Supporting Information

***Ab initio* Chemical Kinetics for the HCCO + H Reaction**

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Figure S1: The IRC profile for the RTS structure, computed at the UB3LYP/6-311+G(d,p) level.

Figure S2: The fitting curve to the Morse function for the out of plane dissociation of singlet ketene on the S_0 surface (C_s^1) at CCSD/6-311++G(d,p) + ZPE

Figure S3. Minimum energy paths (MEPs) for the fitting curve to the Morse function for the barrierless channels a) ${}^1\text{CH}_2\text{CO}(\text{S-I1}) \rightarrow \text{H} + \text{HCCO}$ along the reaction coordinate of C-H b) ${}^1\text{CH}_2\text{CO}(\text{S-I1}) \rightarrow {}^1\text{CH}_2 + \text{CO}$ along the reaction coordinate of C-C calculated at the CASPT2(8,8)/6-311++G(d,p)//CASSCF(8,8)/6-311++G(d,p) level.

Figure S4. Plot of predicted rate constant for the $\text{H} + \text{HCCO}$ reaction *via* H-abstraction forming minor products $\text{H}_2 + {}^3\text{CCO}$ (k_3) channel with respect to temperature.

Figure S5. Predicted rate constant for formation of major product, ${}^1\text{CH}_2\text{CO} \rightarrow {}^1\text{CH}_2 + \text{CO}$ **a)** at high pressure limit Ar pressure compared with experimental data (Wagner et al. 1971; Warnatz 1984). **b)** at low pressure limit Ar pressure compared with experimental data (Frank et al. 1988; Wagner et al. 1971; Warnatz 1984).

Table S1: Frequencies and Rotational constants of the optimized geometries of the related reactants, products, intermediates and transition states for calculating the rate constants of HCCO + H at CCSD/6-311++G(d,p) level

I. Reactants and Products

R&P	Frequencies (cm ⁻¹)	Rotational constants (GHZ)
HCCO (X ² A'')	466.17 496.39 551.84 1248.37 2073.50 3355.15	1015.36 10.86 10.75
CH ₂ (a ¹ A ₁)	1401.95 2923.93 2991.61	586.51 336.54 213.84
CH ₂ (X ³ B ₁)	1118.02 3149.46 3374.51	1575.20 254.17 218.86
CO (X ¹ Σ ⁺)	2221.81	0.00 57.63 57.63
CCO (a ¹ Δ)	358.32 455.94 1109.36	0.00 11.43 11.43
CCO (X ³ Σ _g)	393.39 393.41 1087.29	0.00 11.50 11.50

II. Intermediates (T stands for Triplet and S for singlet)

Int	Frequencies (cm ⁻¹)	Rotational constants (GHZ)
H ₂ CCO(C _{2v} ; ¹ A ₁)	448.30 489.13 581.94	281.51 10.23 9.87
S-II	1005.93 1168.91 1434.25 2230.10 3216.27 3324.27	
H ₂ CCO (C _s ; ³ A'')	372.96 471.26 721.29	109.80 11.04 10.03
T-II	980.76 1066.24 1459.32 1830.29 3143.92 3289.08	
H:HCCO	12.41 35.79 39.06 467.08 496.18 551.71 1248.02 2073.60 3354.35	34.06 10.59 8.08

III. Transition States

TS	Frequencies (cm ⁻¹)	Rotational constants (GHZ)
T-TS0	-1895.33 265.64 432.75 578.24 827.26 856.74 1124.76 1471.90 2063.26	115.95 9.63 8.89
T-TS1	-589.86 210.85 335.32 519.23 548.98 619.54 1223.52 2063.81 3339.59	125.72 9.77 9.06
T-TS2	-406.22 122.59 233.20 331.66 442.91 1181.22 2116.45 3137.07 3349.12	72.82 7.62 6.90

Table S2: Selected calculated results of energy decomposition and optimum geometries along the fragmentation path of singlet ketene (¹HCCO)

	Energies (hartree)		
R _{C-C}	C-O	C-H	∠HCH	∠CCO	∠HCC	CCSD/BS1 ^a	CCSD(T)/BS2 ^b	T1 ^c
1.6	1.146	1.090	117.04	164.09	107.00	-152.2022041	-152.3131067	0.0216
1.9	1.133	1.107	107.25	158.42	96.31	-152.1542349	-152.2624714	0.0202
2.2	1.129	1.113	103.59	157.11	91.22	-152.1324597	-152.2367719	0.0197
2.5	1.129	1.114	102.37	159.31	87.77	-152.1247387	-152.226715	0.0173
2.8	1.129	1.115	101.93	159.33	85.72	-152.1215338	-152.0382434	0.0185
3.1	1.130	1.115	101.73	159.39	84.02	-152.1196774	-152.2199391	0.0160

^a BS1= 6-311++G(d,p); ^b BS2: 6-311++G(3df,2p) and ^c T1: T1 Diagnostic

Table S3: Comparison of Calculated Thermodynamic Properties of Stable Structures Are Formed from Reactions in System HCCO+H with Experimental Data (NIST= Webbook NIST, webbook.nist.gov, ATcT = Active Thermochemical Tables). Notations for Species are given in Figure 1. Unit: $\Delta H_f, 298K$ in kcal.mol⁻¹, S_{298K} and $C_p(T)$ in cal.mol⁻¹.K⁻¹.

Species	Method	$\Delta H_f, 298K$	S_{298K}	$C_p, 300K$	$C_p, 400K$	$C_p, 500K$	$C_p, 600K$	$C_p, 800K$	$C_p, 1000K$	$C_p, 1500K$
HCCO	Ab initio ^a	42.61	58.80	11.91	13.05	13.91	14.61	15.72	16.57	17.91
	NIST	-	-	-	-	-	-	-	-	-
	ATcT	42.61	58.89	11.97	13.27	14.21	14.93	16.08	16.93	18.27
H	Ab initio ^a	52.10	27.39	4.97	4.97	4.97	4.97	4.97	4.97	4.97
	NIST	52.10[78]	27.42[78]	4.97	4.97	4.97	4.97	4.97	4.97	4.97[77]
	ATcT	52.10	27.42	4.97	4.97	4.97	4.97	4.97	4.97	4.97
S-II	Ab initio ^a	-11.75	57.67	12.28	14.09	15.55	16.76	18.66	20.11	22.44
	NIST	-11.40[79]	-	12.41	14.22	15.68	16.89	18.80	20.25	22.55[80]
	ATcT	-11.61	60.09	12.40	14.20	15.68	16.90	18.79	20.25	22.48
T-II	Ab initio ^a	43.07	62.29	12.36	14.23	15.78	17.05	19.01	20.45	22.69
	NIST	-	-	-	-	-	-	-	-	-
	ATcT	-	-	-	-	-	-	-	-	-
T-I2	Ab initio ^a	62.77	62.08	12.13	14.13	15.81	17.18	19.24	20.70	22.90
	NIST	-	-	-	-	-	-	-	-	-
	ATcT	-	-	-	-	-	-	-	-	-
T-I3	Ab initio ^a	61.69	61.96	11.73	13.79	15.53	16.94	19.05	20.54	22.79
	NIST	-	-	-	-	-	-	-	-	-
	ATcT	-	-	-	-	-	-	-	-	-
T-I4	Ab initio ^a	97.26	62.96	12.77	14.78	16.46	17.80	19.76	21.08	22.88
	NIST	-	-	-	-	-	-	-	-	-
	ATcT	-	-	-	-	-	-	-	-	-
T-I5	Ab initio ^a	95.72	64.36	13.12	14.96	16.38	17.47	19.05	20.17	21.98
	NIST	-	-	-	-	-	-	-	-	-
	ATcT	-	-	-	-	-	-	-	-	-
³ CCO	Ab initio ^a	91.30	55.89	10.35	11.10	11.71	12.21	12.98	13.49	14.17
	NIST	-	55.70[77]	10.31	11.10	11.72	12.24	13.06	13.66	14.66[77]
	ATcT	90.54	55.83	10.33	11.13	11.75	12.24	13.03	13.56	14.41
¹ CCO	Ab initio ^a	109.68	53.65	10.23	11.01	11.64	12.16	12.94	13.46	14.16
	NIST	-	-	-	-	-	-	-	-	-
	ATcT	-	-	-	-	-	-	-	-	-
³ CH ₂	Ab initio ^a	94.64	46.66	8.29	8.64	8.97	9.27	9.86	10.46	11.69
	NIST	92.35[77]	46.35[77]	8.28	8.63	9.00	9.38	10.14	10.89	12.25[77]
	ATcT	93.49	46.46	8.37	8.73	9.07	9.39	9.97	10.59	11.77
¹ CH ₂	Ab initio ^a	102.47	45.21	8.06	8.30	8.62	8.98	9.76	10.50	11.84
	NIST	-	-	-	-	-	-	-	-	-
	ATcT	102.48	45.22	8.08	8.33	8.66	9.04	9.83	10.57	11.94
CO	Ab initio ^a	-26.90	47.20	6.96	7.00	7.10	7.24	7.57	7.87	8.34
	NIST	-26.42 [78]	47.24[78]	6.97	7.00	7.13	7.28	7.62	7.93	8.42[77]
	ATcT	-26.41	47.24	6.96	7.02	7.12	7.27	7.62	7.93	8.40
HC≡COH	Ab initio ^a	22.20	59.10	13.39	15.13	16.42	17.43	18.99	20.19	22.28
	NIST	-	-	-	-	-	-	-	-	-
	ATcT	22.30	59.64	13.80	15.44	16.67	17.64	19.19	20.40	22.43

^a This work at CBS-QB3. ΔH_f calculated by atomization method (See main text for more information).