Supporting Information:

New Mechanism for Autocatalytic Decomposition of H_2CO_3 in the Vapor Phase

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Table S1: Calculated total electronic energies (E_{total}) and zero point vibrational energy (ZPE) corrected total electronic energies [E_{total}(ZPE)] of monomers, their complexes and transition states (TSs) at MP2 level in conjunction with the aug-cc-pVDZ, aug-cc-pVTZ and 6-311++G(3df,3pd) basis sets as well as at the CCSD(T)/aug-cc-pVTZ level of calculations. The values given in the parenthesis correspond to the ZPE corrected total electronic energies. The ZPE correction in case of CCSD(T)/aug-cc-pVTZ level of calculations have been done from the MP2/aug-cc-pVTZ level predicted ZPE correction.

Molecules/Complexes/Transition States	MP2/ aug-cc-PVDZ	MP2/ aug-cc-PVTZ	MP2/ 6-311++G(3df,3pd)	CCSD(T)/ aug-cc-PVTZ
H_2O	-76.2609098 (-76.2395788)	-76.3289923 (-76.3075823)	-76.3242865 (-76.3026835)	-76.3423255 (-76.3209155)
CO_2	-188.1697004 (-188.1583194)	-188.3216406 (-188.3101466)	-188.3119924 (-188.3003474)	-188.3405541 (-188.3290601)
cis-cis H_2CO_3	-264.4193605 (-264.3798605)	-264.6419446 (-264.6022286)	-264.6263124 (-264.586288)	-264.6786675 (-264.6389515)
cis-trans H_2CO_3	-264.4165077 (-264.3773507)	-264.6390758 (-264.5996698)	-264.6233828 (-264.5836898)	-264.6759153 (-264.6365093)
cis-trans H_2CO_3···*cis-cis* H_2CO_3	-528.8570275 (-528.7763565)	-529.3025979 (-529.2213279)	-529.2710793 (-529.1891693)	-529.3762165 (-529.2949465)
cis-trans H_2CO_3···*cis-trans* H_2CO_3	-528.8546842 (-528.7742992)	-529.3002275 (-529.2192185)	-529.2687073 (-529.1870443)	-529.3738935 (-529.2928845)
CO_2···H_2O··· *cis-trans* H_2CO_3	-528.8690238 (-528.7928568)	-529.3113346 (-529.2347586)	-529.2811588 (-529.2037848)	-529.3811504 (-529.3045744)
CO_2···H_2O···*cis-cis* H_2CO_3	-528.8710439 (-528.7946109)	-529.3133825 (-529.2365795)	-529.2833315 (-529.2057605)	-529.3830828 (-529.3062798)
TS [*cis-trans* H_2CO_3···*cis-cis* H_2CO_3→ CO_2···H_2O···*cis-trans* H_2CO_3]	-528.8303117 (-528.7571157)	-529.276399 (-529.202248)	-529.2444581 (-529.1697731)	-529.3467457 (-529.2725947)
TS [*cis-trans* H_2CO_3···*cis-trans* H_2CO_3→	-528.8300532 (-528.7568762)	-529.2761529 (-529.2020909)	-529.2441939 (-529.1695899)	-529.3465066 (-529.2724446)

CO_2···H_2O···*cis-cis* H_2CO_3]				
CO_2···H_2O	----	-264.6551204 (-264.6209884)	----	----
TS [*cis-trans* H_2CO_3 → CO_2···H_2O]	----	-264.5740618 (-264.5410278)	----	----
$(H_2O)_2$	----	-152.6662408 (-152.6200698)	----	----
$(H_2O)_3$	----	-229.012934 (-228.940053)	----	----
$(H_2O)_4$	----	-305.3615357 (-305.2626817)	----	----
cis-trans H_2CO_3 ··· H_2O	----	-340.9828535 (-340.9188045)	----	----
cis-trans H_2CO_3··· H_2O···$(H_2O)_2$	----	-493.6742975 (-493.5599145)	----	----
CO_2···$(H_2O)_4$	----	-493.6889697 (-493.5777247)	----	----
TS [*cis-trans* H_2CO_3 ··· H_2O···$(H_2O)_2$ → CO_2···$(H_2O)_4$]	----	-493.6438468 (-493.5330688)	----	----
cis-trans H_2CO_3···*cis-trans* H_2CO_3 [a]	----	-529.2927961 (-529.212165)	----	----
CO_2···H_2O···CO_2···H_2O	----	-529.3227432 (-529.251365)	----	----
TS [*cis-trans* H_2CO_3···*cis-trans* H_2CO_3→ CO_2···H_2O···CO_2···H_2O]	----	-529.2485223 (-529.176158)	----	----

[a] The *cis-trans* H_2CO_3····*cis-trans* H_2CO_3 complex according to Reference 37 and Fig. 5 of our article

Table S2: Imaginary frequencies (ν_{im}) of various transition states (TSs) at the MP2/aug-cc-pVDZ, MP2/aug-cc-pVTZ and MP2/6-311++G(3df,3pd) levels of calculations.

Unimolecular Isomerization Steps	Imaginary frequencies (ν_{im}) cm^{-1}		
	MP2/aug-cc-pVDZ	**MP2/aug-cc-pVTZ**	**MP2/6-311++G(3df,3pd)**
cis-trans $H_2CO_3 \rightarrow CO_2 \cdots H_2O$	----	1685	----
cis-trans $H_2CO_3 \cdots$ *cis-cis*-$H_2CO_3 \rightarrow$ $CO_2 \cdots H_2O \cdots$ *cis-trans* H_2CO_3	966	853	868
cis-trans $H_2CO_3 \cdots$ *cis-trans* $H_2CO_3 \rightarrow$ $CO_2 \cdots H_2O \cdots$ *cis-cis* H_2CO_3	986	895	905
cis-trans $H_2CO_3 \cdots H_2O \cdots (H_2O)_2$ $\rightarrow CO_2 \cdots (H_2O)_4$	----	521	----
cis-trans $H_2CO_3 \cdots$ *cis-trans* $H_2CO_3 \rightarrow$ $CO_2 \cdots H_2O \cdots CO_2 \cdots H_2O$	----	831	----