	O_2 (Triplet)	-150.3046	-150.3013	-150.3245		
	Cl	-460.1327	-460.1303	-460.1483		
	NO	-129.8755	-129.8722	-129.8955		
	NO_2	-205.0415	-205.0376	-205.0655		
	H	-0.4982	-0.4958	-0.5088		

*Values in both **Bold** and *Italics* are the Barrier heights.

Table S34: Corrected zero-point energies (EE+ZPE), enthalpies (H), and Gibbs free energies (G) of the species involved in the loss processes of product radical P1B, in the presence and absence of O_2. Energies are in Hartree and all the calculations are in M06-2X/6-311++G(d,p) level of theory.

P1B						
Pathways	***Species***	***EE+ZPE***	***H***	***G***	***ΔH***	***ΔG***
	P1c	-729.0871	-729.0762	-729.1237		
	AIM1b	-1189.3506	-1189.3391	-1189.3889	-83.1640	-73.3464
	AIM2b	-879.4438	-879.4314	-879.4847	-33.8315	-22.9032
	NO_2	-205.0415	-205.0376	-205.0655		
	AIM3b	-1084.5259	-1084.5112	-1084.5693	-26.4887	-12.0195
	NO	-129.8755	-129.8722	-129.8955		
	AIM4b	-804.3007	-804.2894	-804.3385	-14.7015	-14.9168
C-H	**AIM4b-TS1**	-804.2752	-804.2636	-804.3138	***16.0074***	
	AIM5b	-803.7933	-803.7822	-803.8311	7.1418	-0.8861
	H	-0.4982	-0.4958	-0.5088		
O2	**O_2 (Triplet)**	-150.3046	-150.3013	-150.3245		
	AIM4b-TS2	-954.5929	-954.5788	-954.6367	***7.7574***	
	AIM6b	-803.7933	-803.7822	-803.8311	-40.0000	-41.5318
	HOO	-150.8760	-150.8722	-150.8981		
	Cl	-460.1327	-460.1303	-460.1483		

*Values in both **Bold** and *Italics* are the Barrier heights.

Table S35: Rotational constants of the species involved in the reaction pathways **R1-R8** at the M06-2X/6-311++G(d,p) level of theory.

R1			
Species	***Rotational constants (GHz)***		
A1	1.8426	1.1605	1.0175
OH	564.2914	-	-
CR1a	1.43881	0.8475	0.70337
TS1a	1.49140	0.87335	0.72017
PC1a	1.49657	0.79526	0.67741
P1a	1.90351	1.1286	1.0178
CR1b	1.4394	0.8820	0.7028
TS1b	1.3296	0.8311	0.7782
PC1b	1.3732	0.8786	0.6901
P1b	1.9807	0.9969	0.8871
CR1c	1.6726	0.6517	0.6236
TS1c	1.7590	0.6829	0.6201
PC1c	1.6895	0.6648	0.6154
P1c	1.8680	1.1785	1.0282
H_2O	829.6254	432.6793	284.3702

R2			
Species	***Rotational constants (GHz)***		
A2	1.9109	1.0395	0.9023
OH	564.2914	-	-
CR2a	1.4381	0.88155	0.70218
TS2a	1.3295	0.83109	0.77817
PC2a	1.3734	0.87846	0.69004
P2a	1.9806	0.99692	0.88705
CR2b	1.5570	0.7890	0.6815
TS2b	1.5570	0.7589	0.6815
PC2b	1.5432	0.7414	0.6386
P2b	1.9560	1.0143	0.8893
CR2c	1.5361	0.6447	0.5907
TS2c	1.7469	0.6348	0.5655
PC2c	1.5343	0.7567	0.6526
P2c	1.9114	1.0796	0.9325
H2O	829.6254	432.6793	284.3702

R3			
Species	***Rotational constants (GHz)***		
A3	2.4101	0.8951	0.8724
OH	564.2914	-	-
CR3a	1.69179	0.67739	0.63295
TS3a	1.53648	0.76530	0.66946
PC3a	1.53754	0.70417	0.64142
P3a	2.2817	0.86015	0.80724
CR3b	1.4705	0.8260	0.6825
TS3b	1.5098	0.8354	0.7093
PC3b	1.4625	0.7899	0.6760
P3b	2.4115	0.9288	0.8862
CR3c	1.8277	0.6537	0.6007
TS3c	1.7529	0.7046	0.6253
PC3c	1.4408	0.8340	0.6777
P3c	2.4152	0.9028	0.8940
H_2O	829.6254	432.6793	284.3702

R4			
Species	***Rotational constants (GHz)***		
A4	2.3390	0.8434	0.8026
OH	564.2914	-	-
CR4a	1.6905	0.6780	0.6333
TS4a	1.5361	0.7653	0.6694
PC4a	1.5389	0.7023	0.6403
P4a	2.2813	0.8603	0.8073
CR4c	1.6896	0.6783	0.6336
TS4c	1.6793	0.6310	0.5783
PC4c	1.5637	0.7152	0.6398
P4c	2.3799	0.8664	0.8248
H_2O	829.6254	432.6793	284.3702

R5			
Species	***Rotational constants (GHz)***		
A1	1.8426	1.1605	1.0175
Cl	0.0000	-	-
CR5a	1.2891	0.6080	0.5132
TS5a	1.4362	0.6136	0.5280
PC5a	1.4957	0.5108	0.4554
P5a	1.9034	1.1286	1.0178
CR5b	1.2491	0.7216	0.5632
TS5b	1.1225	0.6760	0.5877
PC5b	1.1268	0.6061	0.5139
P5b	1.9547	1.0154	0.8897
CR5c	1.5389	0.5063	0.4988
TS5c	1.7974	0.4391	0.4139
PC5c	1.6949	0.4239	0.4034
P5c	1.8685	1.1780	1.0279
HCl	314.1814	-	-

R6			
Species	***Rotational constants (GHz)***		
A2	1.9109	1.0395	0.9023
Cl	-	-	-
CR6a	1.2492	0.7223	0.5636
TS6a	1.1208	0.6771	0.5882
PC6a	1.1202	0.6070	0.5141
P6a	1.9806	0.9970	0.8871
CR6b†	1.2862	0.5969	0.5605
TS6b†	1.3414	0.5910	0.4875
PC6b†	1.1552	0.5760	0.4895
P6b†	1.9722	0.9915	0.8841
CR6c	1.3646	0.6020	0.5631
TS6c	1.7325	0.4284	0.3950
PC6c	1.5586	0.4566	0.4128
P6c	1.9117	1.0799	0.9325
HCl	314.1814	-	-

†: Calculations at MP2/6-311++G(d,p) level of theory.

R7			
Species	***Rotational constants (GHz)***		
A3	2.4101	0.8951	0.8724
CR7a	1.5014	0.5349	0.4852
TS7a	1.1349	0.6849	0.5252
PC7a	1.2011	0.5837	0.4919
P7a	2.2811	0.8602	0.8073
CR7b	1.0432	0.7408	0.5323
TS7b	1.1273	0.6949	0.5324
PC7b	1.0789	0.6841	0.5194
P7b	2.4114	0.9288	0.8862
CR7c	1.6169	0.4774	0.4300
TS7c	1.5346	0.4474	0.4029
PC7c	1.4068	0.4537	0.3997
P7c	2.3919	0.9012	0.8913
HCl	314.1814	-	-

R8			
Species	***Rotational constants (GHz)***		
A4	2.3390	0.8434	0.8026
Cl	-	-	-
CR8a	1.5006	0.5354	0.4855
TS8a	1.1367	0.6832	0.5250
PC8a	1.2103	0.5753	0.4876
P8a	2.2816	0.8602	0.8072
CR8c	1.5005	0.5353	0.4854
TS8c	1.4939	0.4394	0.3957
PC8c	1.2903	0.5086	0.4393
P8c	2.3795	0.8665	0.8247
HCl	314.1814	-	-

Degradation products (P1)			
Species	***Rotational constants (GHz)***		
AIM1a	1.4106	0.7685	0.6149
AIM2a	1.4507	0.7302	0.6118
AIM3a	1.0484	0.3930	0.3406
AIM4a	1.6071	0.9507	0.7739
AIM4a-TS1	1.5929	0.9579	0.8091
AIM4a-PC1	1.4728	0.7840	0.7055
AIM5a	3.7742	2.4239	1.9899
AIM6a	20.2452	6.9719	5.3609
AIM4a-TS2	1.6459	0.9255	0.7687
AIM4a-PC2	1.6814	0.8582	0.8077
AIM7a	1.6802	0.9023	0.8062
AIM4a-TS3	1.5311	1.0277	0.8369
AIM4a-PC3	1.4063	0.9433	0.7368
AIM8a	2.2924	1.4630	1.3277
AIM9a	157.6658	27.9715	27.7941
O_2 (Triplet)	44.7098	-	-

Degradation products (AIM5a)			
Species	***Rotational constants (GHz)***		
SIM1	2.6264	1.3602	1.3074
SIM2	1.9913	0.6024	0.5644
SIM3	2.8811	1.9085	1.8931
SIM3-TS1	2.7717	1.8627	1.7309
SIM4	3.8595	2.5001	2.0676
SIM3-TS2	2.9031	1.7403	1.7280
SIM5	10.9370	10.9355	5.6621
CF2O	11.8638	11.8427	5.9266
NO	52.2319		
NO2	252.1291	13.2818	12.6171

Degradation products (P1b)			
Species	***Rotational constants (GHz)***		
AIM1b	1.7906	0.5570	0.5197
AIM2b	1.7982	0.5431	0.5098
AIM3b	1.2398	0.3008	0.2935
AIM4b	1.8082	0.8187	0.7446
AIM4b-TS1	1.9181	0.7694	0.7049
AIM5b	1.9460	0.7860	0.7182
AIM4b-TS2	1.6323	0.3830	0.3725
AIM6b	1.9493	0.7850	0.7177
HOO	631.7962	34.7076	32.9002