Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Theoretical investigation of dissociation chemistry of formyl halides in gas phase

Supporting Information

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Description of Unimolecular Reaction Pathways

Detailed descriptions of the various unimolecular dissociation pathways of formyl halides HXCO (X = F, Cl, Br, and I) are given below. ΔE_1, ΔE_2, etc. are electronic energies (without zero point corrections) computed using B3LYP/6-31G* level of electronic structure theory with LANL2DZ effective core potentials for the halogen atoms. See TABLE I and FIG.2 in main text.

1. Path (1)

   $\mathrm{HXCO} \xrightarrow{\Delta E_2} \mathrm{H + XCO}$

   - ΔE_2 is the electronic energy of $\mathrm{H + XCO}$ relative to HXCO.

2. Path (2)

   $\mathrm{HXCO} \xrightarrow{\Delta E_1} \mathrm{X + HCO}$

   - ΔE_1 is the electronic energy of $\mathrm{X + HCO}$ relative to HXCO.

3. Path (3)

   $\mathrm{HXCO} \xrightarrow{\Delta E_3} \mathrm{TS-1} \xrightarrow{\Delta E_4} \mathrm{HX + CO}$

   - ΔE_3 is the electronic energy of $\mathrm{TS-1}$ relative to HXCO.
   - ΔE_4 is the electronic energy of $\mathrm{HX + CO}$ relative to HXCO.

4. Path (4)

   $\mathrm{HXCO} \xrightarrow{\Delta E_{10}} \mathrm{TS-3\,A} \xrightarrow{\Delta E_{11}} \mathrm{INT-3\,T(trans-HCOX)} \xrightarrow{\Delta E_{12}} \mathrm{TS-3\,B} \xrightarrow{\Delta E_{13}}$
   $\mathrm{INT-3\,C(cis-HCOX)} \xrightarrow{\Delta E_{14}} \mathrm{TS-3\,C} \xrightarrow{\Delta E_4} \mathrm{HX + CO}$

   - ΔE_{10} is the electronic energy of $\mathrm{TS-3\,A}$ relative to HXCO. $\mathrm{TS-3\,A}$ is the transition state connecting HXCO with trans-HCOX following 1,2-X shift.
   - ΔE_{11} is the electronic energy of $\mathrm{INT-3\,T}$ relative to HXCO. $\mathrm{INT-3\,T}$ represents trans-HCOX.

- ΔE_{12} is the electronic energy of TS−3 B relative to HXCO. TS−3 B is the transition state connecting trans-HCOX with cis-HCOX.
- ΔE_{13} is the electronic energy of INT−3 C relative to HXCO. INT−3 C represents cis-HCOX.
- ΔE_{14} is the electronic energy of TS−3 C relative to HXCO. TS−3 C is the transition state connecting cis-HCOX with HX + CO.
- ΔE_4 is the electronic energy of HX + CO relative to HXCO.

5. Path (5)

   $\mathrm{HXCO} \xrightarrow{\Delta E_5} \mathrm{TS-2\,A} \xrightarrow{\Delta E_6} \mathrm{INT-2\,T(trans-HOCX)} \xrightarrow{\Delta E_7} \mathrm{TS-2\,B} \xrightarrow{\Delta E_8}$
   $\mathrm{INT-2\,C(cis-HOCX)} \xrightarrow{\Delta E_9} \mathrm{TS-2\,C} \xrightarrow{\Delta E_4} \mathrm{HX + CO}$

   - ΔE_5 is the electronic energy of TS−2 A relative to HXCO. TS−2 A is the transition state connecting HXCO with trans-HOCX following 1,2-H shift.
   - ΔE_6 is the electronic energy of INT−2 T relative to HXCO. INT−2 T represents trans-HOCX.
   - ΔE_7 is the electronic energy of TS−2 B relative to HXCO. TS−2 B is the transition state connecting trans-HOCX with cis-HOCX.
   - ΔE_8 is the electronic energy of INT−2 C relative to HXCO. INT−2 C represents cis-HOCX.
   - ΔE_9 is the electronic energy of TS−2 C relative to HXCO. TS−2 C is the transition state connecting cis-HOCX with HX + CO.
   - ΔE_4 is the electronic energy of HX + CO relative to HXCO.

Potential energy profile - HFCO

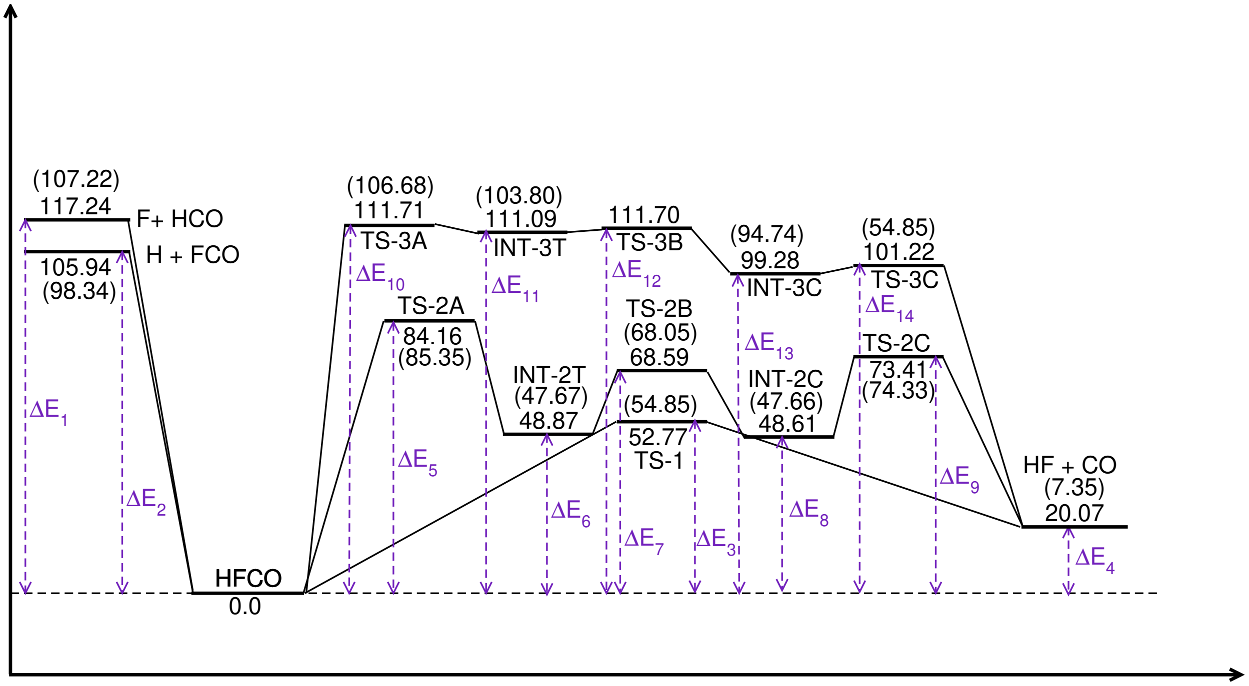

Figure 1: Dissociation energy profile of HFCO computed using B3LYP/6-31G*/ECP level of theory. The given energies are in units of kcal/mol and without zero point energy corrections. The numbers in bracket are CCSD(T)/6-31G*/ECP single point energies computed using MP2/6-31G*/ECP optimized geometries.

Potential energy profile - HClCO

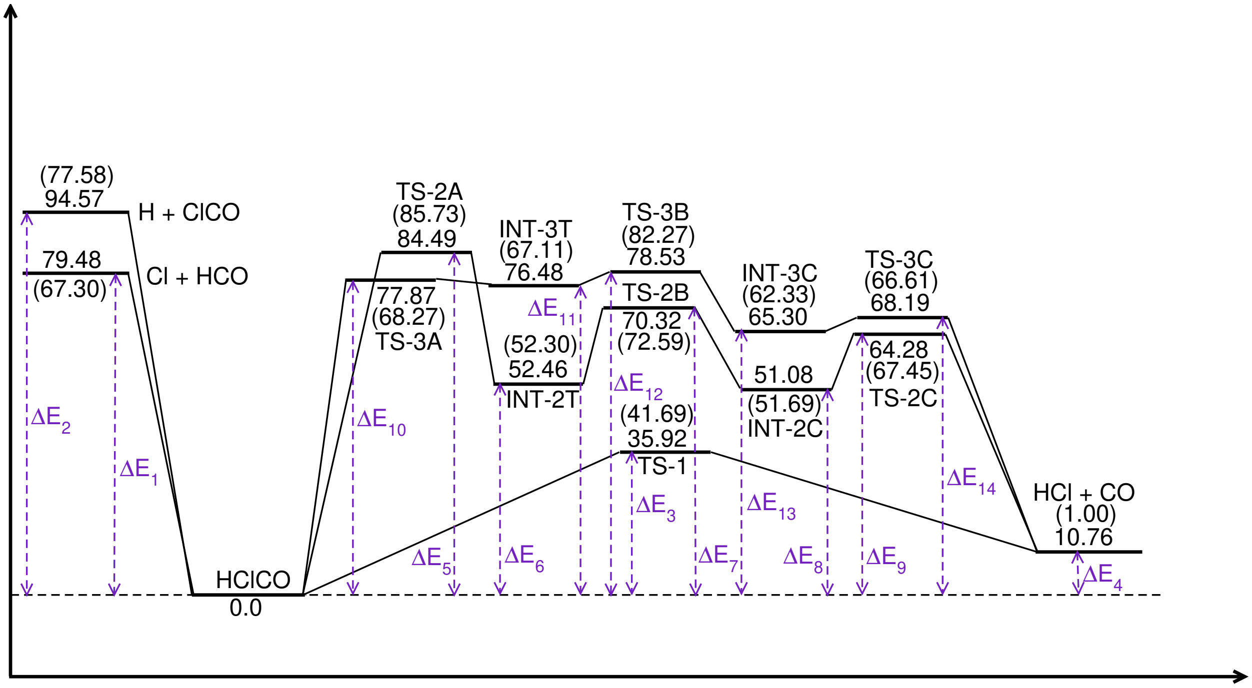

Figure 2: Dissociation energy profile of HClCO computed using B3LYP/6-31G*/ECP level of theory. The given energies are in units of kcal/mol and without zero point energy corrections. The numbers in bracket are CCSD(T)/6-31G*/ECP single point energies computed using MP2/6-31G*/ECP optimized geometries.

Potential energy profile - HBrCO

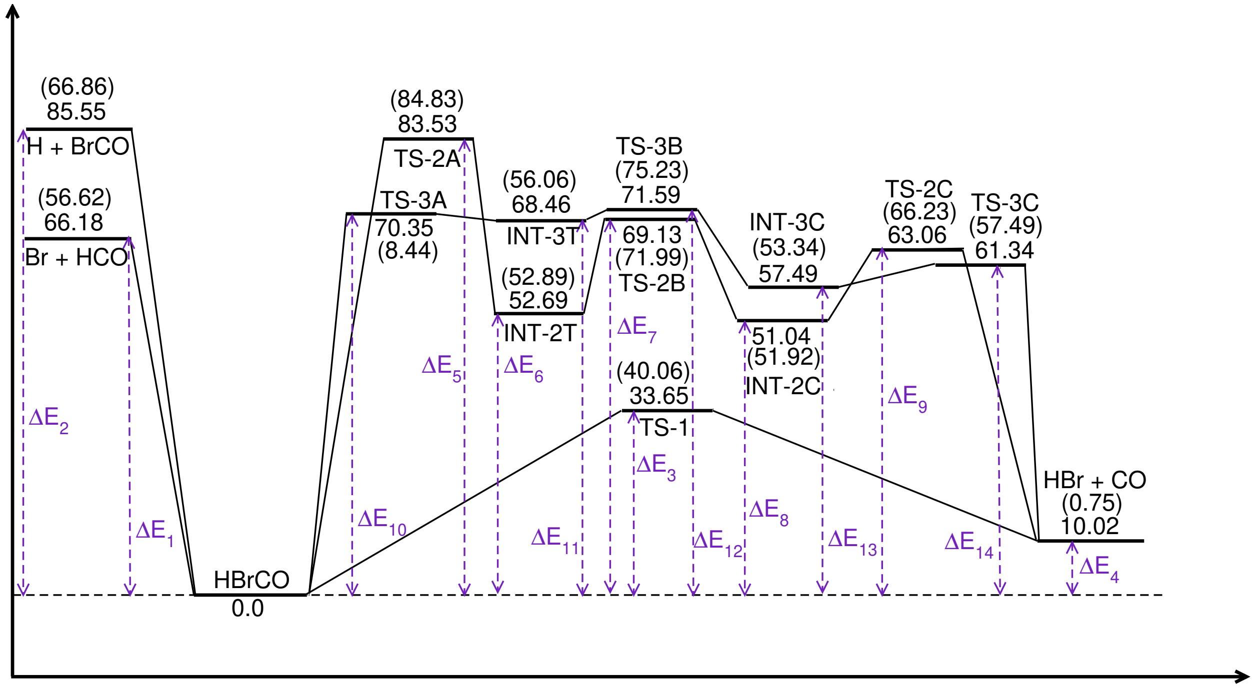

Figure 3: Dissociation energy profile of HBrCO computed using B3LYP/6-31G*/ECP level of theory. The given energies are in units of kcal/mol and without zero point energy corrections. The numbers in bracket are CCSD(T)/6-31G*/ECP single point energies computed using MP2/6-31G*/ECP optimized geometries.

Potential energy profile - HICO

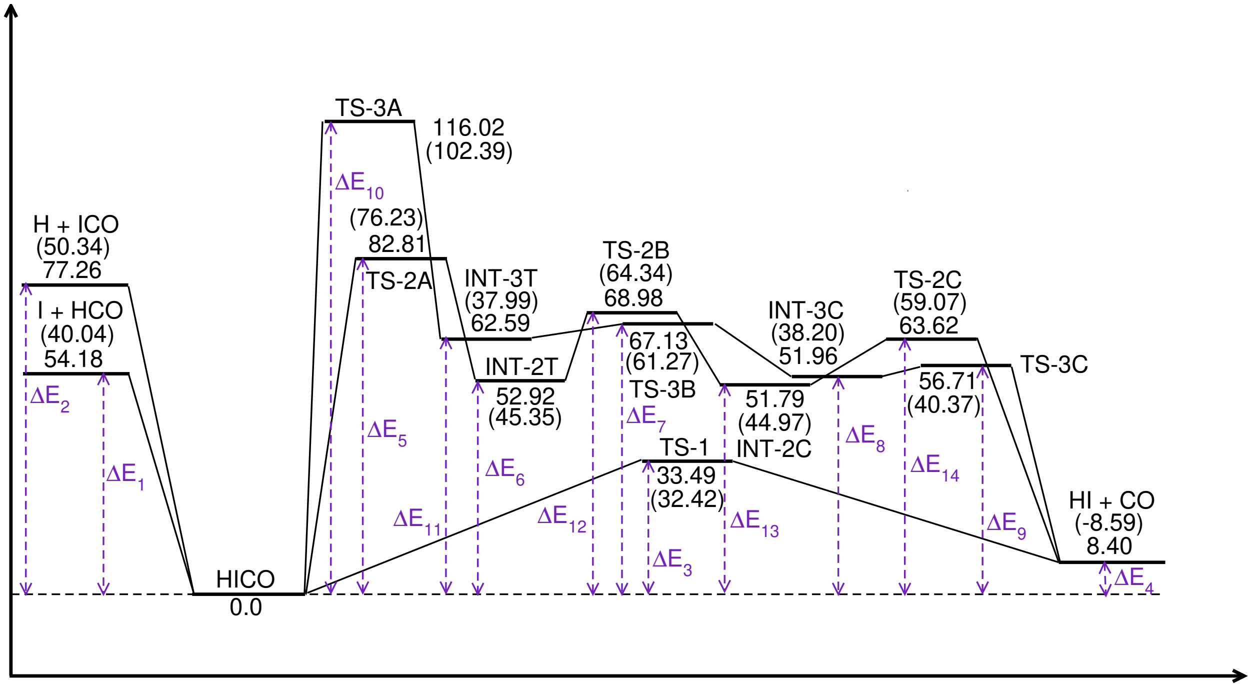

Figure 4: Dissociation energy profile of HICO computed using B3LYP/6-31G*/ECP level of theory. The given energies are in units of kcal/mol and without zero point energy corrections. The numbers in bracket are CCSD(T)/6-31G*/ECP single point energies computed using MP2/6-31G*/ECP optimized geometries.

Table 1: Comparison of stationary point energies of HFCO dissociation with existing work. The numbers given are in units of kcal/mol and relative to the reactant HFCO energy.

Theory	HFCO	HF+CO	INT-2T	INT-2C	INT-3T	INT-3C	F + HCO	H + FCO	Ref.
B3LYP/6-31G* (ECP)	0.0	20.07	48.87	48.61	111.09	99.28	117.24	105.94	p
MP2/6-31G* (ECP)	0.0	8.21	52.35	52.62	107.60	96.49	112.44	98.51	p
CCSD(T)/6-31G* (ECP)// MP2/6-31G* (ECP)	0.0	7.35	47.67	47.66	103.80	94.74	107.22	98.34	p
UHF/6-31G(d)	0.0	4.4	43.6	44.5	149.1	146.2	84.9	86.3	a
UMP2/6-31G(d)	0.0	10.6	51.6	51.8	120.5	109.7	125.4	98.2	a
UMP2/6-311(d,p)	0.0	0.0	47.5	48.8	117.9	106.6	121.9	102.6	a
UMP4SDTQ/6-311++G(d,p)	0.0	-4.5	44.1	46.3	99.9	90	116.2	104.1	a
PMP4SDTQ/6-311++G(d,p)	0.0	-4.5	44.1	46.3	99.9	90	114.4	102.4	a
PMP4SDTQ + ZPE	0.0	-9.0	43.6	45.4	97.8	88.2	109.5	94.4	a
HF/3-21G*	0.0	-0.08	36.54						b
HF/3-21G* + ZPE	0.0	-5.05	35.44						b
MP2/cc-pVQZ	0.0	2.68	46.93						b
MP2/cc-pVQZ + ZPE	0.0	-1.49	46.62						b
HF/3-21G	0.0	10.6							c
HF/6-31G*	0.0	4.4							c
HF/6-31G* + ZPE	0.0	-0.4							c
MP2/6-31G*	0.0	10.6							c
MP2/6-31G* + ZPE	0.0	6.1							c
HF/6-311G*//MP2/6-3IG*	0.0	-3.8							c
MP2/6-311G**//MP2/6-31G*	0.0	0.0							c
MP3/6-311G**//MP2/6-31G*	0.0	-0.5							c
MP4(DQ)/6-311G**//MP2/6-31G*	0.0	-2.4							c
MP4(SDQ)/6-311G**//MP2/6-31G*	0.0	-2.2							c
MP4(SDTQ)/6-311G**//MP2/6-31G*	0.0	-1.7							c
MP4(SDTQ)/6-311G**// MP2/6-31G* + ZPE	0.0	-6.3							c
CI-SD/6-31G**//HF/4-31G	0.0	-1							c
CI-SD/6-31G**//HF/4-31G + ZPE	0.0	-4							c
DZ + P SCF//DZ + P SCF	0.0		39.4	41.2					d
DZ + P CISD//DZ + P CISD	0.0		42.4	43.6					d
DZ + P CCSD//DZ + P CCSD	0.0		42.2	43.1					d
DZ + P CCSD//DZ + P CCSD	0.0		42.5	43.4					d
DZ + P CCSDT-1//DZ + P CCSD	0.0		42.7	43.4					d
TZ + 2P CCSD//DZ + P CCSD	0.0		42.7	43.7					d
CASSCF	0.0						109.8	101	e

Table 2: Comparison of transition state energies of HFCO dissociation with existing work. The numbers given are in units of kcal/mol and relative to the reactant HFCO energy.

	TS-1	TS-2A	TS-2B	TS-2C	TS-3A	TS-3B	TS-3C	Ref.
B3LYP/6-31G* (ECP)	52.77	84.16	68.59	73.41	111.71	111.70	101.22	p
MP2/6-31G* (ECP)	53.01	85.95	73.79	77.69	108.88		53.01	p
CCSD(T)/6-31G* (ECP)// MP2/6-31G* (ECP)	54.85	85.35	68.05	74.33	106.68		54.85	p
UHF/6-31G(d)	72.1	100.6	63.4	82.1	162.5		148.2	a
UMP2/6-31G(d)	57.9	86.1	73.4	75.7	121.4	124.5	111.6	a
UMP2/6-311(d,p)	53.8	81.6	69.5	73.3	118.9		108.7	a
UMP4SDTQ/6-311++G(d,p)	46.9	79	65.1	69.2	102	103	92.8	a
PMP4SDTQ/6-311++G(d,p)	46.9	79	65.1	69.2	102	103	92.8	a
PMP4SDTQ + ZPE	43.2	74.9	62.6	65	99.3	99.8	90.1	a
HF/3-21G*	56.96	101.73						b
HF/3-21G* + ZPE	53.34	96.63						b
MP2/cc-pVQZ	50.75	79.63						b
MP2/cc-pVQZ + ZPE	47.3	75.69						b
HF/3-21G	69.3							c
HF/6-31G*	72.1							c
HF/6-31G* + ZPE	68.2							c
MP2/6-31G*	57.9							c
MP2/6-31G* + ZPE	54.2							c
HF/6-311G*//MP2/6-3IG*	68.1							c
MP2/6-311G**//MP2/6-3IG*	53.7							c
MP3/6-311G**/ /MP2/6-31G*	62.1							c
MP4(DQ)/6-311G**//MP2/6-31G*	60							c
MP4(SDQ)/6-311G**//MP2/6-31G*	56.1							c
MP4(SDTQ)/6-311G**//MP2/6-31G*	50.6							c
MP4(SDTQ)/6-311G**// MP2/6-31G* + ZPE	46.9							c
CI-SD/6-31G**//HF/4-31G	61							c
CI-SD/6-31G**//HF/4-31G + ZPE	58							c
DZ + P SCF//DZ + P SCF	67.6	95.2	58.5					d
DZ + P CISD//DZ + P CISD	60.9	86.9	62.7					d
TZ + 2P CISD//TZ + 2P CISD	58.4							d
DZ + P CCSD//DZ + P CCSD	57.7	83.3	62.4					d
DZ + P CCSD//DZ + P CCSD	57.9	83.5	62.7					d
DZ + P CCSDT-1//DZ + P CCSD	53.2	80.2	62.9					d
TZ + 2P CCSD//DZ + P CCSD	55	84.6						d
MP4/VTZ/SPF5	44.5							f
MP4/VTZ/SPF6	44.4							f
MP4/VTZ/MBE	45.7							f
MP2/6-31G*	46.9							f
CCSD/DZ+P	47							f
MP2/6-31G(d)	43.2							f

Table 3: Comparison of stationary point energies of HClCO dissociation with existing work. The numbers given are in units of kcal/mol and relative to the reactant HClCO energy.

Theory	HClCO	HCl+CO	INT-2T	INT-2C	INT-3T	INT-3C	Cl + HCO	H + ClCO	Ref.
B3LYP/6-31G* (ECP)	0.0	10.76	52.46	51.08	76.48	65.30	79.48	94.57	p
MP2/6-31G* (ECP)	0.0	2.60	57.79	57.71	79.53	67.99	67.78	75.91	p
CCSD(T)/6-31G* (ECP)// MP2/6-31G* (ECP)	0.0	1.00	52.30	51.69	67.11	62.33	67.30	77.58	p
UHF/6-31G(d)	0.0	-10.2	46.8	48	106.7		54	76.7	a
UMP2/6-31G(d)	0.0	2	55.9	56.5	85.8	73.4	82.2	88.9	a
UMP2/6-311(d,p)	0.0	-5.9	51.8	53.4	85.3	72.7	82	93.1	a
UMP4SDTQ/6-311++G(d,p)	0.0	-5.9	48.3	50.6	82	71.9	80.2	93.8	a
PMP4SDTQ/6-311++G(d,p)	0.0	-5.9	48.3	50.6	82	71.9	78.5	91.7	a
PMP4SDTQ+ZPE	0.0	-10.8	48	50	80.3	70.6	74.4	83.8	a
MP2/cc-pVTZ	0.0						94.5	93.9	g
CAS-MP2/cc-pVTZ	0.0						90	95.4	g
	TS-1	TS-2A	TS-2B	TS-2C	TS-3A	TS-3B	TS-3C		Ref.
B3LYP/6-31G* (ECP)	35.92	84.49	70.32	64.28	77.87	78.53	68.19		p
MP2/6-31G* (ECP)	41.40	87.21	79.79	74.20	82.18	84.91	72.36		p
CCSD(T)/6-31G* (ECP)// MP2/6-31G* (ECP)	41.69	85.73	72.59	67.45	68.27	82.27	66.61		p
UHF/6-31G(d)	45.2	99.5	67.9	69.4	116.2				a
UMP2/6-31G(d)	45.8	86.2	79.1	77.5	88	89.1	77.7		a
UMP2/6-311(d,p)	40.1	82.5	75.3	69.7	87.1		76.9		a
UMP4SDTQ/6-311++G(d,p)	41.1	80	70.7	67.5	84.4	86.9	75.7		a
PMP4SDTQ/6-311++G(d,p)	41.1	80	70.7	67.5	84.4	86.9	75.7		a
PMP4SDTQ+ZPE	37.8	76	68.3	62.9	81.9	83.8	73.2		a

Table 4: Comparison of stationary point energies of HBrCO dissociation with existing work. The numbers given are in units of kcal/mol and relative to the reactant HBrCO energy.

Theory	HBrCO	HBr+CO	INT-2T	INT-2C	INT-3T	INT-3C	Br + HCO	H + BrCO	Ref.
B3LYP/6-31G* (ECP)	0.0	10.02	52.69	51.04	68.46	57.49	66.18	85.55	p
MP2/6-31G* (ECP)	0.0	2.77	58.76	58.27	70.78	59.59	56.73	64.80	p
CCSD(T)/6-31G* (ECP)// MP2/6-31G* (ECP)	0.0	0.75	52.89	51.92	56.06	53.34	56.62	66.86	p
UHF/962(d)/6-311G(d,p)	0.0	-16.2					41.4		h
UMP2/962(d)/6-311G(d,p)+ZPE	0.0	-4.8					69.8		h
UMP4SDTQ/962(d)/6-311G(d,p)//									
UMP2/962(d)/6-311G(d,p)	0.0	-8.0					65.8		h
PMP4SDTQ+ZPE	0.0	-12.8					62.4		h
	TS-1	TS-2A	TS-2B	TS-2C	TS-3A	TS-3B	TS-3C		Ref.
B3LYP/6-31G* (ECP)	33.65	83.53	69.13	63.06	70.35	71.59	61.34		p
MP2/6-31G* (ECP)	39.67	86.70	79.62	73.24	73.90	79.07	65.46		p
CCSD(T)/6-31G* (ECP)// MP2/6-31G* (ECP)	40.06	84.83	71.99	66.23		75.23	57.49		p
UMP2/962(d)/6-311G(d,p)+ZPE	35.3								h
UMP2/962(d)/6-311G(d,p)+ZPE	34.3								h
UMP4SDTQ/962(d)/6-311G(d,p)//									
UMP2/962(d)/6-311G(d,p)	33.7								h
PMP4SDTQ+ZPE	31								h

Table 5: Comparison of stationary point energies of HICO dissociation with existing work. The numbers given are in units of kcal/mol and relative to the reactant HICO energy.

Theory	HICO	HI+CO	INT-2T	INT-2C	INT-3T	INT-3C	I + HCO	H + ICO	Ref.
B3LYP/6-31G* (ECP)	0.0	8.40	52.92	51.79	62.59	51.96	54.18	77.26	p
MP2/6-31G* (ECP)	0.0	1.74	59.42	59.45	63.42	53.02	47.97	56.06	p
CCSD(T)/6-31G* (ECP)// MP2/6-31G* (ECP)	0.0	-8.59	45.35	44.97	37.99	38.20	40.04	50.34	p
B3LYP/6-31G*	0.0	7.34	52.26	51.09	65.06	53.97			i
CCSD(T)/6-31G **//B3LYP/6-31G*	0.0	-3.51	49.40	48.33	55.07	49.40			i
CCSD(T)/6-31G **//B3LYP/6-31G* + ZPE	0.0	-7.14	48.92	47.61	53.22	48.07			i
	TS-1	TS-2A	TS-2B	TS-2C	TS-3A	TS-3B	TS-3C		Ref.
B3LYP/6-31G* (ECP)	33.49	82.81	68.98	63.62	116.02	67.13	56.71		p
MP2/6-31G* (ECP)	39.90	86.30	80.21	74.41	116.63	74.89	60.04		p
CCSD(T)/6-31G* (ECP)// MP2/6-31G* (ECP)	32.42	76.23	64.34	59.07	102.39	61.27	40.37		p
B3LYP/6-31G*	33.44	82.87	69.21	62.90	111.20	68.72	58.27		i
CCSD(T)/6-31G **//B3LYP/6-31G*	35.03	81.53	68.00	61.26	108.30	71.19	54.51		i
CCSD(T)/6-31G **//B3LYP/6-31G* + ZPE	32.34	77.68	65.93	56.98	105.20	68.94	52.47		i

References

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(i) C.-l. Lin, M.-D. Su, and S.-Y. Chu, Chem. Phys. Lett. 308, 142 (1999).

(p) present work

HFCO - Optimized Geometries

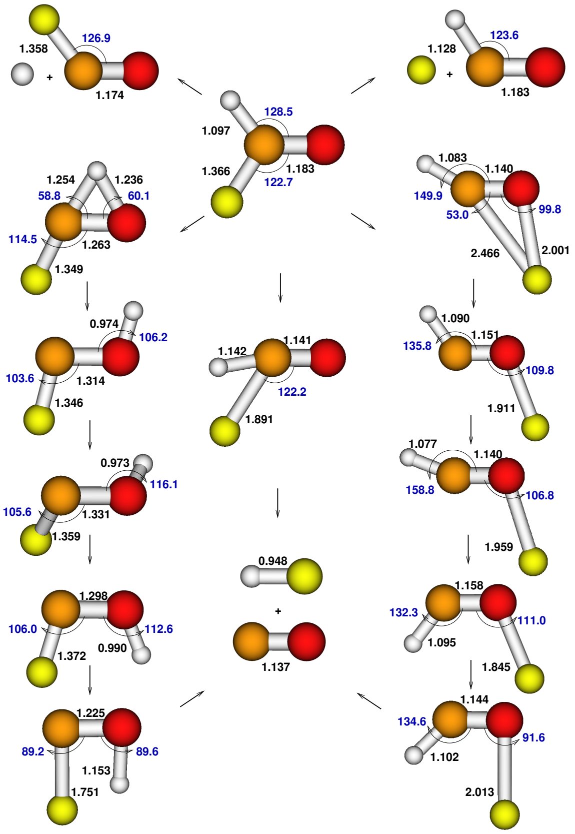

Figure 5: Optimized geometries (B3LYP/6-31G*/ECP) of various stationary points on the potential energy surface of HFCO. Bond distances are in Å and angles are in degrees.

HClCO - Optimized Geometries

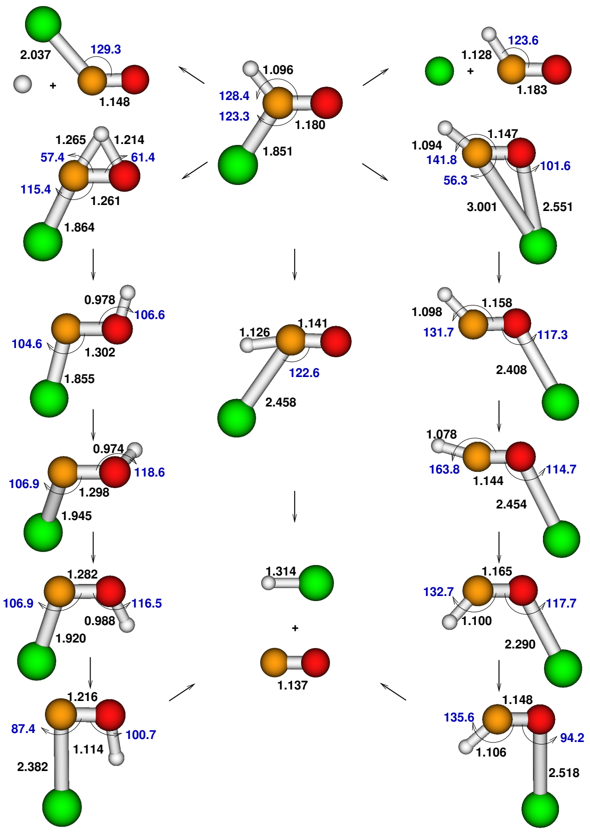

Figure 6: Optimized geometries (B3LYP/6-31G*/ECP) of various stationary points on the potential energy surface of HClCO. Bond distances are in Å and angles are in degrees.

HBrCO - Optimized Geometries

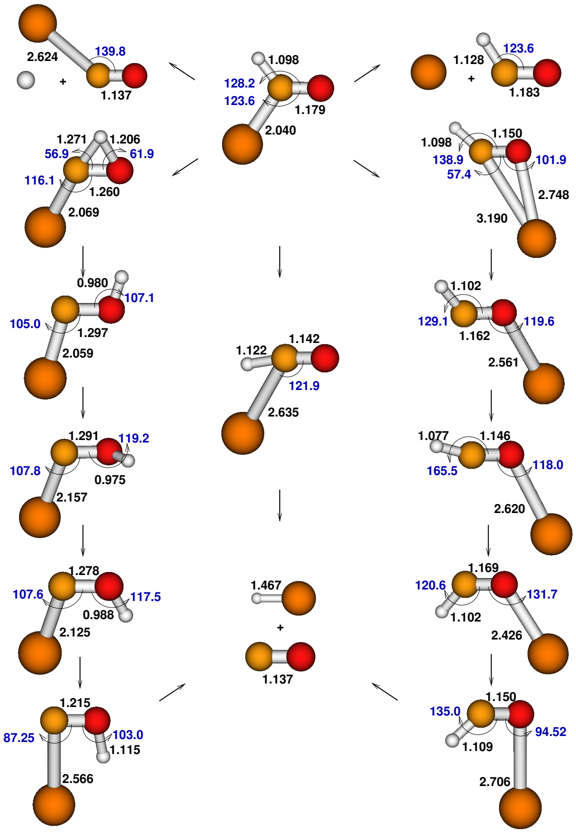

Figure 7: Optimized geometries (B3LYP/6-31G*/ECP) of various stationary points on the potential energy surface of HBrCO. Bond distances are in Å and angles are in degrees.

HICO - Optimized Geometries

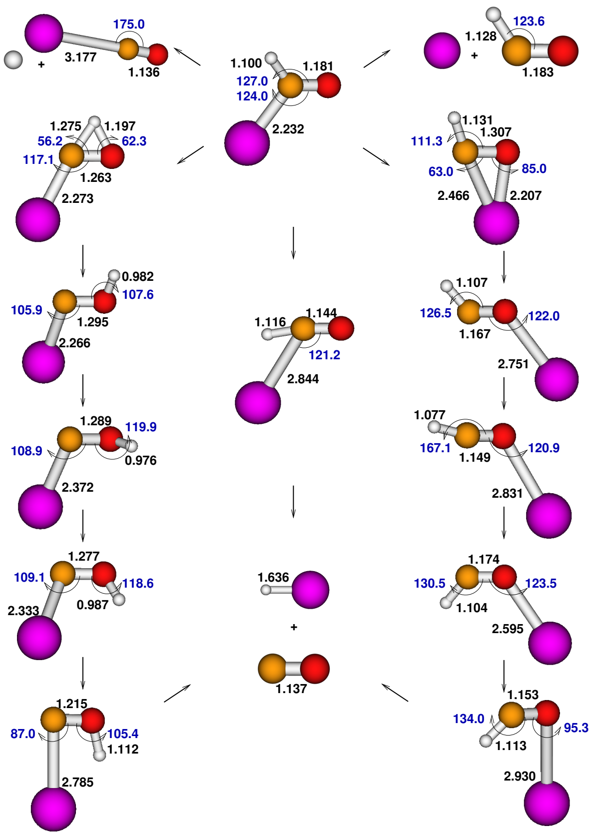

Figure 8: Optimized geometries (B3LYP/6-31G*/ECP) of various stationary points on the potential energy surface of HICO. Bond distances are in Å and angles are in degrees.

Spin-orbit (SO) included energies

The table below shows comparison of potential energy profiles for the HBrCO and HICO molecules computed using the B3LYP/6-31G*/ECP(Stuttgart group, SO included, *Ref:* Mol. Phys. **80**, 1431 (1993)) and B3LYP/6-31G*/ECP(LANL2DZ) theory used for the direct dynamics simulations.

Table 6: Comparison of potential energy profiles for the HBrCO and HICO species with and without the spin-orbit corrections.

species	B3LYP/6-31G* ECP,Stuttgart (SO included)	B3LYP/6-31G* ECP, LANL2DZ	species	B3LYP/6-31G* ECP, Stuttgart (SO included)	B3LYP/6-31G* ECP, LANL2DZ
HBrCO	0.0	0.0	HICO	0.0	0.0
Br + HCO	62.7	66.2	I + HCO	49.8	54.2
H + BrCO	86.0	85.6	H + ICO	73.2	77.3
TS−1	33.5	33.7	TS−1	33.6	33.5
HBr + CO	11.3	10.0	HI + CO	10.8	8.4
TS−2 A	83.3	83.5	TS−2 A	82.5	82.8
INT−2 T	52.0	52.7	INT−2 T	52.2	52.9
TS−2 B	68.7	69.1	TS−2 B	65.3	69.0
INT−2 C	50.8	51.0	INT−2 C	51.5	51.8
TS−2 C	63.1	63.1	TS−2 C	63.6	63.6
TS−3 A	68.6	70.4	TS−3 A	**61.4**	**116.0**
INT−3 T	67.9	68.5	INT−3 T	60.7	62.6
TS−3 B	69.8	71.6	TS−3 B	65.3	67.1
INT−3 C	57.0	57.5	INT−3 C	50.9	52.0
TS−3 C	60.3	61.3	TS−3 C	54.6	56.7

Transition state frequencies

Table 7: Imaginary frequencies (in cm^{-1}) associated with the transition states of all the four molecules computed using B3LYP/6-31G*/ECP theory.

transition state	HFCO	HClCO	HBrCO	HICO
TS-1 HXCO $\longrightarrow$ HX + CO (concerted path)	-1485	-1065	-1049	-1075
TS-2A HXCO $\longrightarrow$ trans-HOCX (INT-2T)	-1918	-1934	-1942	-1956
TS-2B trans-HOCX (INT-2T) $\longrightarrow$ cis-HOCX (INT-2C)	-903	-883	-863	-867
TS-2C cis-HOCX (INT-2C) $\longrightarrow$ HX + CO	-1573	-1160	-1180	-1213
TS-3A HXCO $\longrightarrow$ trans-HCOX (INT-3T)	-490	-384	-404	-1133
TS-3B trans-HCOX (INT-3T) $\longrightarrow$ cis-HCOX (INT-3C)	-746	-721	-796	-868
TS-3C cis-HCOX (INT-3C) $\longrightarrow$ HX + CO	-479	-404	-414	-423

Isomerization Pathways

Table 8: B3LYP/6-31G*/ECP computed energies of the trans $\longrightarrow$ cis isomerization pathways of HCOX isomers. Energies are in kcal/mol and relative to reactant HXCO molecule.

	HXCO	*trans*-HCOX	*inv*-TS[a]	*tor*-TS[b]	*cis*-HCOX
X=F	0.0	111.1	111.7	192.3	99.3
X=Cl	0.0	76.5	78.5	146.5	65.3
X=Br	0.0	68.5	71.6	131.9	57.5
X=I	0.0	62.6	67.1	115.7	52.0

[a] in-plane *inversion* transition state (TS-3B), low energy pathway, shown in main text.

[b] out-of-plane *torsion* transition state, high energy pathway.

Table 9: B3LYP/6-31G*/ECP computed energies of the trans $\longrightarrow$ cis isomerization pathways of HOCX isomers. Energies are in kcal/mol and relative to reactant HXCO molecule.

	HXCO	*trans*-HOCX	*inv*-TS[a]	*tor*-TS[b]	*cis*-HOCX
X=F	0.0	48.9	182.9	68.6	48.6
X=Cl	0.0	52.5	154.2	70.3	51.1
X=Br	0.0	52.7	128.3	69.1	51.0
X=I	0.0	52.9	119.9	69.0	51.8

[a] in-plane *inversion* transition state, high energy pathway.

[b] out-of-plane *torsion* transition state (TS-2B), low energy pathway, shown in main text.

Total Energy Conservation

Total energy in the classical trajectories reported here was conserved within E_{tot} ± 1.0 kcal/mol. Figure below shows total energy as a function of time for a few trajectories.

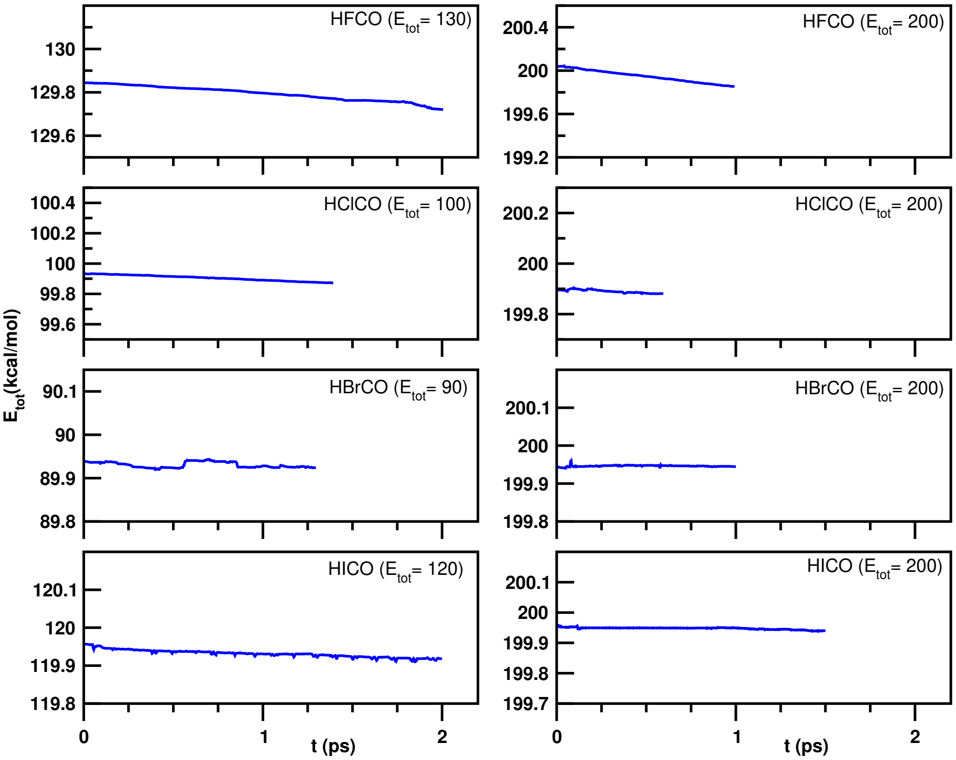

Figure 9: Total energy E_{tot} as a function of time for a few sample classical trajectories. In all plots, x-axes ranges are same.

HFCO - Trajectory Snapshots

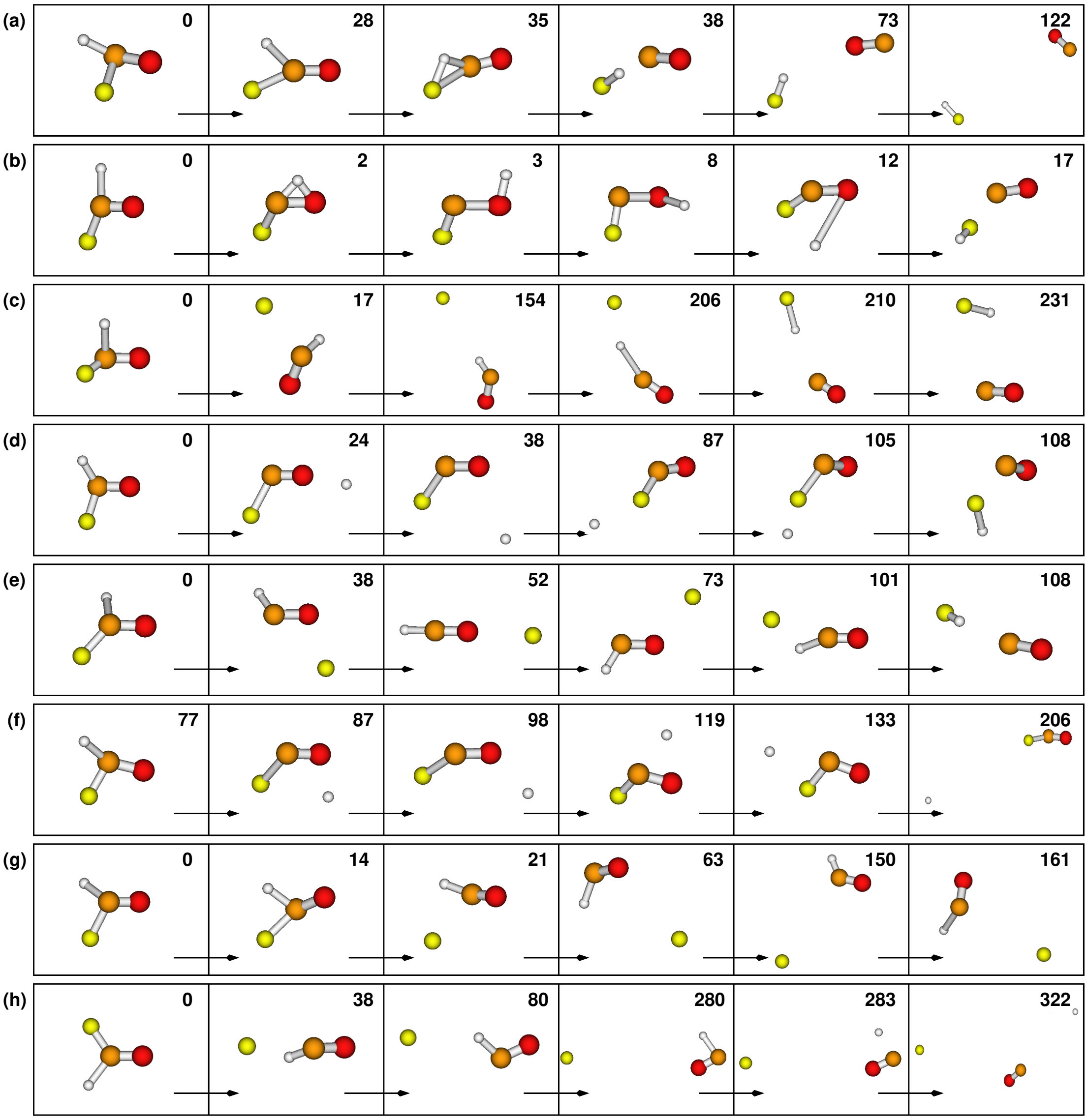

Figure 10: Snapshots of HFCO Trajectories. The numbers inside the frames are time in fs at which the snapshot was taken.

Descriptions of the trajectories:

(a) HFCO $\longrightarrow$ HF + CO (concerted)

(b) HFCO $\longrightarrow$ HOCF $\longrightarrow$ HF + CO (1,2-H shift)

(c) HFCO $\longrightarrow$ F + HCO $\longrightarrow$ HF + CO (radical recombination)

(d) $\mathrm{HFCO} \longrightarrow \mathrm{H} + \mathrm{FCO} \longrightarrow \mathrm{HF} + \mathrm{CO}$ (H roaming)

(e) $\mathrm{HFCO} \longrightarrow \mathrm{F} + \mathrm{HCO} \longrightarrow \mathrm{HF} + \mathrm{CO}$ (F roaming)

(f) $\mathrm{HFCO} \longrightarrow \mathrm{H} + \mathrm{FCO}$ (radical path)

(g) $\mathrm{HFCO} \longrightarrow \mathrm{F} + \mathrm{HCO}$ (radical path)

(h) $\mathrm{HFCO} \longrightarrow \mathrm{F} + \mathrm{HCO} \longrightarrow \mathrm{F} + \mathrm{H} + \mathrm{CO}$

HClCO - Trajectory Snapshots

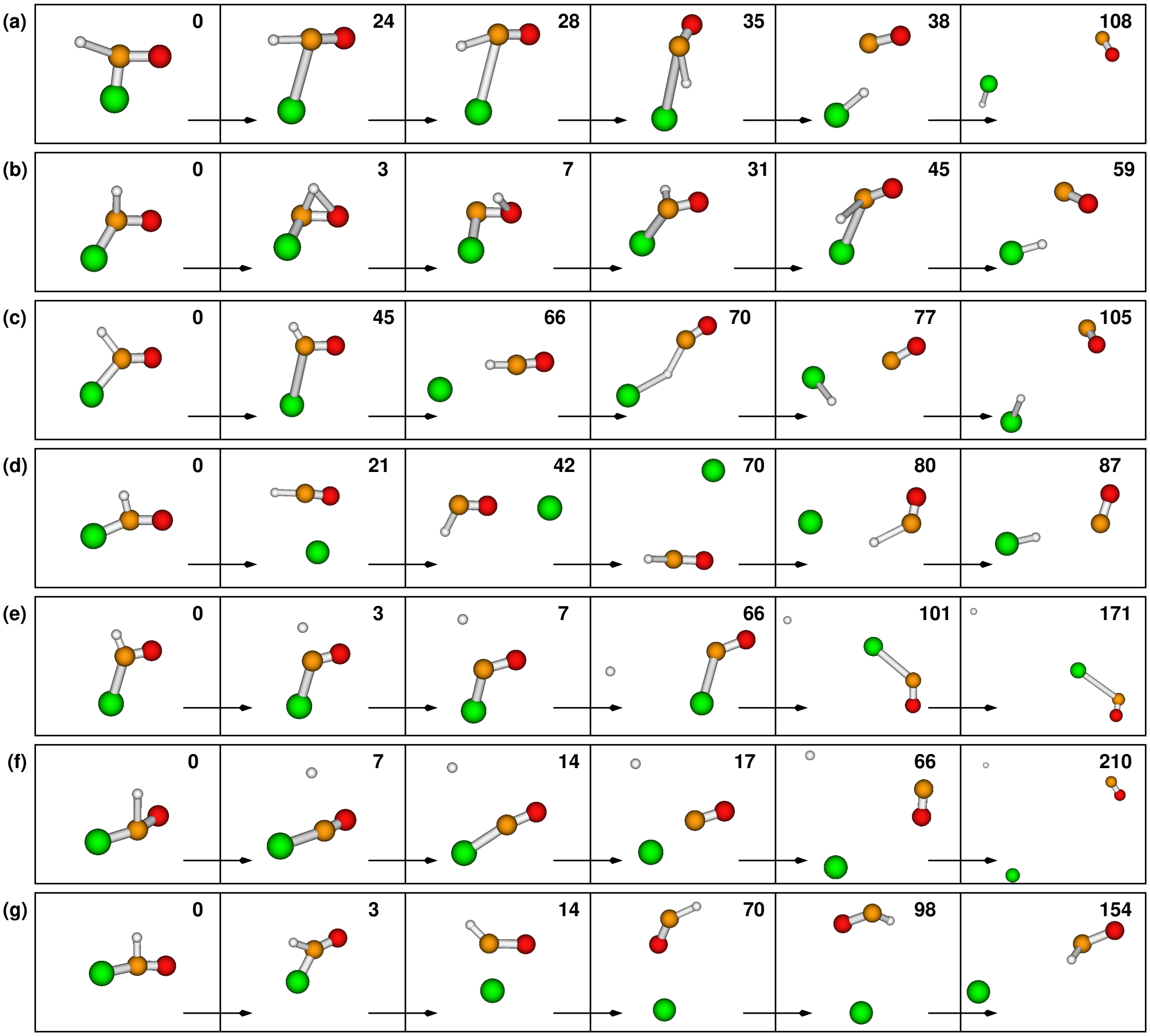

Figure 11: Snapshots of HClCO Trajectories. The numbers inside the frames are time in fs at which the snapshot was taken.

Descriptions of the trajectories:

(a) $\mathrm{HClCO} \longrightarrow \mathrm{HCl} + \mathrm{CO}$ (concerted)

(b) $\mathrm{HClCO} \longrightarrow \mathrm{HOCCl} \longrightarrow \mathrm{HClCO} \longrightarrow \mathrm{HCl} + \mathrm{CO}$ (1,2-H-shift and recross)

(c) $\mathrm{HClCO} \longrightarrow \mathrm{Cl} + \mathrm{HCO} \longrightarrow \mathrm{HCl} + \mathrm{CO}$ (radical recombination)

(d) $\mathrm{HClCO \longrightarrow Cl + HCO \longrightarrow HCl + CO}$ (Cl roaming)

(e) $\mathrm{HClCO \longrightarrow H + ClCO}$ (radical pathway)

(f) $\mathrm{HClCO \longrightarrow H + ClCO \longrightarrow H + Cl + CO}$

(g) $\mathrm{HClCO \longrightarrow Cl + HCO}$ (radical pathway)

HBrCO - Trajectory Snapshots

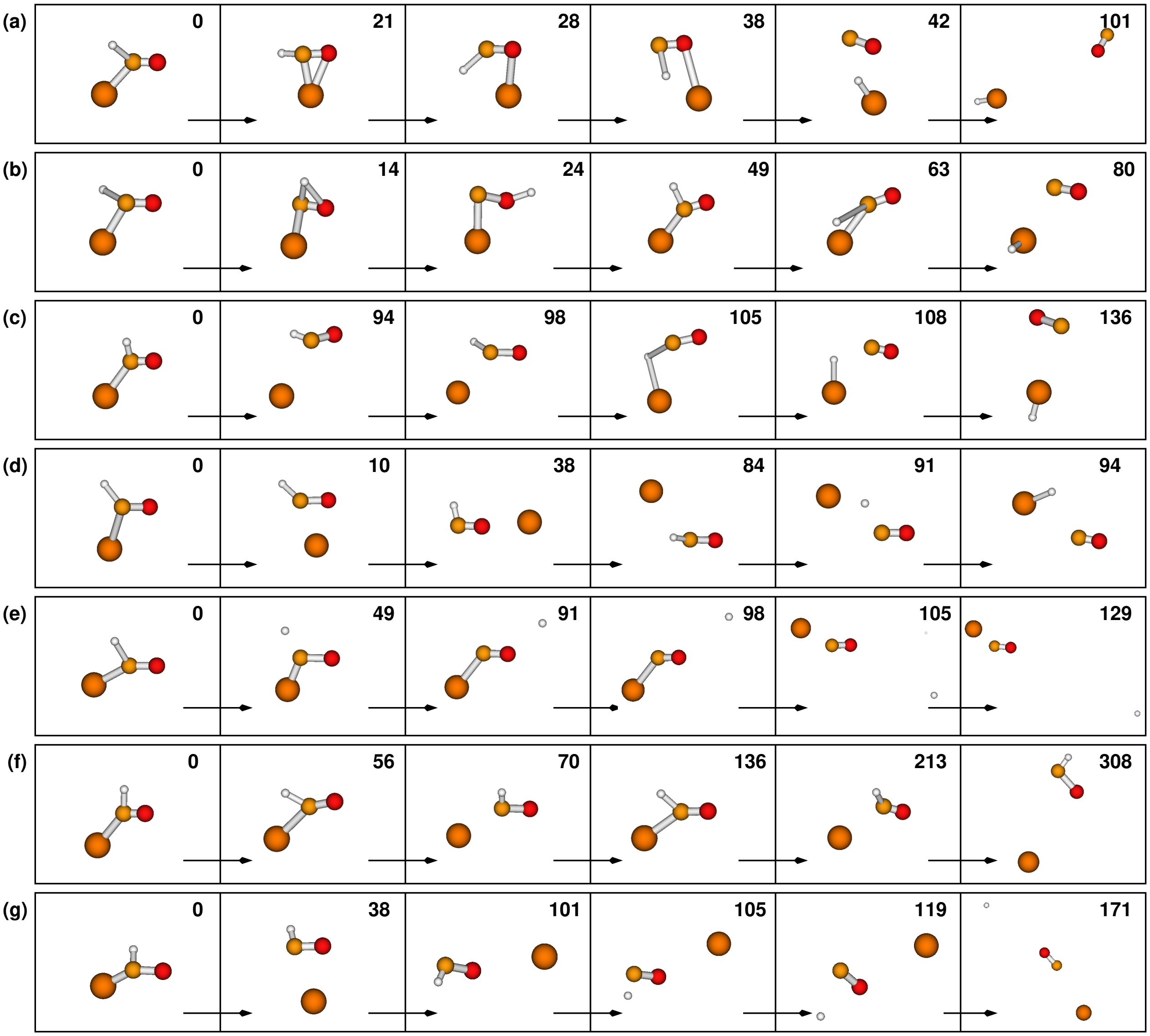

Figure 12: Snapshots of HBrCO Trajectories. The numbers inside the frames are time in fs at which the snapshot was taken.

Descriptions of the trajectories:

(a) HBrCO ⟶ HBr + CO (concerted)

(b) HBrCO ⟶ HOCBr ⟶ HBrCO ⟶ HBr + CO (1,2-H-shift and recross)

(c) HBrCO ⟶ Br + HCO ⟶ HBr + CO (radical recombination)

(d) $\mathrm{HBrCO} \longrightarrow \mathrm{Br} + \mathrm{HCO} \longrightarrow \mathrm{HBr} + \mathrm{CO}$ (Br roaming)

(e) $\mathrm{HBrCO} \longrightarrow \mathrm{H} + \mathrm{BrCO} \longrightarrow \mathrm{H} + \mathrm{Br} + \mathrm{CO}$

(f) $\mathrm{HBrCO} \longrightarrow \mathrm{Br} + \mathrm{HCO}$ (radical pathway)

(g) $\mathrm{HBrCO} \longrightarrow \mathrm{Br} + \mathrm{HCO} \longrightarrow \mathrm{Br} + \mathrm{H} + \mathrm{CO}$

HICO - Trajectory Snapshots

Descriptions of the trajectories:

(a) $\mathrm{HICO} \longrightarrow \mathrm{HI} + \mathrm{CO}$ (concerted)

(b) $\mathrm{HICO} \longrightarrow \mathrm{HOCI} \longrightarrow \mathrm{HICO} \longrightarrow \mathrm{HI} + \mathrm{CO}$ (1,2-H-shift and recross)

(c) $\mathrm{HICO} \longrightarrow \mathrm{I} + \mathrm{HCO} \longrightarrow \mathrm{HI} + \mathrm{CO}$ (radical recombination)

(d) $\mathrm{HICO} \longrightarrow \mathrm{I} + \mathrm{HCO} \longrightarrow \mathrm{HI} + \mathrm{CO}$ (I roaming)

(e) $\mathrm{HICO} \longrightarrow \mathrm{HOCI} \longrightarrow \mathrm{H} + \mathrm{ICO} \longrightarrow \mathrm{H} + \mathrm{I} + \mathrm{CO}$

(f) $\mathrm{HICO} \longrightarrow \mathrm{I} + \mathrm{HCO}$ (radical pathway)

(g) $\mathrm{HICO} \longrightarrow \mathrm{I} + \mathrm{HCO} \longrightarrow \mathrm{I} + \mathrm{H} + \mathrm{CO}$

(h) $\mathrm{HICO} \longrightarrow \mathrm{H} + \mathrm{ICO} \longrightarrow \mathrm{H} + \mathrm{I} + \mathrm{CO}$

(i) $\mathrm{HICO} \longrightarrow \mathrm{HCOI} \longrightarrow \mathrm{HI} + \mathrm{CO}$ (1,2-I-shift)

(j) $\mathrm{HICO} \longrightarrow \mathrm{HOCI} \longrightarrow \mathrm{HI} + \mathrm{CO}$ (1,2-H-shift)

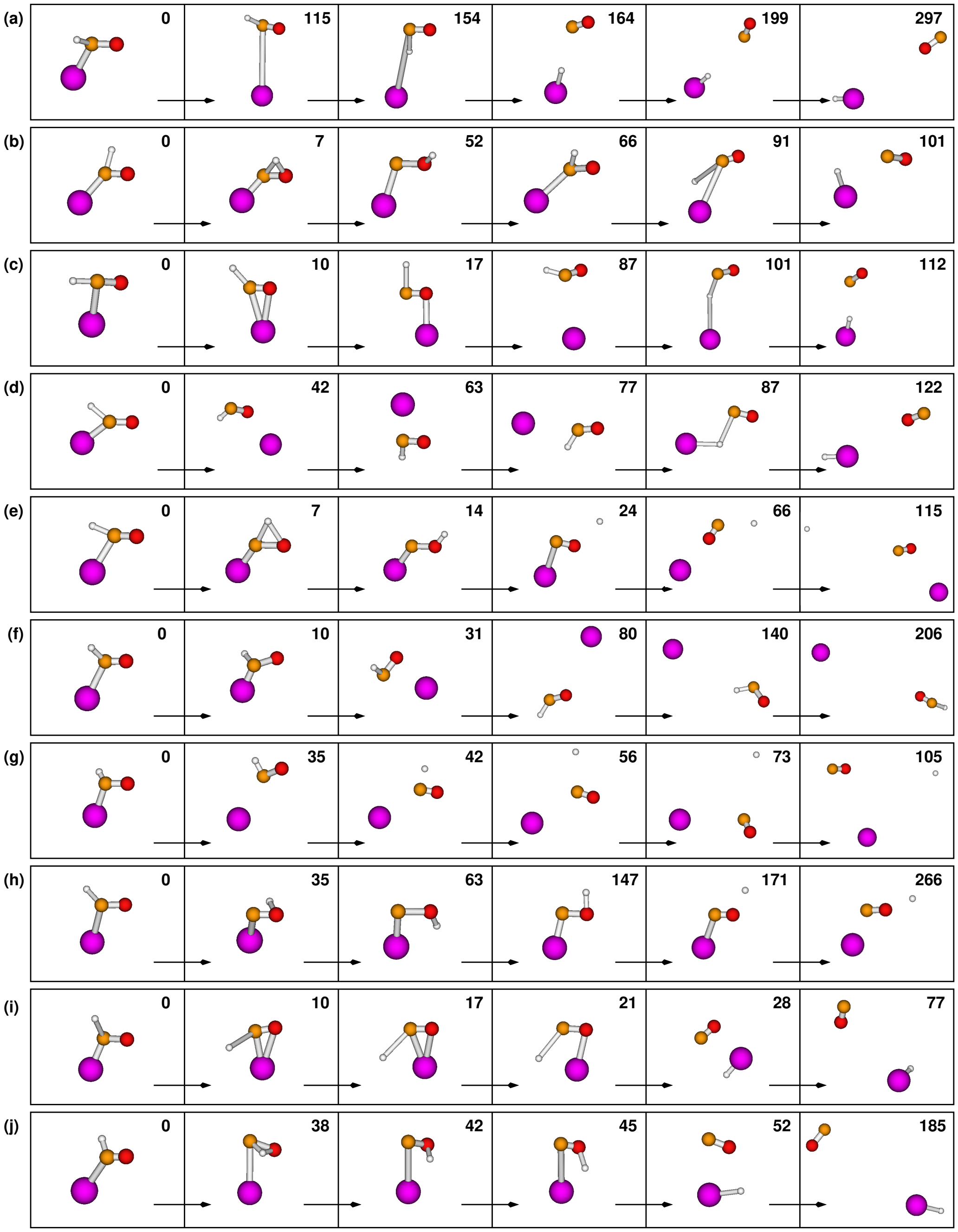

Figure 13: Snapshots of HICO Trajectories. The numbers inside the frames are time in fs at which the snapshot was taken.