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New insights on atmospheric acids-catalyzed gas phase hydrolysis of Formaldehyde: A theoretical study

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Table S1 The T1 diagnostic values of all species for the reactions HCHO + H_2O catalyzed by HNO_3, CH_3COOH and HCOOH.

	HCHO	H_2O	HNO_3	HCHO···H_2O	HNO_3···H_2O	CR1a	TS1a
T1 diagnostic value	0.015	0.009	0.018	0.013	0.016	0.016	0.016
	CR1b	TS1b	CP1	$H_2C(OH)_2$	CH_3COOH	CH_3COOH···H_2O	CR2a
T1 diagnostic value	0.016	0.017	0.015	0.011	0.014	0.013	0.014
	TS2a	CR2b	TS2b	CP2	HCOOH	HCOOH···H_2O	CR3a
T1 diagnostic value	0.014	0.014	0.015	0.013	0.016	0.014	0.015
	TS3a	CR3b	TS3b	CP3			
T1 diagnostic value	0.015	0.015	0.016	0.014			

Table S2 The enthalpies, Gibbs free energies, and relative energies of the various configurations for the HCHO···H_2O, HNO_3···H_2O, CH_3COOH···H_2O, HCHO···H_2O···HNO_3, and

HCHO···H_2O···CH_3COOH complexes with zero-point energy correction included (in kcal/mol).

species	ΔH^a	ΔG^a	ΔE^a	ΔH^b	ΔG^b	ΔE^b
HCHO···H_2O_{global}	-4.63	3.10	-4.16	-3.74	3.99	-3.27
HNO_3···H_2O-1	-1.41	3.08	-1.74	-0.98	3.51	-1.31
HNO_3···H_2O-2	-1.84	4.24	-2.01	-1.35	4.73	-1.52
CH_3COOH···H_2O-1	-5.80	0.58	-5.66	-4.87	1.51	-4.74
CH_3COOH···H_2O-2	-4.07	2.84	-3.99	-2.72	4.18	-2.65
CR1-1	-17.46	-0.94	-17.00	-14.11	2.42	-13.65
CR1-2	-14.61	2.41	-14.42	-11.87	5.15	-11.68
CR1-3	-17.84	-0.56	-17.31	-14.56	2.72	-14.03
CR1-4	-20.06	-2.25	-19.55	-15.86	1.96	-15.34
CR1-5	-15.88	1.03	-15.73	-12.77	4.14	-12.62
CR1-6	-18.45	0.45	-17.84	-13.54	5.35	-12.93
CR2-1	-12.66	4.54	-12.45	-10.91	6.28	-10.70
CR2-2	-15.01	2.33	-14.45	-12.71	4.63	-12.14
CR2-3	-16.80	0.81	-16.45	-14.12	3.49	-13.76
CR2-4	-14.54	2.20	-14.39	-12.82	3.92	-12.67
CR2-5	-12.85	3.71	-12.71	-10.96	5.60	-10.82
CR2-6	-12.36	3.99	-12.21	-10.34	6.00	-10.19

[a] ΔH, ΔG, and ΔE are obtained at the M06-2X/6-311++G(d,p) level of theory.

[b] ΔH, ΔG, and ΔE are calculated at the CCSD(T)-F12A/VTZ-F12//M06-2X/6-311++G(d,p) level of theory.

Table S3 The enthalpies, Gibbs free energies, and relative energies of all species for the reaction HCHO + H_2O + HCOOH with zero-point energy correction included (in kcal/mol).

species	ΔH^a	ΔG^a	ΔE^a	ΔH^b	ΔG^b	ΔE^b

HCHO + H_2O + HCOOH	0.00	0.00	0.00	0.00	0.00	0.00
HCHO···H_2O + HCOOH	-1.75	4.91	-1.67	-1.84	4.81	-1.77
HCHO + HCOOH···H_2O	-8.53	0.46	-7.86	-8.64	0.35	-7.97
CR3a	-9.98	8.65	-9.35	-10.51	8.12	-9.88
TS3a	-9.71	9.20	-8.91	-10.30	8.61	-9.50
CR3b	-13.73	4.79	-13.04	-14.37	4.15	-13.67
TS3b	-4.25	18.71	-1.68	-5.07	17.88	-2.51
CP3	-22.07	-0.58	-20.08	-22.54	-1.05	-20.55
$H_2C(OH)_2$ + HCOOH	-10.16	0.69	-8.36	-10.08	0.77	-8.27

[a] ΔH, ΔG, and ΔE are obtained at the CCSD(T)-F12A/VTZ-F12//M06-2X/6-311++G(d,p) level of theory.

[b] ΔH, ΔG, and ΔE are calculated at the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(d,p) level of theory.

Table S4 Calculated equilibrium constants (molecules cm^{-3}) for the formation of the complex HCOOH···H_2O, the rate constants (cm^3 $molecule^{-1}$ s^{-1}) for the individual reaction pathway and the ratio of rate expressions of between the HCHO + HCOOH···H_2O path and the HCHO···H_2O +

HCOOH path for the reaction of HCHO with H_2O catalyzed by HCOOH with the temperature range 200−300 K

reaction	200 K	220 K	240 K	260 K	280 K	298 K	300 K
$K_{HCOOH \cdot H_2O}$	1.55×10^{-17}	2.37×10^{-18}	5.02×10^{-19}	1.36×10^{-19}	4.47×10^{-20}	1.88×10^{-20}	1.72×10^{-20}
k_3	1.26×10^{-16}	8.54×10^{-17}	6.19×10^{-17}	4.70×10^{-17}	3.71×10^{-17}	3.08×10^{-17}	3.02×10^{-17}
K_3'	3.65×10^{-26}	2.63×10^{-25}	1.38×10^{-24}	5.65×10^{-24}	1.90×10^{-23}	4.92×10^{-23}	5.43×10^{-23}
ratio 3	6.66×10^{-5}	1.56×10^{-4}	3.18×10^{-4}	5.80×10^{-4}	9.73×10^{-4}	1.46×10^{-3}	1.52×10^{-3}

Table S5 The Cartesian coordinates, vibrational frequencies, and total energies of all species for the reactions HCHO + H_2O + HNO_3, HCHO + H_2O + CH_3COOH and HCHO + H_2O + HCOOH. The Cartesian coordinates and vibrational frequencies are obtained at the M06-2X/6-311++G(d,p)

level of theory, while the total energies are obtained at the CCSD(T)-F12A/VTZ-F12//M06-2X/6-311++G(d,p) level of theory.

HCHO

C	0.00000500	0.52564700	0.00000000
H	-0.93961300	1.10737500	0.00000000
H	0.93954100	1.10752700	0.00000000
O	0.00000500	-0.67109800	0.00000000

1219.4280 1273.2843 1544.1469
1874.8458 2943.1116 3016.8832
CCSD(T)-F12A: -114.38932218

H_2O

O	0.00000000	0.00000000	0.11676300
H	0.00000000	0.76103600	-0.46705200
H	0.00000000	-0.76103600	-0.46705200

1599.7961 3892.1190 3996.8634
CCSD(T)-F12A： -76.37493660

HNO_3

N	0.00000000	0.14588500	0.00000000
O	1.16441400	0.44360800	0.00000000
O	-0.96169700	0.83992800	0.00000000
O	-0.27725200	-1.20760900	0.00000000
H	0.59628200	-1.62860700	0.00000000

469.0596 624.1164 709.1354
811.3871 983.3814 1370.0301
1427.4262 1830.0281 3802.1546
CCSD(T)-F12A： -280.65951087

$HCHO\cdots H_2O$

C	-0.96674300	0.55736700	0.00017600
H	-0.84815200	1.12607400	-0.93748800
H	-0.84306000	1.12506300	0.93776900
O	-1.21364800	-0.61702900	0.00012900
O	1.66279400	0.03435100	-0.00033400
H	1.28383400	-0.84957000	-0.00104100
H	2.61466300	-0.08434400	0.00134500

95.3153 100.2561 145.5931
162.8887 267.0389 284.4704

1219.1581	1273.6675	1546.2310
1599.5901	1862.0537	2970.6848
3047.8632	3869.2876	3982.7655

CCSD(T)-F12A： -190.76935223

$HNO_3\cdots H_2O$

N	0.83921400	0.07302600	0.00224300
O	0.22068000	1.11578500	-0.00177300
O	2.01939800	-0.07477800	0.01429100
O	0.11354000	-1.07242500	-0.00641700
H	-0.83827700	-0.78751400	-0.01807500
O	-2.33193500	-0.02594800	-0.06549600
H	-2.08627300	0.90211300	0.01873300
H	-3.12341300	-0.16684700	0.45879900

69.2223	139.2889	180.2339
227.1863	301.2992	446.5152
671.6991	727.1669	809.8817
833.0857	1024.4918	1416.1787
1519.6209	1596.1991	1817.8437
3287.1930	3857.0059	3973.8733

CCSD(T)-F12A： -357.05063992

CR1a

N	1.17185000	0.03824200	0.08500400
O	0.73170900	0.24366600	1.19473500
O	1.82869200	-0.89978900	-0.26475800
O	0.89570300	0.94331900	-0.86968400
H	0.11347700	1.47744000	-0.51732700
O	-1.31853700	1.95002300	0.00576500
H	-1.74601000	1.07918900	0.02067700
H	-1.26965700	2.22976000	0.92441700
O	-1.67940500	-0.85462300	-0.29400000
C	-1.17990900	-1.89126200	0.05899600
H	-1.40203400	-2.83373200	-0.46622700
H	-0.48456500	-1.93354600	0.91298700

50.3969	71.9644	96.5517
104.6229	121.9490	148.3979
193.2277	234.3851	253.5973
255.3598	426.9063	608.0886
678.5095	729.4792	833.9333
1035.3265	1055.6889	1234.7321
1278.3994	1427.7839	1513.5396

1542.0420	1640.1322	1786.8907
1850.0546	2953.5814	2984.4973
3077.3958	3767.6383	3931.0544

CCSD(T)-F12A： -471.45006187

TS1a

O	-0.57726200	0.29879500	-1.03856700
O	-0.79655600	-0.02191200	1.11636200
H	0.14207800	0.25885900	1.01090600
O	1.26550400	1.79123500	0.45288000
H	0.74487400	2.03224600	-0.32040000
H	1.46507400	2.60716800	0.91757800
O	1.68499500	-1.12967700	0.40488700
C	2.29261700	-0.91113900	-0.60611900
H	2.00930700	-0.08648100	-1.27953600
H	3.15748100	-1.53114900	-0.89908200
N	-1.28289000	-0.11349300	-0.14068300
O	-2.37254700	-0.58361100	-0.23150400

-107.4450	72.0299	87.8351
92.8423	102.6864	116.6821
158.3947	166.5767	195.1293
206.8416	282.6647	350.3105
558.9065	664.6499	728.1665
826.4867	1031.8483	1215.7350
1275.9615	1417.2297	1489.8978
1537.6121	1586.9735	1807.3898
1865.3478	2967.8565	3055.5900
3546.4737	3859.3705	3973.7009

CCSD(T)-F12A：-471.44228853

CR1b(HCHO…H_2O…HNO_3)

N	1.52847500	0.17305600	0.05615900
O	0.55339700	0.80857400	0.41690100
O	2.64940900	0.56223600	-0.02612300
O	1.32532500	-1.11126200	-0.27870400
H	0.32956800	-1.26674500	-0.22745900
O	-1.24785200	-1.49724700	-0.27223000
H	-1.16862100	1.73220300	-0.22268500
O	-2.11855200	1.57160900	-0.25779000
H	-2.47067500	2.17183100	-0.91794700
C	-1.99634500	-0.88432300	0.45362600
H	-1.62279000	-0.27630200	1.28643100
H	-3.08254700	-0.93772000	0.31035800

46.0668	63.3779	101.8724
117.1132	140.8717	151.1857
182.5174	223.3312	260.7516
325.3701	388.3718	436.4762
672.8779	729.4857	826.1291
937.5547	1048.1765	1228.4689
1273.6803	1413.9604	1522.3599
1534.4148	1608.1893	1800.8332
1822.5555	2959.2676	3045.3957
3135.6400	3849.1470	3971.0284

CCSD(T)-F12A： -471.44916058

TS1b

N	-1.49685700	-0.06793300	0.00727600
O	-0.74289800	-1.05631000	-0.10669400
O	-2.68482500	-0.16804800	0.08795000
O	-0.96497100	1.11073200	0.04930700
H	0.23179100	1.13596100	-0.25307600
O	1.37685600	1.16291300	-0.45499700
H	0.86802300	-1.33904000	-0.05958400
O	1.85864600	-1.27899600	0.00741800
H	2.20360300	-1.40948100	-0.88460800
C	1.97906100	0.50875600	0.43887700
H	1.49027000	0.33665900	1.40174300
H	3.06748300	0.53656200	0.44746200

-497.9787	38.5352	71.0707
160.8901	182.2301	256.2462
381.8694	427.7316	486.9152
696.1850	731.9560	744.7039
809.5707	840.7250	935.7118
1077.7622	1129.9900	1246.4402
1313.3543	1420.5958	1450.4300
1491.4654	1619.3086	1657.7882
1672.8855	1720.4795	3084.1598
3188.9616	3257.9118	3870.1946

CCSD(T)-F12A：-471.43031294

CP1

N	1.58825400	-0.13646000	0.02272100
O	1.18951400	1.14574500	-0.08849100
O	2.76189900	-0.31795800	-0.02099600
O	0.71684800	-0.97457300	0.16177300

H	-1.22714400	-1.40015000	-0.48711300
O	-2.12069000	-1.04143300	-0.42211800
H	0.18503000	1.13474700	-0.07646400
O	-1.42399500	1.15141200	-0.07957000
H	-1.86123300	1.39249800	-0.90390300
C	-2.09023700	0.01134600	0.47038900
H	-1.53844500	-0.21903600	1.38284400
H	-3.12317700	0.27353000	0.69847400

47.2138	74.5399	137.9696
146.8544	192.9701	236.3922
399.9371	512.8344	599.9522
669.5726	730.9110	821.9473
927.0056	1009.0047	1044.1773
1060.2934	1148.2972	1231.1320
1379.9913	1411.6140	1424.2683
1465.6484	1527.9666	1535.9843
1807.5233	3057.1939	3101.1489
3159.7155	3851.7747	3868.9273

CCSD(T)-F12A：-471.46645258

$H_2C(OH)_2$

C	0.00016600	0.53224600	-0.00000200
H	-0.00143100	1.15892100	0.89475200
H	0.00149200	1.15905100	-0.89468800
O	-1.15915500	-0.24738400	-0.09392800
H	-1.23137000	-0.77622200	0.70632700
O	1.15906100	-0.24747000	0.09391500
H	1.23106500	-0.77639800	-0.70628200

374.1640	407.8412	578.7513
1019.5029	1082.0312	1122.3408
1216.0538	1371.7931	1401.4388
1463.8716	1539.5778	3076.1521
3127.8633	3883.7716	3884.5537

CCSD(T)-F12A：-190.78711912

CH_3COOH

C	-1.38983300	-0.12177800	0.00001100
H	-1.66012400	-0.70560100	-0.88079500
H	-1.66001500	-0.70628600	0.88040400
H	-1.91573500	0.82866400	0.00042600
C	0.09023500	0.12675200	-0.00002700
O	0.62728000	1.19871200	0.00000200

O	0.78625400	-1.02955100	-0.00001300
H	1.72518500	-0.79990100	0.00014600

82.3639	428.7299	540.3277
599.7942	658.5124	886.5686
1012.6130	1074.2897	1236.2379
1349.7110	1423.7612	1477.5160
1480.4942	1884.1344	3090.3807
3160.6797	3206.5967	3834.7630

CCSD(T)-F12A：-228.86551546

$CH_3COOH\cdots H_2O$

C	2.16006600	-0.00710400	0.00111000
H	2.48876100	-0.58187200	0.86785000
H	2.48226300	-0.54434000	-0.89203600
H	2.59155400	0.98965900	0.01901800
C	0.66222100	0.09042700	0.00535100
O	0.04622900	1.13260800	0.00467200
O	0.07839800	-1.10622400	0.00867100
H	-0.89536600	-0.98548600	0.00476700
O	-2.43417100	-0.05050600	-0.07689000
H	-1.92323200	0.77122900	-0.02039800
H	-3.20135600	0.04384000	0.49041100

69.8097	91.6445	174.3148
205.2370	213.7684	356.6787
450.9153	578.8897	599.6966
640.9463	873.1619	912.7899
1027.7345	1076.3555	1321.2593
1394.9888	1458.3472	1478.3333
1482.1559	1593.2785	1837.2785
3088.9933	3159.3363	3204.0964
3539.7445	3765.8210	3965.7253

CCSD(T)-F12A： -305.25690174

CR2a

C	-2.34433300	0.41558900	0.10088800
H	-2.08287300	1.41822200	-0.24466700
H	-3.06003800	-0.01284400	-0.59976500
H	-2.75801200	0.46684100	1.10435500
C	-1.08033100	-0.38518300	0.11335200
O	-0.46371800	-0.67756100	1.11776000
O	-0.68677800	-0.73496700	-1.10865900
H	0.20790800	-1.12334100	-1.05742300

O	1.81096700	-1.45843700	-0.10843300
H	1.23675300	-1.43952500	0.67528500
H	2.37906200	-2.22841200	-0.04084500
O	0.66986700	1.82068300	-0.36003600
C	1.63228100	1.43843300	0.24609200
H	1.53483300	0.94447000	1.22728200
H	2.65396300	1.56380700	-0.15127300

63.8733	79.6723	93.4990
109.3035	114.2720	129.2790
152.4131	183.3958	213.4928
267.3712	280.8081	371.3746
451.4869	587.1655	624.7300
650.1089	809.5208	915.3040
1034.0736	1074.7239	1216.5840
1272.3413	1312.7982	1382.9596
1450.7904	1476.7126	1485.6816
1536.2437	1575.0176	1818.8129
1862.0642	2967.0631	3048.9727
3087.5557	3163.6636	3203.7886
3630.1005	3717.1593	3956.6610

CCSD(T)-F12A： -419.65227932

TS2a

C	-2.80317500	-0.31749500	-0.20138900
H	-2.89205200	-1.40479100	-0.16820400
H	-3.36230300	0.08531600	0.64336600
H	-3.19633400	0.06031000	-1.14091600
C	-1.35464500	0.05068000	-0.07387900
O	-0.69858500	0.55777600	-0.95822000
O	-0.86417600	-0.24146600	1.12448900
H	0.10106100	-0.11069800	1.11776600
O	1.50728500	1.62071400	0.34288300
H	0.77771400	1.55038100	-0.29195100
H	1.58418800	2.54732900	0.57761800
O	1.65919900	-1.36980900	0.26086300
C	2.30985000	-0.77860100	-0.55715700
H	1.84384900	-0.33056100	-1.45016200
H	3.40191300	-0.66251700	-0.45308300

-82.6103	39.4798	61.5777
78.7420	97.4025	117.0782
138.9971	158.9502	196.0611
249.3908	273.0476	346.9395

450.6193	538.4584	593.5382
624.0612	717.5571	910.7158
1028.9350	1075.4685	1222.1911
1274.1980	1291.0322	1376.2813
1448.9857	1477.8479	1482.1769
1538.8140	1595.6698	1823.7281
1859.9409	2972.2048	3054.0905
3089.2533	3160.4855	3204.4797
3718.3788	3748.8660	3959.4107

CCSD(T)-F12A： -419.64930599

CR2b(HCHO…H_2O…CH_3COOH)

C	2.91574300	0.37637600	0.06928200
H	3.37344500	-0.22290600	0.85751600
H	3.37419900	0.08098300	-0.87546700
H	3.07669000	1.43444400	0.25528200
C	1.44318800	0.08666400	0.01745700
O	0.58185900	0.92757400	0.16551600
O	1.18421600	-1.19159100	-0.20235800
H	0.20718400	-1.33566600	-0.24761600
O	-1.50690900	-1.48915200	-0.29853600
C	-2.15038300	-0.81599000	0.46995700
H	-1.15235500	1.60863400	-0.13892400
O	-2.11869900	1.67162500	-0.15887600
H	-3.24277100	-0.74505400	0.38737900
H	-1.67482700	-0.26529500	1.29370800
H	-2.33657900	2.21491300	-0.91802400

40.7093	59.5124	78.6632
83.0258	115.2414	137.7072
175.0325	177.2330	205.1419
242.4995	368.2557	418.8268
456.4776	547.8287	602.7257
625.1970	917.6827	938.9276
1031.2488	1076.3104	1217.0753
1269.3454	1329.7453	1390.5814
1461.8888	1479.4465	1481.7218
1533.3719	1616.9839	1812.2812
1839.7522	3012.1280	3089.2658
3107.6718	3159.2423	3204.5325
3352.3104	3777.1391	3964.3528

CCSD(T)-F12A： -419.65656006

TS2b

C	2.84351200	0.09238900	0.07690400
H	3.19394700	-0.57783300	0.86159800
H	3.25210400	-0.26822000	-0.86905900
H	3.17526700	1.11097300	0.25880600
C	1.34276100	0.03517700	0.00031200
O	0.68606700	1.09155500	-0.02405600
O	0.84120200	-1.14232000	-0.04091400
H	-0.28176600	-1.18909500	-0.20035800
O	-1.54667400	-1.17515600	-0.35959300
C	-2.07315800	-0.36978600	0.46624600
H	-0.74033500	1.25722600	-0.10347700
O	-1.78673000	1.26788400	-0.09223600
H	-3.16326600	-0.31291900	0.50347200
H	-1.58255900	-0.19713100	1.43298000
H	-2.08300000	1.29461800	-1.01034100

-514.4674	43.1421	84.6314
91.5076	160.6337	183.0252
314.1971	374.9042	488.9080
549.8387	594.5282	627.0215
659.1670	820.0078	932.9831
992.6132	1047.6271	1079.1271
1099.0583	1241.2095	1292.5270
1358.1771	1383.3919	1401.0375
1443.4556	1471.0023	1480.6041
1506.7604	1595.6197	1638.7568
1682.6702	1777.1563	2410.5383
3036.8168	3088.0450	3127.3990
3159.4311	3202.2635	3866.2047

CCSD(T)-F12A： -419.63751164

CP2

C	2.96253500	-0.21171100	0.05312900
H	3.24053100	-1.26050100	0.10516300
H	3.39543300	0.25403300	-0.83322200
H	3.33944400	0.32616600	0.92410300
C	1.46766400	-0.08517800	0.00037900
O	1.06479100	1.17550100	-0.06586900
O	0.70651300	-1.02870600	0.01994100
H	-1.13998300	-1.35826200	-0.38958800
O	-2.07831700	-1.11818600	-0.34320000
C	-2.16524500	-0.02234900	0.49015600
H	0.07884700	1.20960600	-0.11007500
O	-1.64428800	1.15645800	-0.12651300

H	-3.21867700	0.12663300	0.73095500
H	-1.57659100	-0.13838300	1.40338900
H	-2.09832300	1.27559200	-0.96758700

49.4358	77.5955	86.6606
112.9390	147.2108	188.1151
209.7930	405.0793	456.1556
555.7744	604.4090	629.0469
700.2809	914.0050	943.8567
1024.5984	1031.0042	1052.9459
1077.0610	1152.5664	1235.7475
1329.2596	1376.2274	1392.6456
1437.7703	1461.4742	1472.5595
1479.6518	1481.9586	1532.5923
1824.8469	3083.4293	3088.8852
3141.2846	3158.7050	3204.8012
3379.0447	3764.4496	3875.0520

CCSD(T)-F12A： -419.67417662

HCOOH

C	0.13533100	0.39857300	0.00005300
H	0.11015800	1.49478500	-0.00002400
O	1.12728000	-0.26500800	-0.00008200
O	-1.11083800	-0.08887300	0.00004400
H	-1.05367500	-1.05518400	0.00001500

646.4672	677.2334	1075.8281
1169.2011	1313.5119	1418.8272
1879.5331	3103.7164	3817.1832

CCSD(T)-F12A： -189.59579218

HCOOH…H_2O

C	1.19879900	-0.05452600	-0.00467000
H	2.28927600	0.05794100	-0.00303200
O	0.64371300	-1.12384000	-0.00479200
O	0.60117900	1.12402800	-0.00779400
H	-0.37258700	0.98758500	-0.00635800
O	-1.87408200	0.02037300	0.07086300
H	-1.39413000	-0.81792100	0.00992100
H	-2.68184000	-0.06494100	-0.43872100

155.0848	192.9116	212.4552
229.3682	367.3069	537.9244
704.4860	888.8650	1088.2392

1249.8404	1396.1272	1454.9137
1590.7667	1836.2595	3103.5109
3508.6186	3789.9899	3968.8037

CCSD(T)-F12A： -265.98709144

CR3a

C	1.28671200	-0.82596100	0.19536700
O	0.99599800	-0.18583900	1.17764200
O	1.25544100	-0.38110700	-1.04664800
H	0.85048200	0.51002500	-1.05786500
O	-0.02300300	1.93262500	-0.19320100
H	0.33476700	1.59481400	0.64256800
H	0.09727000	2.88443100	-0.20422700
O	-1.54032000	-1.08568000	-0.37419400
C	-1.96637600	-0.16229000	0.26114300
H	-1.55496100	0.09231000	1.25303600
H	-2.78733400	0.47149500	-0.11626800
H	1.63282500	-1.86356000	0.23490400

59.7880	86.1300	118.5528
129.7099	151.2388	180.3958
204.9014	221.8864	273.5008
301.9540	379.0916	608.5476
702.9269	836.0867	1082.2187
1216.7556	1246.8169	1273.7180
1391.7275	1444.0849	1536.8730
1577.1727	1819.1207	1865.4407
2962.4134	3041.1015	3122.5809
3601.8616	3752.7749	3957.9016

CCSD(T)-F12A： -380.38106115

TS3a

C	1.61534500	-0.60326100	0.21109400
O	1.05064900	-0.14773300	1.17667300
O	1.30781500	-0.36392300	-1.04518800
H	0.49073000	0.17472600	-1.07706000
O	-0.31707100	1.87365800	-0.17701600
H	0.11881300	1.51574500	0.60920900
H	-0.04742400	2.79137800	-0.24972400
O	-1.48939700	-0.81460800	-0.59369100
C	-2.07312200	-0.52898400	0.41413100
H	-1.55477400	-0.06452700	1.26901200
H	-3.15385900	-0.72646700	0.52638900
H	2.47720800	-1.27654100	0.28460700

-93.3685	70.2146	94.9435
114.1892	130.3910	141.7292
179.3695	199.4851	215.0262
246.9880	324.3128	554.6220
696.8750	756.0133	1085.9803
1221.2779	1254.2685	1278.7097
1397.2092	1443.9562	1540.2674
1590.7731	1820.6679	1867.7815
2962.8146	3049.8391	3101.4085
3646.2284	3786.0188	3962.3308

CCSD(T)-F12A： -380.37943174

CR3b

O	-0.85143800	-1.22438000	0.18648000
O	-1.87474400	0.74390600	-0.15175700
H	-0.95124000	1.10161100	-0.22516500
O	0.66531700	1.59875900	-0.32212200
H	1.00760000	-1.51917500	-0.13118400
O	1.95842600	-1.33982700	-0.15457300
H	2.31149800	-1.85030600	-0.88519700
C	1.45413000	1.09587800	0.44193100
H	1.12546200	0.46858300	1.28232900
H	2.53322800	1.26593200	0.33789100
C	-1.84565000	-0.55036600	0.06328100
H	-2.85791100	-0.96738300	0.12582700

44.4232	89.7165	94.6042
139.8817	180.8440	183.0696
206.1584	238.1417	247.7478
366.3860	421.5108	532.8413
699.9667	968.8104	1096.2582
1217.5916	1269.1164	1278.0026
1404.9888	1451.4319	1534.6388
1614.5902	1809.2819	1841.5861
3015.1167	3097.4213	3113.1841
3269.0935	3790.1129	3965.4920

CCSD(T)-F12A： -380.38702034

TS3b

C	1.80503600	0.13988700	0.05533700
O	1.12196000	1.17163800	0.02341000
O	1.38569300	-1.05990900	-0.00731000
H	0.25436300	-1.17260700	-0.19314800

O	-0.98587600	-1.21665000	-0.37389000
C	-1.56805600	-0.44909000	0.44762400
H	-0.34100900	1.28432800	-0.09637200
O	-1.37447600	1.22443400	-0.10862600
H	-2.65922800	-0.45105600	0.46687700
H	-1.09608800	-0.24136400	1.41581200
H	-1.65169600	1.24272700	-1.03285200
H	2.89336300	0.23708900	0.15324200

-574.7363	85.8202	159.5620
174.9707	261.8046	336.8012
461.5848	525.5836	587.0995
729.1523	803.8548	867.7370
1059.1531	1095.9834	1233.8756
1260.9690	1343.7847	1391.7176
1421.4952	1434.6208	1449.9509
1598.8095	1640.6388	1681.3230
1784.4813	2559.4594	3047.6789
3089.9440	3142.4583	3867.5767

CCSD(T)-F12A： -380.36874022

CP3

O	1.65420900	1.00630300	-0.03431500
O	1.12674900	-1.17415500	0.04619700
H	-0.76529000	-1.35482800	-0.38176700
O	-1.67305000	-1.01850800	-0.34360400
H	0.67374700	1.13593300	-0.09881000
O	-1.02576800	1.20716500	-0.14813100
H	-1.46218900	1.36070400	-0.99306000
C	-1.65717900	0.08857100	0.47885200
H	-1.08474000	-0.07303500	1.39542300
H	-2.69205300	0.33962800	0.71415600
C	1.93356900	-0.27654500	0.03871900
H	3.01506400	-0.44699300	0.09745300

60.4865	117.6530	136.6334
189.2820	226.9117	241.1708
395.6775	552.9343	672.2057
701.6939	961.9517	1023.3018
1052.4837	1099.8587	1152.8852
1233.4170	1272.8541	1376.3911
1405.0952	1431.1925	1457.2624
1471.3281	1534.8109	1825.1386
3084.0348	3101.3895	3143.5072

3320.1453 3781.3776 3874.1849
CCSD(T)-F12A： -380.40443183

Table S6 The atomic Cartesian coordinates of the various configurations for the HCHO···H_2O, HNO_3···H_2O, CH_3COOH···H_2O, HCHO···H_2O···HNO_3, and HCHO···H_2O···CH_3COOH complexes obtained at the M06-2X/6-311++G(d,p) level of theory

HCHO···H_2O_{global}

C	1.11392400	0.70576900	0.00000000
H	1.99539900	1.36871900	0.00000000
H	1.28840800	-0.38262400	0.00000000
O	0.00000000	1.15801700	0.00000000
O	-0.89510300	-1.50350000	0.00000000
H	-1.76376900	-1.90765900	0.00000000
H	-1.04276000	-0.54918800	0.00000000

HNO_3···H_2O-1

N	-0.81861500	0.09250500	-0.00039000
O	0.08503900	-0.71025900	-0.00284400
O	-0.77320100	1.27456800	0.00042000
O	-2.08648600	-0.43593900	0.00175200
H	-1.94791800	-1.39629000	0.00054000
H	2.09280200	-0.03562100	-0.00413300
H	3.39568000	-0.82116200	0.01602400
O	3.04836500	0.07232200	-0.00054000

HNO_3···H_2O-2

N	-0.89684100	-0.13741800	-0.00227600
O	-2.09304800	-0.19440100	0.02021400
O	-0.09676500	-1.02247000	-0.01700400
O	-0.33678700	1.11622100	-0.01315300
H	-1.09171300	1.72563500	0.00190600
H	1.91001100	-0.28069700	-0.00961900
O	2.78482200	0.11809300	0.01111600
H	3.39380500	-0.62255100	0.01425500

CH_3COOH···H_2O-1

C	0.32725600	1.34326200	-0.00026900
H	0.74133500	1.83367800	0.88201100
H	0.74755500	1.83586200	-0.87832800
H	-0.75784500	1.41361000	-0.00370400
C	0.74752200	-0.09425700	-0.00018000
O	0.01364900	-1.05192600	-0.00003700
O	2.08243500	-0.23514500	0.00004600

H	2.27575000	-1.18263200	0.00050200
H	-3.40536800	-0.54163900	-0.00577500
O	-2.61899200	0.00576900	0.00092000
H	-1.86683000	-0.60249600	0.00055200

$CH_3COOH\cdots H_2O$-2

C	-0.23229500	1.30420700	0.00200000
H	0.41494600	1.36421300	0.87830300
H	0.42159200	1.36338400	-0.86938600
H	-0.95654800	2.11362400	-0.00100800
C	-0.95893200	-0.00446000	0.00002400
O	-2.14362300	-0.17218200	-0.00444300
O	-0.09727800	-1.06085700	0.00410200
H	-0.63034200	-1.86739800	0.00289900
O	2.57241300	0.02456300	-0.00046400
H	1.85883100	-0.62357800	0.00107900
H	3.38678800	-0.48091800	-0.01759500

CR1-1

N	-2.24154400	-0.05059600	-0.02236900
O	-1.91608000	1.11376700	0.07461400
O	-3.34413900	-0.49024400	-0.12637500
O	-1.24948900	-0.96822800	-0.01375500
H	-0.39596300	-0.44719400	0.08112000
O	0.84745200	0.54731500	0.27753200
H	0.43251100	1.41301500	0.20293000
H	1.66847000	0.55704700	-0.24147700
O	3.44174600	0.15554600	-0.62262200
C	3.91284100	-0.43426300	0.31375600
H	3.31784900	-0.63918400	1.21930600
H	4.95497700	-0.78917400	0.29701800

CR1-2

C	1.52160800	1.07365100	0.00100500
H	2.57113600	1.39648900	0.00193400
H	0.71710700	1.82128700	-0.00086800
O	1.25849600	-0.10859900	0.00200100
O	4.05833700	-0.37965200	-0.00320400
H	3.24628600	-0.89749300	0.00084200
H	4.78054800	-1.00976300	0.00842200
H	-0.32405000	-0.73291600	0.00091800
O	-1.54562700	1.05182000	-0.00031200
O	-1.24113800	-1.11191400	0.00060800
N	-2.07099200	-0.03962400	-0.00031700

O	-3.23303400	-0.29442300	-0.00097600

CR1-3

C	2.55744800	-1.19242700	-0.11007200
H	3.22121700	-2.05251600	-0.28980100
H	1.55017700	-1.40156200	0.28760300
O	2.92423700	-0.06965400	-0.34273900
O	0.85301600	1.63891500	0.39065600
H	0.46313300	2.16673200	-0.31324900
H	1.69440300	1.28323600	0.05679000
H	-0.15093700	0.49861600	0.72040200
O	-1.75174300	0.82996400	-0.71886600
O	-0.73836400	-0.32126600	0.83745500
N	-1.74625800	-0.18271100	-0.05546100
O	-2.52450600	-1.08557900	-0.09314200

CR1-4

C	-2.59280100	-1.19814200	-0.00971600
H	-3.50894200	-1.80052500	0.10145200
H	-1.65151200	-1.72229700	-0.22633000
O	-2.63403600	-0.00019500	0.10751500
H	-0.96995300	2.68104100	0.34994000
H	-1.29190100	1.21198600	-0.06226000
O	-0.62495600	1.92123300	-0.12345700
H	0.82034200	1.35778100	0.00166100
O	0.40191700	-0.77459400	-0.12249800
O	1.73994300	0.93785800	0.06713000
N	1.54890000	-0.38919900	-0.00305200
O	2.53169200	-1.06114600	0.06070900

CR1-5

C	2.03071200	-1.21814200	0.07067200
H	3.02900500	-1.68109900	0.09688900
H	1.96354700	-0.12351900	0.12518200
O	1.05150000	-1.92261400	-0.02107600
O	2.02579800	2.04473800	-0.16140900
H	2.37346900	2.93406800	-0.07422600
H	1.07472100	2.11259400	-0.02429100
H	-0.49137900	-1.39892500	-0.09572100
O	-0.37446700	0.72220600	0.30796700
O	-1.44833300	-1.10988000	-0.17611100
N	-1.44886000	0.21612500	0.04238200
O	-2.50344900	0.75965700	-0.04293700

CR1-6

N	1.10510400	-0.39807000	-0.05225500
O	0.80181400	-1.00881500	-1.04563200
O	1.93607300	0.45967700	0.05441700
O	0.43609200	-0.68942500	1.08622700
H	-0.40568600	-1.15978300	0.78775900
O	-1.85701400	-1.42858800	0.15756500
H	-1.78799400	-1.96121400	-0.64039500
H	-2.02080900	-0.52190800	-0.14551500
O	-1.28542500	1.29744100	-0.41393100
C	-0.55850500	2.08059800	0.14189400
H	-0.15138400	1.87571400	1.14447700
H	-0.27115200	3.02778000	-0.34107400

CR2-1

C	-1.58727800	1.03218800	0.00071200
H	-2.61406700	1.42606300	-0.00305600
H	-0.73146000	1.72063100	0.00392200
O	-1.40514700	-0.16509700	0.00103300
O	-4.20648600	-0.36252800	0.00535300
H	-3.34318700	-0.79298900	-0.00092400
H	-4.85597400	-1.06513200	-0.04753300
H	0.28600500	-0.82934500	0.00310500
O	1.49411500	1.12573000	-0.00222600
O	1.23053000	-1.09147700	0.00242600
C	1.97151100	0.01677800	-0.00060500
C	3.44333400	-0.28289400	-0.00110500
H	3.69033600	-0.88531900	-0.87627700
H	3.69319500	-0.86993900	0.88374400
H	4.00565800	0.64656900	-0.00968100

CR2-2

C	-3.60633700	-0.20519500	-0.06765400
H	-3.83597400	-0.71087400	-1.00650200
H	-3.89204900	-0.87418700	0.74525300
H	-4.15253300	0.73124600	0.00260800
C	-2.13045500	0.06318400	0.00542500
O	-1.64359100	1.16455500	0.12973700
O	-1.40864000	-1.05130100	-0.08183100
H	-0.45473000	-0.81241100	-0.02828400
O	0.96563500	0.20648100	0.18621800
H	0.39837500	0.99068100	0.17500100
H	1.71530900	0.36589000	-0.40371800
O	3.64377700	0.16080500	-0.65683700

C	3.98305600	-0.28285100	0.40787200
H	5.03537300	-0.54396600	0.60642700
H	3.25119300	-0.44152400	1.21706700

CR2-3

C	-2.56362600	-1.34585700	-0.00567600
H	-3.40148700	-2.05888700	0.07711100
H	-1.55279100	-1.73934400	-0.17787700
O	-2.76357000	-0.16213900	0.09571000
H	-1.37696000	2.64739100	0.32652600
H	-1.46017400	1.15309000	-0.07212800
O	-0.89526200	1.94480100	-0.11368900
H	0.71541800	1.49984000	0.02032500
O	0.42790000	-0.78687100	-0.10736900
O	1.61801800	1.09404500	0.06469800
C	1.49495900	-0.22236900	-0.00946800
C	2.82281500	-0.92683500	0.04066300
H	3.34203800	-0.65660300	0.96113200
H	2.67285700	-2.00186200	-0.00840200
H	3.43953000	-0.59194400	-0.79460900

CR2-4

C	-2.82158300	-0.82657200	-0.00038200
H	-3.75547700	-1.41405200	-0.00515800
H	-2.88451600	0.27044400	0.00669900
O	-1.75766500	-1.39573300	-0.00323900
O	-1.68679500	2.01314600	0.00609300
H	-1.63166800	2.96982000	0.00767400
H	-0.76914700	1.69801100	-0.00308800
H	0.01150800	-1.11818200	0.00227700
O	0.94695200	1.03315100	-0.01221000
O	0.98879500	-1.20174700	0.00576600
C	1.56364100	-0.00893100	-0.00207100
C	3.06259800	-0.09704000	0.00332600
H	3.39387700	-0.66145200	-0.86932900
H	3.48909300	0.90193000	-0.00617000
H	3.38809300	-0.64179400	0.89058700

CR2-5

C	0.41516300	1.70563100	0.00956000
H	0.24990500	2.37684000	-0.83430900
H	0.30663200	2.29648400	0.92090100
H	1.40976000	1.26788400	-0.03882600
C	-0.63321700	0.63449600	0.00094400

O	-0.39811500	-0.55784500	0.00353600
O	-1.86755100	1.12620500	-0.00567500
H	-2.50917700	0.38347600	-0.00187400
O	-3.04085500	-1.33089200	0.06284900
H	-2.11353600	-1.60512500	0.00253400
H	-3.55080700	-1.89384000	-0.52241400
H	1.81106700	-1.29020800	0.06394300
O	3.39904500	-0.06162100	-0.05045000
C	2.90481900	-1.15374500	0.03143300
H	3.53537600	-2.06057300	0.07634300

CR2-6

C	-0.48112000	1.69120100	0.26493000
H	-1.33287900	1.30887600	-0.30265100
H	-0.76630100	1.71206900	1.31840600
H	-0.21546300	2.68942000	-0.07152600
C	0.69058900	0.77408000	0.08839700
O	1.75746000	1.09864500	-0.38011200
O	0.43150900	-0.46941100	0.50907700
H	1.23037700	-1.02301800	0.37038500
O	2.93390400	-1.36704100	-0.07869200
H	3.01506700	-0.45720600	-0.40361700
H	3.36056100	-1.94212200	-0.71642500
O	-3.12167800	-0.23253600	-0.62981400
C	-2.85185400	-1.06419200	0.19246500
H	-1.92985800	-1.00369900	0.79488100
H	-3.51675100	-1.92810800	0.37211200

Table S7 The atomic Cartesian coordinates of all species for the reactions $(HCO)_2$ + H_2O + HNO_3 and $(HCO)_2$ + H_2O + CH_3COOH obtained at the M06-2X/6-311++G(d,p) level of theory

$(HCO)_2$

C	0.65447100	-0.39122500	0.00000200
H	0.54568800	-1.49111400	0.00000000
O	1.71044200	0.17169500	-0.00000100
C	-0.65450100	0.39155800	0.00000100
H	-0.54649500	1.49149700	0.00000200
O	-1.71031800	-0.17199300	-0.00000100

$(HCO)_2\cdots H_2O$

O	1.67391200	-0.93022500	0.14749000
C	0.89905100	-0.19507200	-0.39314600
H	-1.86530700	-1.97682500	0.25056200
O	-1.59462100	-1.08419000	0.02483200

H	0.68396700	-0.21724900	-1.47589300
H	-2.39155000	-0.61940000	-0.24231400
C	0.15626000	0.88311900	0.38744400
O	-0.45575300	1.74852300	-0.17032700
H	0.25271200	0.81232800	1.48589300

CR4a

O	1.28825500	0.25607900	1.14093500
O	1.71607400	0.56934100	-0.98551400
H	0.86474300	1.04521200	-0.84210500
O	-0.59955100	1.78257100	-0.16823900
H	-0.35060300	1.80174200	0.76397300
H	-1.06025000	2.60407900	-0.35972800
O	-0.42781700	-1.37708300	-0.67898400
C	-1.22394700	-1.00806800	0.13646200
H	-1.07620200	-1.11825300	1.22586500
C	-2.52001600	-0.32738800	-0.28928900
H	-2.63051800	-0.18099500	-1.37916800
O	-3.33955300	0.01310500	0.51422100
N	2.00519400	-0.02155200	0.20012800
O	2.94762300	-0.74253700	0.19098300

TS4a

O	-1.75617300	0.33739700	-1.04412000
O	-1.62539100	-0.07826600	1.10664800
H	-0.69281800	0.07844600	0.84850800
O	0.55785400	1.58644700	-0.03341200
H	-0.07691700	1.49903300	-0.75643100
H	0.64574100	2.52746600	0.13783000
O	0.67124600	-1.26299100	-0.03372800
C	1.77562300	-0.99027900	-0.41404600
H	2.20327700	-1.38072800	-1.35430800
C	2.69671300	-0.07826000	0.39108700
H	2.29685400	0.26012300	1.36136300
O	3.78142100	0.20904000	-0.02431700
N	-2.34070200	-0.02751400	-0.04657100
O	-3.48211300	-0.33919100	0.05727800

CR4b

N	2.34579100	0.07970000	0.13266200
O	1.39726000	0.80483400	0.36966800
O	3.49902100	0.35863800	0.17949900
O	2.06469400	-1.19280200	-0.21421500
H	1.07102200	-1.25227700	-0.26500700

O	-0.58598300	-1.24611600	-0.47295400
H	-0.20708700	1.79900600	-0.43369600
O	-1.16082000	1.74886300	-0.56911300
H	-1.51651600	2.59891600	-0.29891700
C	-1.33447500	-0.63520800	0.25037300
H	-1.04135600	-0.25424900	1.24030500
C	-2.77784000	-0.39094000	-0.16084300
H	-2.99322000	-0.55979200	-1.22957100
O	-3.59660800	-0.06499400	0.64725000

TS4b

N	-2.26663600	-0.02150700	-0.12096600
O	-1.61731500	1.04162900	0.02197400
O	-3.43915700	-0.02671700	-0.33585500
O	-1.63757600	-1.14659800	-0.04215500
H	-0.48811700	-1.06669700	0.38694900
O	0.62428100	-0.98505000	0.72967900
H	-0.11797900	1.36472800	0.16077300
O	0.88890700	1.43805400	0.25307300
H	1.06330500	1.63219500	1.18443000
C	1.28009600	-0.27379700	-0.09007700
H	0.96750100	-0.19969400	-1.13682800
C	2.78468900	-0.22268500	0.13176200
H	3.09742300	-0.34047700	1.18637300
O	3.55031200	-0.10389500	-0.77484700

CP4

N	-2.36482000	-0.00053200	0.06922000
O	-1.83722300	-1.20494000	-0.22355400
O	-3.55026500	0.06058700	0.06065200
O	-1.58008700	0.89809500	0.31656600
H	0.13038700	1.58849200	-0.57499700
O	1.06140900	1.34892500	-0.66210200
H	-0.84681000	-1.09413200	-0.17271200
O	0.78041200	-0.88407600	-0.04465400
H	1.46697800	-1.43669300	-0.44927900
C	1.33921100	0.36643200	0.27518000
H	0.96648300	0.63990500	1.26775100
C	2.86183400	0.24561900	0.28325400
H	3.41685500	1.16582100	0.52448600
O	3.40245200	-0.78508800	-0.00070600

$CHOCH(OH)_2$

H	2.22062500	-0.47636400	-0.32764000

O	1.32608600	-0.82854500	-0.35970200
C	0.49792700	0.00785700	0.40869000
O	0.52910300	1.33085600	0.01453100
H	0.78911500	-0.02639800	1.46563100
H	-0.18039400	1.47149800	-0.62722300
C	-0.89214500	-0.60066100	0.22615600
H	-1.00474200	-1.65434500	0.53137400
O	-1.78760200	0.02799300	-0.26123100

CR5a

C	2.98253900	-0.83247100	0.16920000
H	2.54508300	-1.76958900	-0.18325600
H	3.78892500	-0.55702800	-0.50920600
H	3.34698200	-0.95628700	1.18527000
C	1.89831900	0.19861600	0.14158000
O	1.30957700	0.60089300	1.12353000
O	1.62325500	0.61491900	-1.09241800
H	0.82967000	1.18215300	-1.07185400
O	-0.74664600	1.75976400	-0.16309500
H	-0.21086400	1.66156300	0.64230000
H	-1.30502300	2.53366600	-0.05754400
O	-0.38171400	-1.51585500	-0.42584400
C	-1.18359200	-0.95009700	0.26315100
H	-1.04634000	-0.78795800	1.34708300
C	-2.48694300	-0.42120400	-0.32324600
H	-2.53166100	-0.41995500	-1.42733500
O	-3.38931200	-0.06667500	0.37913200

TS5a

C	-3.67827200	-0.32193800	-0.10222400
H	-3.72739000	-1.40998100	-0.17171300
H	-4.18425300	-0.02593200	0.81694700
H	-4.15420600	0.12945400	-0.96802100
C	-2.23848200	0.09232600	-0.04475800
O	-1.67317800	0.72100500	-0.91206900
O	-1.64272800	-0.31148800	1.07350600
H	-0.69051300	-0.11560100	1.02670700
O	0.70210700	1.51394500	0.21353300
H	-0.05718300	1.43985600	-0.39150200
H	0.84287000	2.45060100	0.36792600
O	0.76755700	-1.37470500	-0.09310600
C	1.76837600	-0.88806600	-0.54029100
H	2.04702200	-0.94914700	-1.60758100
C	2.76845700	-0.15918100	0.35007500

H	2.46368100	-0.05146300	1.40461400
O	3.81367900	0.22541400	-0.08863700

CR5b

C	3.81328600	0.21048400	0.19725300
H	4.15863600	-0.36056100	1.06002500
H	4.31256300	-0.19263900	-0.68496600
H	4.04990300	1.26367000	0.31820800
C	2.33026500	0.03714700	0.04677800
O	1.53538300	0.95143900	0.04919800
O	1.97995300	-1.23444200	-0.08724400
H	1.00723600	-1.30228200	-0.19490100
O	-0.76696000	-1.25024800	-0.41949200
C	-1.55625500	-0.68353500	0.29258800
H	-0.18303600	1.56388100	-0.27893400
O	-1.14135800	1.71094900	-0.33032400
H	-1.36855800	-0.46964800	1.35732700
H	-1.30211000	2.58741600	0.02500300
C	-2.92078200	-0.26182300	-0.23036200
O	-3.81481900	-0.01083800	0.52410500
H	-3.01131300	-0.23836200	-1.32925400

TS5b

C	-3.67211800	-0.20044400	-0.11813500
H	-4.12509200	0.37962900	0.68609400
H	-4.01623000	0.22378600	-1.06305400
H	-3.96008500	-1.24574300	-0.05088000
C	-2.17865600	-0.07003900	-0.04874100
O	-1.44909500	-1.06273400	-0.05296200
O	-1.75210200	1.15294000	0.01002300
H	-0.71021400	1.21025800	-0.04447700
O	0.71854200	1.19231300	-0.23355200
C	1.45455400	0.48743500	0.51300400
H	0.03509300	-1.16709500	0.14618600
O	1.03073100	-1.18136800	0.39206000
H	1.33779400	0.52891000	1.60640800
H	1.56981600	-1.55567300	-0.32222100
C	2.90172200	0.41579300	0.01995200
H	3.46319200	1.35985500	0.13275900
O	3.37351500	-0.54245100	-0.52648200

CP5

C	3.78274100	0.02134600	-0.09815600
H	4.13320000	1.03948000	-0.24096700

H	4.18447600	-0.39426600	0.82693700
H	4.11797900	-0.61590200	-0.91760700
C	2.28374400	0.00432800	-0.03846000
O	1.79351100	-1.21246400	0.14048200
O	1.58930600	0.99372800	-0.14608200
H	-0.11528300	1.46321900	0.47684400
O	-1.07009300	1.31919200	0.57833100
C	-1.41363900	0.30650700	-0.30090600
H	0.81063300	-1.17415800	0.16290700
O	-0.92544000	-0.95581100	0.07712600
H	-1.02915600	0.50418700	-1.30854400
H	-1.62515500	-1.42719400	0.55234500
C	-2.93937000	0.28515200	-0.30549400
H	-3.43114200	1.22629200	-0.60038600
O	-3.55308500	-0.68535300	0.03846400

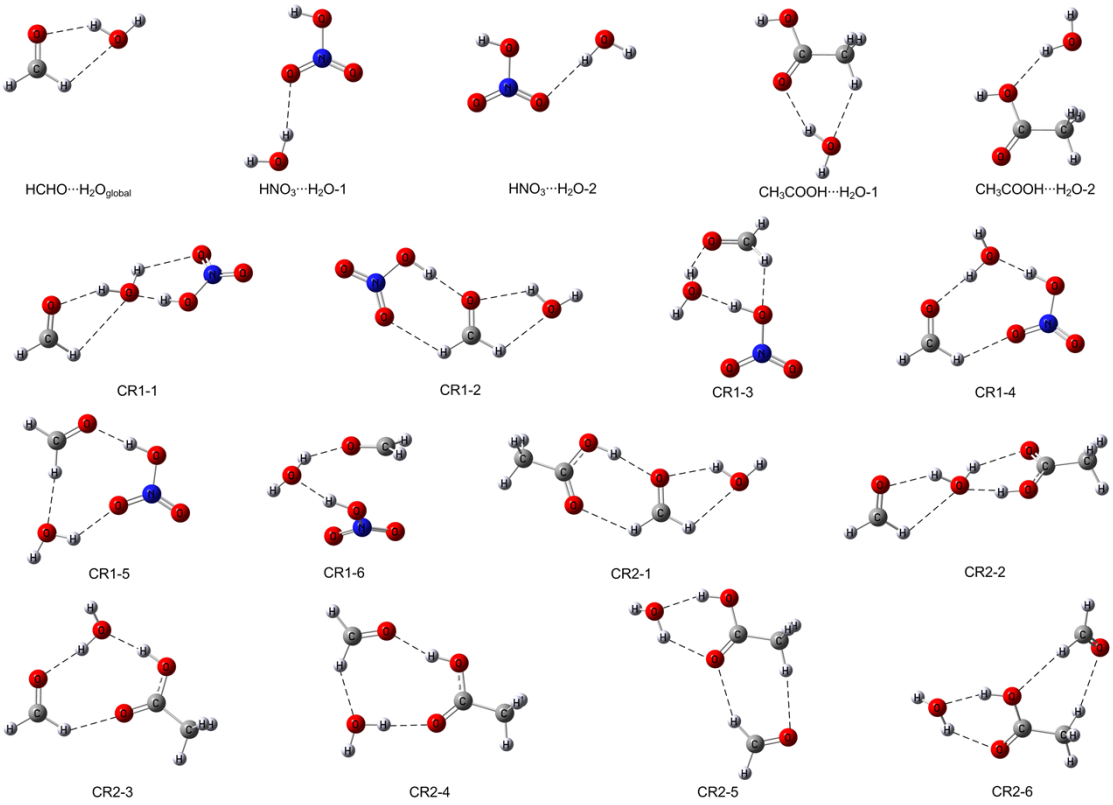

Figure S1 The various optimized structures for the $HCHO\cdots H_2O$, $HNO_3\cdots H_2O$, $CH_3COOH\cdots H_2O$, $HCHO\cdots H_2O\cdots HNO_3$, and $HCHO\cdots H_2O\cdots CH_3COOH$ complexes computed at the M06-2X/6-311++G(d,p) level.

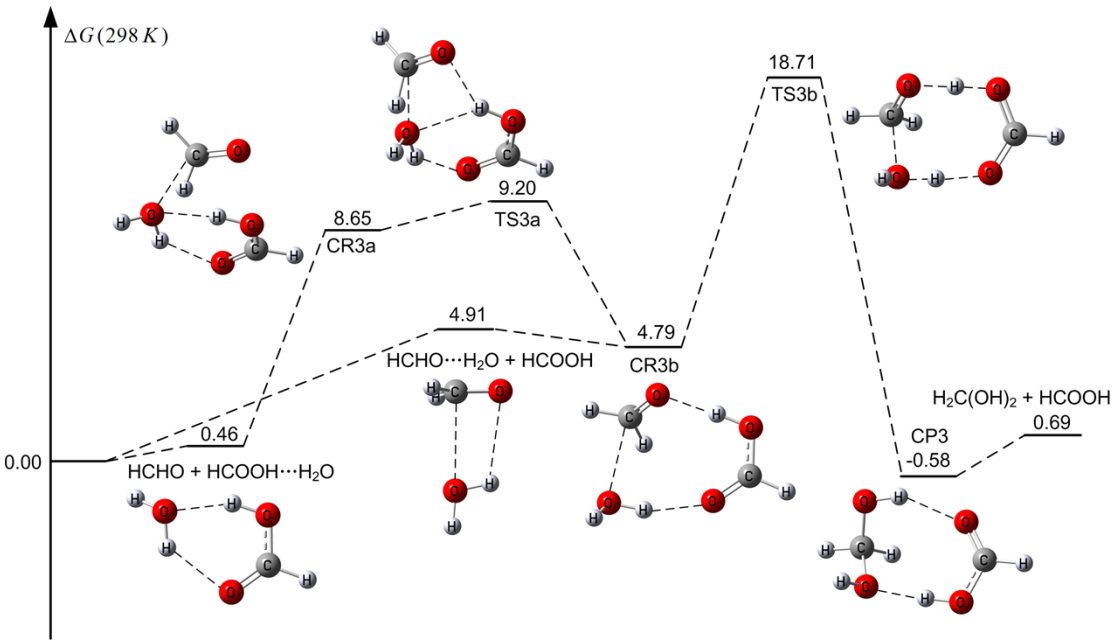

Figure S2 Free energy profile for the HCHO + H_2O + HCOOH → $H_2C(OH)_2$ + HCOOH reaction calculated at the CCSD(T)-F12A/VTZ-F12//M06-2X/6-311++G(d,p) level of theory (in kcal/mol).

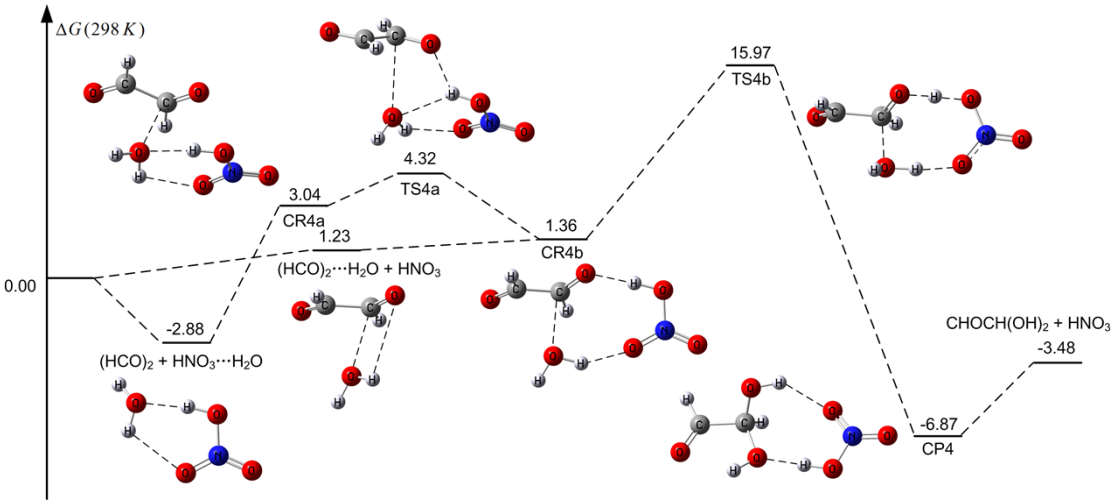

Figure S3 Free energy profile for the $(HCO)_2 + H_2O + HNO_3 \rightarrow CHOCH(OH)_2 + HNO_3$ reaction calculated at the M06-2X/6-311++G(d,p) level of theory (in kcal/mol).

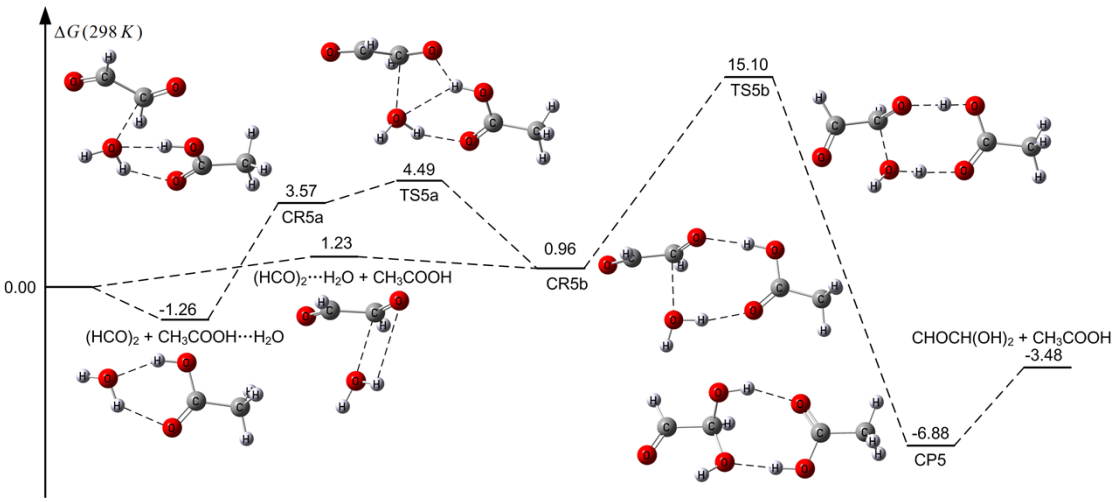

Figure S4 Free energy profile for the $(HCO)_2$ + H_2O + CH_3COOH → $CHOCH(OH)_2$ + CH_3COOH reaction calculated at the M06-2X/6-311++G(d,p) level of theory (in kcal/mol).