

A PROPOSAL FOR THE MECHANISM OF THE CH + CO₂ REACTION

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SUPPORTING INFORMATION

Table S1. Equilibrium bond lengths (in Angstrom), r , bond angles (in degree), θ , dihedral angles (in degree), d , and T_1 diagnostic for stable molecular structures involved in the CH + CO₂ ↔ HCO + CO and HCO ↔ H + CO reactions.^a

Molecule	Parameters	UCCSD/ cc-pVDZ	ROCCSD/ cc-pVDZ	Experimental (1)
CH	r (H – C)	1.1419 [2.0]	1.1419 [2.0]	1.1199
	T_1	0.010	0.016	...
CO ₂	r (O _a – C)	1.1681 [0.7]	1.1681 [0.7]	1.1600
	r (C – O _b)	1.1681 [0.7]	1.1681 [0.7]	1.1600
	θ (O _a – C – O _b)	180.0	180.0	180.0
	T_1	0.019	0.019	...
Pre- Complex	r (H – C _a)	1.1381	1.1381	...
	r (C _a – O _a)	2.4928	2.4908	...
	r (O _a – C _b)	1.1724	1.1724	...
	r (C _b – O _b)	1.1642	1.1642	...
	θ (H – C _a – O _a)	84.3	84.3	...
	θ (C _a – O _a – C _b)	107.7	107.8	...
	θ (O _a – C _b – O _b)	179.2	179.2	...
	d (H – C _a – O _a – C _b)	180.0	180.0	...
	d (C _a – O _a – C _b – O _b)	180.0	180.0	...
	T_1	0.019	0.019	...
IM1	r (H – C _a)	1.0947	1.0947	...
	r (C _a – O _a)	1.4433	1.4440	...
	r (O _a – C _b)	1.4039	1.4029	...
	r (C _b – O _b)	1.1850	1.1851	...
	θ (H – C _a – O _a)	122.9	122.9	...
	θ (C _a – O _a – C _b)	59.6	59.6	...
	θ (O _a – C _b – O _b)	137.3	137.3	...
	d (H – C _a – O _a – C _b)	131.5	131.4	...
	d (C _a – O _a – C _b – O _b)	179.0	179.0	...
	T_1	0.022	0.027	...

Molecule	Parameters	UCCSD/ cc-pVDZ	ROCCSD/ cc-pVDZ	Experimental
IM2	$r(\text{H} - \text{C}_a)$	1.1082	1.1083	...
	$r(\text{C}_a - \text{O}_a)$	1.2525	1.2510	...
	$r(\text{O}_a - \text{C}_b)$	2.3228	2.3214	...
	$r(\text{C}_b - \text{O}_b)$	1.1647	1.1642	...
	$\theta(\text{H} - \text{C}_a - \text{O}_a)$	125.4	125.5	...
	$\theta(\text{C}_a - \text{O}_a - \text{C}_b)$	31.1	31.2	...
	$\theta(\text{O}_a - \text{C}_b - \text{O}_b)$	152.0	151.9	...
	$d(\text{H} - \text{C}_a - \text{O}_a - \text{C}_b)$	180.0	180.0	...
	$d(\text{C}_a - \text{O}_a - \text{C}_b - \text{O}_b)$	180.0	179.9	...
	T_1	0.031	0.024	...
IM3	$r(\text{H} - \text{C}_a)$	1.1156	1.1158	...
	$r(\text{C}_a - \text{O}_a)$	1.2115	1.2102	...
	$r(\text{O}_a - \text{C}_b)$	2.4003	2.4029	...
	$r(\text{C}_b - \text{O}_b)$	1.1798	1.1801	...
	$\theta(\text{H} - \text{C}_a - \text{O}_a)$	124.5	124.5	...
	$\theta(\text{C}_a - \text{O}_a - \text{C}_b)$	32.3	32.3	...
	$\theta(\text{O}_a - \text{C}_b - \text{O}_b)$	131.8	131.0	...
	$d(\text{H} - \text{C}_a - \text{O}_a - \text{C}_b)$	169.5	169.9	...
	$d(\text{C}_a - \text{O}_a - \text{C}_b - \text{O}_b)$	112.3	111.6	...
	T_1	0.031	0.031	...
IM4	$r(\text{H} - \text{C}_a)$	1.1274	1.1273	...
	$r(\text{C}_a - \text{O}_a)$	1.3369	1.3371	...
	$r(\text{O}_a - \text{C}_b)$	1.4271	1.4256	...
	$r(\text{C}_b - \text{O}_b)$	1.1733	1.1734	...
	$\theta(\text{H} - \text{C}_a - \text{O}_a)$	100.0	100.0	...
	$\theta(\text{C}_a - \text{O}_a - \text{C}_b)$	114.2	114.1	...
	$\theta(\text{O}_a - \text{C}_b - \text{O}_b)$	124.0	124.1	...
	$d(\text{H} - \text{C}_a - \text{O}_a - \text{C}_b)$	180.0	180.0	...
	$d(\text{C}_a - \text{O}_a - \text{C}_b - \text{O}_b)$	180.0	180.0	...
	T_1	0.024	0.028	...
PoC1	$r(\text{H} - \text{C}_a)$	1.1356	1.1356	...
	$r(\text{C}_a - \text{O}_a)$	1.1846	1.1845	...
	$r(\text{O}_a - \text{C}_b)$	3.9567	3.9583	...
	$r(\text{C}_b - \text{O}_b)$	1.1377	1.1377	...
	$\theta(\text{H} - \text{C}_a - \text{O}_a)$	124.6	124.6	...
	$\theta(\text{C}_a - \text{O}_a - \text{C}_b)$	52.3	52.2	...
	$\theta(\text{O}_a - \text{C}_b - \text{O}_b)$	142.4	142.4	...
	$d(\text{H} - \text{C}_a - \text{O}_a - \text{C}_b)$	84.6	84.8	...
	$d(\text{C}_a - \text{O}_a - \text{C}_b - \text{O}_b)$	134.5	134.4	...
	T_1	0.022	0.024	...
PoC2	$r(\text{H} - \text{C}_a)$	3.9238	3.9235	...
	$r(\text{C}_a - \text{O}_a)$	1.1384	1.1384	...
	$\theta(\text{H} - \text{C}_a - \text{O}_a)$	116.9	116.9	...
	T_1	0.019	0.019	...

Molecule	Parameters	UCCSD/ cc-pVDZ	ROCCSD/ cc-pVDZ	Experimental
HCO	r (H – C)	1.1373 [2.5]	1.1373 [2.5]	1.1100
	r (C – O)	1.1844 [1.1]	1.1842 [1.1]	1.1712
	θ (H – C – O)	124.4 [2.4]	124.4 [2.4]	127.43
	T_1	0.023	0.028	...
CO	r (C – O)	1.1384 [0.9]	1.1384 [0.9]	1.1283
	T_1	0.020	0.020	...

^a The values between brackets are absolute deviations (in %) in relation to experimental data. Reference. (1) Lide (2004).

Table S2. Equilibrium bond lengths (in Angstrom), r , bond angles (in degree), θ , dihedral angles (in degree), d , and T_1 diagnostic for transition state structures involved in the $\text{CH} + \text{CO}_2 \leftrightarrow \text{HCO} + \text{CO}$ and $\text{HCO} \leftrightarrow \text{H} + \text{CO}$ reactions.

Molecule	Parameters	UCCSD/ cc-pVDZ	ROCCSD/ cc-pVDZ
TSR1	r (H – C _a)	1.1195	1.1195
	r (C _a – O _a)	1.9580	1.9584
	r (O _a – C _b)	1.2086	1.2085
	r (C _b – O _b)	1.1636	1.1636
	θ (H – C _a – O _a)	91.9	91.8
	θ (C _a – O _a – C _b)	72.1	72.1
	θ (O _a – C _b – O _b)	162.8	162.8
	d (H – C _a – O _a – C _b)	167.7	166.8
	d (C _a – O _a – C _b – O _b)	179.2	179.2
	T_1	0.022	0.023
TS12	r (H – C _a)	1.0908	1.0906
	r (C _a – O _a)	1.3880	1.3871
	r (O _a – C _b)	1.5722	1.5744
	r (C _b – O _b)	1.1758	1.1758
	θ (H – C _a – O _a)	130.0	130.2
	θ (C _a – O _a – C _b)	54.8	54.8
	θ (O _a – C _b – O _b)	134.4	134.4
	d (H – C _a – O _a – C _b)	148.4	149.2
	d (C _a – O _a – C _b – O _b)	177.9	177.9
	T_1	0.021	0.025
TS23	r (H – C _a)	1.1105	1.1105
	r (C _a – O _a)	1.2385	1.2381
	r (O _a – C _b)	2.3435	2.3404
	r (C _b – O _b)	1.1689	1.1680
	θ (H – C _a – O _a)	125.0	125.2
	θ (C _a – O _a – C _b)	31.3	31.3
	θ (O _a – C _b – O _b)	148.2	148.8
	d (H – C _a – O _a – C _b)	170.8	171.4
	d (C _a – O _a – C _b – O _b)	141.8	144.7
	T_1	0.033	0.027

Molecule	Parameters	UCCSD/ cc-pVDZ	ROCCSD/ cc-pVDZ
TS3P	$r(\text{H} - \text{C}_a)$	1.1230	1.1230
	$r(\text{C}_a - \text{O}_a)$	1.1881	1.1878
	$r(\text{O}_a - \text{C}_b)$	2.7328	2.7330
	$r(\text{C}_b - \text{O}_b)$	1.1580	1.1578
	$\theta(\text{H} - \text{C}_a - \text{O}_a)$	126.9	126.9
	$\theta(\text{C}_a - \text{O}_a - \text{C}_b)$	37.3	37.3
	$\theta(\text{O}_a - \text{C}_b - \text{O}_b)$	118.1	118.1
	$d(\text{H} - \text{C}_a - \text{O}_a - \text{C}_b)$	154.9	155.2
	$d(\text{C}_a - \text{O}_a - \text{C}_b - \text{O}_b)$	109.3	109.3
	T_1	0.025	0.027
TS14	$r(\text{H} - \text{C}_a)$	1.1224	1.1228
	$r(\text{C}_a - \text{O}_a)$	1.3807	1.3822
	$r(\text{O}_a - \text{C}_b)$	1.3590	1.3571
	$r(\text{C}_b - \text{O}_b)$	1.1841	1.1841
	$\theta(\text{H} - \text{C}_a - \text{O}_a)$	106.5	106.4
	$\theta(\text{C}_a - \text{O}_a - \text{C}_b)$	88.1	88.3
	$\theta(\text{O}_a - \text{C}_b - \text{O}_b)$	130.2	130.4
	$d(\text{H} - \text{C}_a - \text{O}_a - \text{C}_b)$	148.0	148.0
	$d(\text{C}_a - \text{O}_a - \text{C}_b - \text{O}_b)$	155.2	156.2
	T_1	0.045	0.065
TS4P	$r(\text{H} - \text{C}_a)$	1.1302	1.1297
	$r(\text{C}_a - \text{O}_a)$	1.3074	1.3059
	$r(\text{O}_a - \text{C}_b)$	1.5411	1.5472
	$r(\text{C}_b - \text{O}_b)$	1.1632	1.1627
	$\theta(\text{H} - \text{C}_a - \text{O}_a)$	100.0	100.4
	$\theta(\text{C}_a - \text{O}_a - \text{C}_b)$	116.0	116.2
	$\theta(\text{O}_a - \text{C}_b - \text{O}_b)$	121.4	121.2
	$d(\text{H} - \text{C}_a - \text{O}_a - \text{C}_b)$	180.0	180.0
	$d(\text{C}_a - \text{O}_a - \text{C}_b - \text{O}_b)$	179.6	180.0
	T_1	0.056	0.034
TSRP	$r(\text{H} - \text{C}_a)$	1.8061	1.7965
	$r(\text{C}_a - \text{O}_a)$	1.1436	1.1435
	$\theta(\text{H} - \text{C}_a - \text{O}_a)$	117.7	117.8
	T_1	0.024	0.031

Table S3. Scaled fundamental vibrational frequencies (in cm^{-1}) for stable molecular structures involved in the $\text{CH} + \text{CO}_2 \leftrightarrow \text{HCO} + \text{CO}$ and $\text{HCO} \leftrightarrow \text{H} + \text{CO}$ reactions.^a

Molecule	UCCSD/ cc-pVDZ scale=0.947	ROCCSD/ cc-pVDZ scale=0.947 ^b	Experimental (1)	Ref.
CH	2680.5 [6.3]	2680.9 [6.3]	2861	(1)
CO_2	636.7 [4.6]	636.7 [4.6]	667	(2)
	636.7 [4.6]	636.7 [4.6]	667	(2)
	1306.1 [2.0]	1306.1 [2.0]	1333	(2)
	2303.9 [1.9]	2303.9 [1.9]	2349	(2)
Pre- Complex	51.4	49.8
	89.7	94.9
	139.9	139.6
	477.4	477.5
	632.9	633.2
	637.2	636.1
	1304.1	1304.1
	2297.2	2297.4
	2716.4	2716.6
IM1	481.6	482.5
	508.7	509.6
	588.2	589.9
	740.9	742.5
	864.0	863.4
	1077.9	1077.8
	1133.3	1132.4
	1973.7	1974.0
	3075.8	3075.4
IM2	167.6	176.5
	194.2	191.9
	643.9	641.8
	749.3	750.5
	943.9	939.4
	1284.8	1283.6
	1424.4	1412.5
	2051.3	2051.7
	2916.1	2914.6
IM3	146.1	140.3
	247.0	260.0
	487.5	484.1
	729.6	729.2
	915.1	916.0
	1297.1	1296.9
	1675.5	1685.4
	1886.7	1883.9
	2846.9	2845.0

Molecule	UCCSD/ cc-pVDZ scale=0.947	ROCCSD/ cc-pVDZ scale=0.947 ^b	Experimental	Ref.
IM4	116.1	113.9
	334.7	334.7
	530.2	535.1
	648.4	644.4
	794.5	802.1
	1187.8	1187.9
	1345.5	1346.0
	1860.6	1863.0
	2754.6	2755.5
PoC1	20.2	11.1
	32.5	25.3
	53.4	49.0
	80.8	78.4
	184.7	183.9
	1072.4	1072.6
	1837.0	1839.2
	2097.5	2097.8
	2560.5	2561.9
PoC2	5.8	10.4
	39.1	38.9
	2092.1	2092.5
HCO	1070.6 [1.0]	1071.4 [0.9]	1081	(2)
	1837.4 [1.6]	1840.3 [1.5]	1868	(2)
	2540.9 [2.3]	2541.9 [2.3]	2485	(2)
CO	2092.1 [2.4]	2092.1 [2.4]	2143	(3)

^a The values between brackets are absolute deviations (in %) in relation to experimental data.

^b We adopted the same scaling factor value as that suggested by Johnson III (2015) for UCCSD/cc-pVDZ calculations.

References. (1) Irikura (2007), (2) Lide (2004), and (3) Bishop & Cheung (1982).

Table S4. Scaled fundamental vibrational frequencies (in cm^{-1}) for transition state structures involved in the $\text{CH} + \text{CO}_2 \leftrightarrow \text{HCO} + \text{CO}$ and $\text{HCO} \leftrightarrow \text{H} + \text{CO}$ reactions.^a

Molecule	UCCSD/ cc-pVDZ scale=0.947	ROCCSD/ cc-pVDZ scale=0.947 ^b
TSR1	479.7 <i>i</i> 99.0 303.0 573.7 607.0 862.8 1224.2 2173.7 2872.1	487.5 <i>i</i> 102.8 299.2 565.9 607.1 861.7 1222.1 2174.0 2871.7
TS12	462.5 <i>i</i> 390.6 501.3 550.5 916.7 1137.1 1202.1 2029.1 3115.3	458.4 <i>i</i> 384.7 500.4 548.6 916.3 1138.4 1202.6 2031.2 3116.9
TS23	195.5 <i>i</i> 189.2 602.5 763.6 913.2 1298.1 1486.0 2002.0 2894.3	208.1 <i>i</i> 187.7 607.2 764.1 914.4 1298.6 1490.2 2010.2 2894.8
TS3P	481.6 <i>i</i> 69.7 242.4 328.2 629.4 1154.3 1779.0 1908.0 2739.6	510.6 <i>i</i> 58.5 238.2 325.9 624.1 1153.7 1780.8 1906.6 2738.9
TS14	994.1 <i>i</i> 193.7 539.7 594.6 860.0 1111.3 1215.8 1802.8 2790.9	1078.8 <i>i</i> 200.3 536.9 587.5 853.9 1101.1 1202.6 1800.3 2785.8

Molecule	UCCSD/ cc-pVDZ scale=0.947	ROCCSD/ cc-pVDZ scale=0.947 ^b
TS4P	687.8 <i>i</i> 94.8 333.3 576.7 671.7 1205.0 1293.0 1894.2 2722.6	727.1 <i>i</i> 96.9 333.4 571.0 664.4 1203.8 1283.7 1897.5 2726.5
TSRP	875.7 <i>i</i> 403.1 2034.2	886.3 <i>i</i> 410.2 2035.7

^a The symbol *i* represents the imaginary frequency.

^b We adopted the same scaling factor value as that suggested by Johnson III (2015) for UCCSD/cc-pVDZ calculations.

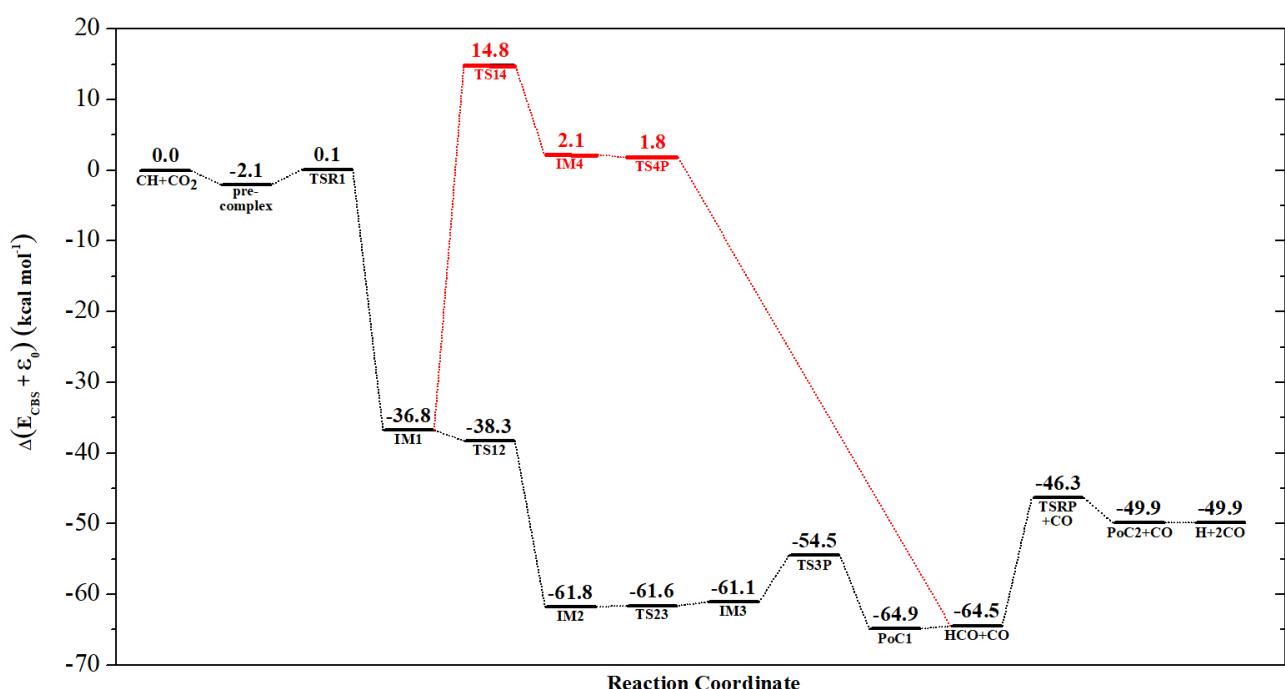


Figure S1. Relative energetic profile (electronic energies, E_{CBS} , plus scaled zero-point corrections, ε_0) (in kcal mol^{-1}) for the stationary point structures involved in the $\text{CH} + \text{CO}_2 \leftrightarrow \text{HCO} + \text{CO}$ and $\text{HCO} \leftrightarrow \text{H} + \text{CO}$ reactions, calculated at the ROCCSD(T)/CBS//UCCSD/cc-pVDZ level.

Table S5. Enthalpies (in kcal mol⁻¹) relative to reactants (CH + CO₂) for the stationary point structures involved in the CH + CO₂ ↔ HCO + CO and HCO ↔ H + CO reactions, calculated from the ROCCSD(T)/CBS//UCCSD/cc-pVDZ treatment at different temperatures (in K), T.

Molecule	T												
	50	100	200	300	500	700	1000	1500	2000	2500	3000	3500	4000
CH + CO ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pre-Complex	-2.4	-2.4	-2.5	-2.3	-2.0	-1.7	-1.1	-0.2	0.8	1.8	2.8	3.8	4.8
TSR1	-0.2	-0.3	-0.7	-0.9	-1.0	-1.2	-1.2	-1.3	-1.4	-1.4	-1.4	-1.4	-1.4
IM1	-37.1	-37.3	-37.9	-38.2	-38.4	-38.4	-38.0	-37.3	-36.4	-35.5	-34.6	-33.6	-32.6
TS12	-38.7	-38.9	-39.5	-39.8	-40.2	-40.5	-40.7	-41.0	-41.1	-41.2	-41.2	-41.3	-41.3
IM2	-62.1	-62.3	-62.7	-62.9	-63.1	-63.1	-62.8	-62.2	-61.3	-60.4	-59.5	-58.5	-57.6
TS23	-61.9	-62.1	-62.6	-63.0	-63.5	-63.9	-64.3	-64.6	-64.7	-64.8	-64.9	-64.9	-64.9
IM3	-61.4	-61.6	-61.9	-62.1	-62.3	-62.3	-62.0	-61.3	-60.5	-59.5	-58.6	-57.7	-56.7
TS3P	-54.8	-54.9	-55.2	-55.3	-55.5	-55.7	-55.9	-56.1	-56.1	-56.1	-56.2	-56.2	-56.2
PoC1	-65.0	-64.8	-64.6	-64.3	-63.9	-63.7	-63.2	-62.3	-61.3	-60.3	-59.3	-58.4	-57.4
TS14	14.5	14.3	13.8	13.5	13.1	12.9	12.7	12.6	12.7	12.7	12.7	12.7	12.7
IM4	1.8	1.7	1.3	1.1	1.1	1.2	1.6	2.4	3.4	4.4	5.4	6.3	7.3
TS4P	1.6	1.4	1.0	0.8	0.5	0.3	0.2	0.1	0.1	0.1	0.1	0.1	0.1
HCO + CO	-64.5	-64.4	-64.4	-64.4	-64.6	-64.9	-65.3	-65.9	-66.4	-66.9	-67.4	-67.9	-68.4
TSRP + CO	-46.3	-46.2	-46.1	-46.0	-46.1	-46.3	-46.7	-47.8	-49.0	-50.3	-51.6	-53.0	-54.4
PoC2 + CO	-49.7	-49.5	-49.0	-48.6	-48.2	-48.0	-47.9	-47.9	-48.1	-48.4	-48.8	-49.2	-49.6
H + 2 CO	-49.6	-49.4	-48.9	-48.6	-48.2	-48.0	-47.8	-47.8	-48.1	-48.4	-48.7	-49.1	-49.6

Table S6. Gibbs free energies (in kcal mol⁻¹) relative to reactants (CH + CO₂) for the stationary point structures involved in the CH + CO₂ ↔ HCO + CO and HCO ↔ H + CO reactions, calculated from the ROCCSD(T)/CBS//UCCSD/cc-pVDZ treatment at different temperatures (in K), T.

Molecule	T												
	50	100	200	300	500	700	1000	1500	2000	2500	3000	3500	4000
CH + CO ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pre-Complex	-1.4	-0.6	1.3	3.2	6.8	10.2	15.4	23.4	31.1	38.5	45.7	52.8	59.7
TSR1	0.9	1.9	4.4	6.9	12.3	17.5	25.7	39.1	52.6	66.1	79.5	93.0	106.5
IM1	-36.0	-34.8	-32.1	-29.1	-22.9	-16.8	-7.5	7.7	22.5	37.1	51.5	65.8	79.9
TS12	-37.5	-36.4	-33.7	-30.7	-24.5	-18.2	-8.5	7.6	23.8	40.1	56.3	72.5	88.8
IM2	-61.0	-59.9	-57.4	-54.8	-49.2	-43.8	-35.4	-21.9	-8.6	4.5	17.3	30.1	42.7
TS23	-60.8	-59.7	-57.0	-54.1	-48.1	-41.9	-32.2	-16.1	0.0	16.2	32.4	48.6	64.8
IM3	-60.3	-59.2	-56.7	-54.1	-48.6	-43.3	-35.0	-21.7	-8.7	4.2	16.8	29.3	41.6
TS3P	-53.8	-52.8	-50.5	-48.1	-43.1	-38.2	-30.5	-17.8	-5.1	7.6	20.4	33.1	45.9
PoC1	-64.4	-63.8	-62.9	-62.2	-60.8	-59.7	-58.0	-55.6	-53.5	-51.7	-50.1	-48.6	-47.2
TS14	15.6	16.7	19.4	22.3	28.3	34.3	43.7	59.2	74.6	90.1	105.6	121.1	136.6
IM4	3.0	4.1	6.6	9.3	14.9	20.3	28.6	41.9	54.9	67.6	80.1	92.5	104.8
TS4P	2.6	3.7	6.3	9.0	14.5	20.1	28.8	43.0	57.3	71.6	85.8	100.1	114.4
HCO + CO	-64.7	-65.0	-65.6	-66.2	-67.3	-68.4	-69.7	-71.8	-73.7	-75.5	-77.2	-78.8	-80.3
TSRP + CO	-46.6	-46.9	-47.6	-48.4	-50.0	-51.5	-53.7	-57.0	-59.8	-62.4	-64.7	-66.8	-68.7
PoC2 + CO	-50.5	-51.4	-53.4	-55.7	-60.6	-65.6	-73.1	-85.8	-98.4	-110.9	-123.3	-135.7	-148.1
H + 2 CO	-50.6	-51.6	-54.0	-56.7	-62.2	-67.8	-76.4	-90.7	-105.0	-119.2	-133.3	-147.3	-161.3

Table S7. Traditional Arrhenius' parameters [A (in s^{-1}) and E_{ARR} (in kcal mol $^{-1}$)], which were obtained from ICVT/SCT rate constants calculated for different temperature ranges (in K), T_{R} , for each elementary process involved in the forward $\text{CH} + \text{CO}_2 \rightarrow \text{HCO} + \text{CO}$ and $\text{HCO} \rightarrow \text{H} + \text{CO}$ reactions.

Chemical Process	A	E_{ARR}	MAD ^b	T_{R}
$\text{CH} + \text{CO}_2 \rightarrow \text{IM1}$	6.422×10^{-12} ^a	0.64	7.7	300 – 700
$\text{IM1} \rightarrow \text{IM2}$	1.576×10^{13}	0.22	1.2	300 – 700
$\text{IM2} \rightarrow \text{IM3}$	5.618×10^{12}	0.82	0.6	300 – 700
$\text{IM3} \rightarrow \text{HCO} + \text{CO}$	4.688×10^{13}	7.19	2.6	300 – 700
$\text{IM1} \rightarrow \text{IM4}$	1.101×10^{13}	50.62	12.6	300 – 700
$\text{IM4} \rightarrow \text{HCO} + \text{CO}$	1.207×10^{13}	-0.99	5.7	300 – 700
$\text{HCO} \rightarrow \text{H} + \text{CO}$	4.732×10^{13}	18.55	10.8	300 – 700
$\text{CH} + \text{CO}_2 \rightarrow \text{IM1}$	2.086×10^{-10} ^a	10.18	1.6	2500 – 3500
$\text{IM1} \rightarrow \text{IM2}$	1.496×10^{13}	-0.02	<0.1	2500 – 3500
$\text{IM2} \rightarrow \text{IM3}$	5.590×10^{12}	0.83	0.1	2500 – 3500
$\text{IM3} \rightarrow \text{HCO} + \text{CO}$	7.412×10^{12}	-0.02	<0.1	2500 – 3500
$\text{IM1} \rightarrow \text{IM4}$	2.792×10^{13}	51.67	0.2	2500 – 3500
$\text{IM4} \rightarrow \text{HCO} + \text{CO}$	9.025×10^{12}	-0.91	0.1	2500 – 3500
$\text{HCO} \rightarrow \text{H} + \text{CO}$	1.514×10^{14}	20.14	0.2	2500 – 3500

^a Values given in units of $\text{cm}^3 \text{ particle}^{-1} \text{ s}^{-1}$.

^b MAD means maximum absolute deviations (in %) found between rate constants obtained from traditional Arrhenius' equations and those presented in Table 1.

Table S8. Concentrations at chemical equilibrium (in particle cm⁻³), [X]_{eq}, and time to reach this equilibrium (in seconds), $t_{\text{eq},X}$, for stable species involved in the CH + CO₂ ↔ HCO + CO and HCO ↔ H + CO reactions at different temperatures (in K), T . ^a

T	200	300	500	700	2500	3500
[CH] _{eq}	1.92×10^{-64}	3.32×10^{-41}	1.68×10^{-26}	2.41×10^{-20}	2.99×10^{-9}	6.93×10^{-8}
[CO ₂] _{eq}	1.00×10^{16}					
[IM1] _{eq}	6.53×10^{-33}	2.30×10^{-23}	1.26×10^{-19}	3.96×10^{-18}	5.88×10^{-15}	2.59×10^{-14}
[IM2] _{eq}	3.13×10^{-5}	1.10×10^{-4}	4.03×10^{-8}	1.05×10^{-9}	4.11×10^{-12}	4.30×10^{-12}
[IM3] _{eq}	5.63×10^{-6}	3.66×10^{-5}	2.24×10^{-8}	7.35×10^{-10}	4.38×10^{-12}	4.82×10^{-12}
[IM4] _{eq}	2.15×10^{-67}	2.28×10^{-43}	8.52×10^{-34}	1.29×10^{-27}	1.02×10^{-16}	2.35×10^{-15}
[HCO] _{eq}	1.00×10^{12}	3.67×10^{11}	2.39×10^7	2.74×10^5	1.04×10^2	4.97×10^1
[CO] _{eq}	1.00×10^{12}	1.63×10^{12}	2.00×10^{12}	2.00×10^{12}	2.00×10^{12}	2.00×10^{12}
[H] _{eq}	8.62×10^6	6.33×10^{11}	1.00×10^{12}	1.00×10^{12}	1.00×10^{12}	1.00×10^{12}
$t_{\text{eq,CH}}$ ^b	6.5×10^{-3}	5.8×10^{-3}	3.6×10^{-3}	2.2×10^{-3}	2.6×10^{-4}	1.5×10^{-4}
$t_{\text{eq,CO}_2}$ ^b	6.2×10^{-4}	5.5×10^{-4}	4.2×10^{-4}	3.1×10^{-4}	5.0×10^{-5}	2.9×10^{-5}
$t_{\text{eq,HCO}}$ ^b	1.4×10^2	1.0×10^1	1.0×10^{-3}	6.9×10^{-4}	1.1×10^{-4}	7.2×10^{-5}
$t_{\text{eq,CO}}$ ^b	1.1×10^2	8.0×10^0	6.5×10^{-4}	5.5×10^{-4}	8.1×10^{-5}	4.7×10^{-5}
$t_{\text{eq,H}}$ ^b	3.2×10^2	1.0×10^1	7.2×10^{-4}	5.5×10^{-4}	8.5×10^{-5}	5.3×10^{-5}

^a These simulations were performed considering initial concentrations of 1.0×10^{12} and 1.0×10^{16} particle cm⁻³ for CH and CO₂, respectively. In addition, the initial concentrations for the other molecules were taken as zero.

^b Time for the derivatives of concentration with respect to time, $d[X]/dt$, to stabilize below 1×10^{-40} particle cm⁻³ s⁻¹.