Atmospheric Chemistry of CF_3O_2: A Theoretical Study on Mechanism and Pathways of the CF_3O_2 + IO Reaction

Supporting information

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Table S1. The Zero-point energy correction (ZPE), relative energies (ΔE) and reaction enthalpies (ΔH) (in kJ/mol) of various species at the different methods and basis sets for I atom in the CF_3O_2 + IO reaction on the singlet and triplet potential energy surfaces.

Species	CCSD(T) ΔE				B3LYP		ZPE
	LANL2DZ	CEP[a]	SDD	ADZ[b]	ΔE	ΔH	
CF_3O_2+IO	0.0	0.0	0.0	0.0	0.0	0.0	55.6
$CF_3OOI+O(^3P)$	68.8				106.7	108.2	55.1
$CF_3OIO+O(^3P)$	68.1				160.7	163.9	51.1
$CF_3OI+O_2(^3\sum)$	-249.4				-237.6	-236.7	56.6
$CF_3OI+O_2(^1\Delta)$	-121.0				-76.3	-75.4	56.6
$CF_3IO+O_2(^1\Delta)$	165.4				243.6	247.2	49.3
CF_3O+OIO	37.5				115.7	116.2	49.9
CF_2O+FOOI	-3.9				-34.6	-33.9	55.0
CF_2O+FOIO	49.8				94.4	96.4	51.3
CF_2O+FIO_2	-132.8				11.6	12.8	52.1
IM1	-93.4	-97.4	-100.0	-89.7	-86.5	-87.9	62.3
IM2	-56.9	-54.3	-50.0	-61.6	11.2	10.9	60.1
IM2a	-58.0				10.3	10.0	59.9
IM2b	-40.0				21.2	21.3	59.8
IM3	-143.9	-124.5	-107.4	-143.9	18.3	18.8	57.8
IM4	176.1				394.2	395.6	54.4
TS1	9.5	10.9	12.4	12.6	68.2	65.9	59.7

TS2	0.1	131.4	130.6	55.3
TS3	302.6	482.8	483.5	51.7
TS4	91.0	62.5	62.2	55.9
TS5	139.5	84.7	84.9	55.4
TS6	220.3	234.7	234.2	55.1
TS7	125.1	239.1	240.1	50.3
TS8	20.4	147.9	148.2	52.2
TS9	192.2	201.1	199.8	57.0
TS10	42.0	176.4	176.9	52.6
TS11	96.4	262.9	263.7	54.7
^{3}TS1	244.1	154.5	156.2	52.7
^{3}TS2	61.5	101.4	101.9	21.5
^{3}TS3	170.3	181.1	181.5	51.9
^{3}TS4	161.8	171.1	173.2	49.4

[a]: the basis set of CEP is CEP-121G.

[b]: the basis set of CEP is aug-cc-pVDZ-PP.

Table S2. The Zero-point energy correction (ZPE), relative energies (ΔE) and reaction enthalpies (ΔH) (in kJ/mol) of various species at the different methods for the FIO_2 potential energy surface.

Species	CCSD(T)	B3LYP		ZPE
	ΔE	ΔE	ΔE	
FIO_2	0.0	0.0	0.0	15.6
FOIO	182.6	82.8	83.6	14.8
FOOI	128.9	-46.1	-46.8	18.6
TSa	204.3	184.7	184.2	12.3
FO+IO	258.2	101.1	103.6	10.0
F+OIO	253.8	191.4	194.3	9.2

Table S3. The excitation energy T_V (in eV), oscillator strength f (in atomic units) and wavelength λ (in nm) of the first ten excited states of CF_3OOOI, CF_3OOIO and CF_3OIO_2.

Excited states	CF_3OOOI			CF_3OOIO			CF_3OIO_2		
	T_V	f	λ	T_V	f	λ	T_V	f	λ
1	2.30	0.0001	538.85	1.45	0.000	852.21	3.11	0.0058	398.97
2	2.71	0.0003	457.37	3.28	0.0002	378.56	3.18	0.0003	390.24
3	4.28	0.0954	289.57	3.44	0.0162	360.08	3.87	0.0058	320.34
4	4.49	0.0373	276.22	3.91	0.1031	316.98	4.09	0.0023	302.8
5	4.67	0.0227	265.56	4.51	0.0213	275.03	4.77	0.0603	259.86
6	4.94	0.0024	251.13	4.73	0.0005	262.06	4.94	0.0607	250.96
7	4.95	0.0013	250.32	4.95	0.0293	250.49	5.05	0.0039	245.45
8	5.33	0.2034	232.83	5.74	0.0025	216.13	5.10	0.0023	243.04
9	6.11	0.0004	202.95	5.89	0.0158	210.41	5.37	0.0374	230.74
10	6.86	0.0259	180.74	6.25	0.0364	198.45	5.52	0.0019	224.54