Supporting Information

Stepwise Hydration of Protonated Carbonic Acid: A Theoretical Study

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Table S1: Binding Energies (in kcal/mol) of $PCAW_n^x$ (AW_n^x, BW_n^x and CW_n^x) Clusters Calculated at HF method Using 6-31+G* and 6-311++G Basis Sets**

Isomer A	6-31+G*	6-311 ++G**	**Isomer B**	6-31+G*	6-311 ++G**	**Isomer C**	6-31+G*	6-311 ++G**
AW_1^l	27.3	28.6	BW_1^m	22.4	23.1	CW_1^m	21.6	22.2
AW_2^l	57.9	59.3	BW_2^m	60.9	62.0	CW_2^m	36.2	38.4
AW_3^l	71.3	72.8	BW_3^m	73.4	74.8	CW_3^m	75.7	77.4
AW_4^l	82.4	84.0	BW_4^m	83.4	85.4	CW_4^m	90.8	86.9
AW_5^l	91.7	93.6	BW_5^m	93.1	94.6	CW_5^m	99.6	96.1
AW_6^l	100.9	102.3	BW_6^m	101.3	102.8	CW_6^m	110.4	104.2
AW_2^b	47.8	48.7	BW_2^d	41.2	42.0	CW_1^d	28.0	27.4
AW_3^b	61.0	62.3	BW_3^d	76.9	79.7	CW_2^d	43.9	43.7
AW_4^b	73.0	74.1	BW_4^{d1}	87.8	111.3	CW_3^d	58.4	58.2
AW_5^b	82.4	83.6	BW_4^{d2}	65.2	66.4	CW_4^d	83.6	83.1
AW_6^b	91.4	93.0	BW_5^{d1}	95.6	97.2	CW_5^d	95.7	96.3
			BW_5^{d2}	98.0	100.2	CW_6^d	105.6	105.6
AW_3^c	71.1	71.4	BW_5^{d3}	74.3	75.0			
AW_4^c	83.6	85.0	BW_6^{d1}	79.5	81.9	CW_3^t	60.0	59.7
AW_5^c	97.8	97.2	BW_6^{d2}	82.4	84.1	CW_6^t	92.7	92.5
AW_5^{c1}	83.6	83.9	BW_6^{d3}	106.6	108.9			
AW_6^c	107.8	107.5	BW_6^{d4}	107.3	108.6			
			BW_3^t	57.7	58.4			
			BW_6^t	89.8	90.5			

$\mathbf{AW_n^x}$, (where n= 1-6, *x* = *l*, *b* and *c*); $\mathbf{BW_n^x}$ and $\mathbf{CW_n^x}$ (where n= 1-6, *x* = *m*, *d* and *t*);

Table S2: Calculated Contribution of Electron Correlation Energy to the Binding Energy (in %) Using Basis Set 6-311++G**

$PCAW_n^x$ Clusters	Correlation Energy Contribution (%)	
	B3LYP	M05-2X
AW_1^l	19.23	27.76
AW_2^l	15.87	20.02
AW_3^l	17.56	21.98
AW_4^l	16.89	21.83
AW_5^l	18.51	22.91
AW_6^l	18.47	23.53
AW_2^b	12.37	17.00
AW_3^b	16.33	22.84
AW_4^b	15.21	20.68
AW_5^b	17.12	22.81
AW_6^b	16.67	22.42
AW_3^c	16.74	21.21
AW_4^c	14.08	22.73
AW_5^c	13.38	20.45
AW_5^{c1}	15.99	21.57
AW_6^c	13.73	18.10
BW_1^m	23.85	32.63
BW_2^m	13.25	17.57
BW_3^m	16.30	20.11
BW_4^m	16.05	19.99
BW_5^m	18.72	22.50
BW_6^m	17.70	22.61
BW_2^d	16.57	23.77
BW_3^d	28.08	30.67
BW_4^{d1}	16.96	21.89
BW_4^{d2}	21.61	29.16
BW_5^{d1}	19.84	23.05
BW_5^{d2}	17.11	22.61
BW_5^{d3}	23.15	30.50
BW_6^{d1}	35.85	39.86
BW_6^{d2}	36.16	39.84
BW_6^{d3}	17.69	25.89
BW_6^{d4}	17.45	24.12
BW_3^t	13.75	19.87
BW_6^t	16.36	23.76
CW_1^m	23.57	32.15
CW_2^m	47.44	50.10
CW_3^m	15.15	18.42

Table S2 continued

$PCAW_n^x$ Clusters	Correlation Energy Contribution (%)	
	B3LYP	M05-2X
CW_4^m	15.32	19.64
CW_5^m	17.72	22.08
CW_6^m	17.44	21.94
CW_1^d	10.50	15.70
CW_2^d	14.90	22.17
CW_3^d	15.56	22.94
CW_4^d	12.87	18.22
CW_5^d	12.21	19.10
CW_6^d	13.31	19.34
CW_3^t	13.31	19.65
CW_6^t	17.80	25.38

$\mathbf{AW_n}^x$, (where n= 1-6, x = *l*, *b* and *c*); $\mathbf{BW_n}^x$ and $\mathbf{CW_n}^x$ (where n= 1-6, x = *m*, *d* and *t*);

Table S3: Calculated Thermochemical Parameters of $PCAW_n^x$ (where, n= 1-6, *x* = *l*, *b*, *c*, *m*, *d* and *t*) Clusters at B3LYP/6-31+G* Level

$PCAW_n^x$ Clusters	E (kcal/mol)	H (kcal/mol)	G (kcal/mol)	S (cal/mol/K)
Isomer A	-33.67	-34.26	-11.78	-75.41
Isomer B	-34.58	-35.18	-15.82	-64.93
Isomer C	-34.43	-35.03	-15.49	-65.54
AW_1^l	-50.15	-50.74	-23.06	-92.83
AW_2^l	-67.30	-67.89	-34.54	-111.86
AW_3^l	-83.94	-84.53	-44.93	-132.85
AW_4^l	-101.43	-102.02	-57.06	-150.81
AW_5^l	-118.40	-118.99	-68.33	-169.94
AW_6^l	-135.69	-136.28	-79.17	-191.55
AW_2^b	-67.82	-68.41	-34.96	-112.19
AW_3^b	-84.61	-85.20	-46.39	-130.16
AW_4^b	-102.03	-102.63	-58.08	-149.40
AW_5^b	-118.80	-119.39	-67.68	-173.44
AW_6^b	-136.12	-136.71	-78.43	-195.47
AW_3^c	-85.05	-85.64	-49.68	-120.61
AW_4^c	-102.17	-102.76	-59.87	-143.88
AW_5^c	-120.34	-120.93	-72.92	-161.01
AW_5^{c1}	-119.85	-120.44	-73.33	-158.01
AW_6^c	-137.49	-138.08	-84.14	-180.92
BW_1^m	-50.33	-50.92	-27.87	-77.32
BW_2^m	-68.23	-68.83	-38.93	-100.26
BW_3^m	-84.95	-85.54	-49.95	-119.38
BW_4^m	-102.32	-102.91	-62.48	-135.61
BW_5^m	-119.01	-119.61	-72.75	-157.16
BW_6^m	-136.70	-137.29	-84.16	-178.21
BW_2^d	-68.13	-68.72	-38.52	-101.31
BW_3^d	-84.06	-84.65	-49.29	-118.58
BW_4^{d1}	-102.16	-102.76	-61.48	-138.44
BW_4^{d2}	-101.58	-102.18	-61.34	-136.95
BW_5^{d1}	-118.82	-119.41	-72.75	-156.52
BW_5^{d2}	-119.02	-119.62	-72.87	-156.79
BW_5^{d3}	-119.26	-119.85	-78.22	-139.64
BW_6^{d1}	-136.53	-137.12	-84.93	-175.04
BW_6^{d2}	-136.24	-136.84	-84.22	-176.46
BW_6^{d3}	-135.84	-136.43	-84.23	-176.09
BW_6^{d4}	-136.97	-137.57	-88.84	-163.42
BW_3^t	-85.27	-85.86	-49.57	-121.74

Table S3 continued

$PCAW_n^x$ Clusters	E (kcal/mol)	H (kcal/mol)	G (kcal/mol)	S (cal/mol/K)
BW_6^t	-136.47	-137.06	-83.71	-178.94
CW_1^m	-50.77	-51.36	-26.53	-83.31
CW_2^m	-67.98	-68.57	-38.62	-100.46
CW_3^m	-84.63	-85.22	-49.39	-120.18
CW_4^m	-102.17	-102.77	-61.29	-139.12
CW_5^m	-118.92	-119.51	-71.95	-159.51
CW_6^m	-136.41	-137.00	-84.18	-177.17
CW_1^d	-52.34	-52.94	-29.83	-77.51
CW_2^d	-68.71	-69.30	-41.46	-93.40
CW_3^d	-85.83	-86.42	-54.00	-108.74
CW_4^d	-104.63	-105.22	-70.23	-117.36
CW_5^d	-120.64	-121.23	-81.64	-132.78
CW_6^d	-138.94	-139.53	-92.57	-157.51
CW_3^t	-85.98	-86.57	-53.22	-111.85
CW_6^t	-137.47	-138.07	-90.96	-158.00

$\mathbf{AW_n^x}$, (where n= 1-6, *x* = *l*, *b* and c); $\mathbf{BW_n^x}$ and $\mathbf{CW_n^x}$ (where n= 1-6, *x* = *m*, *d* and *t*); calculated E, H, G and S are zero point energy corrected Energy, Enthalpy, Free energy and Entropy respectively at 298.15 K and 1 atm.

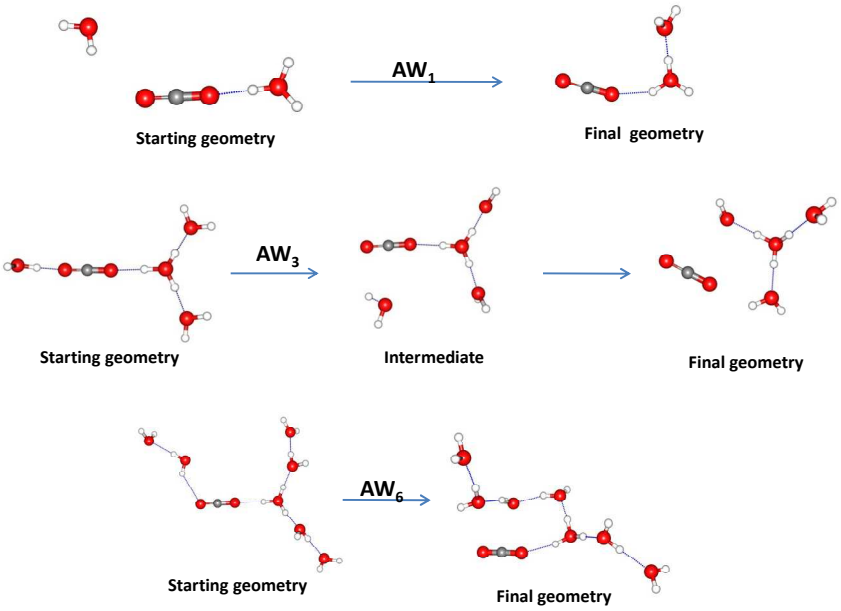

Figure S1: Starting and final optimized geometries of $\mathbf{AW_n}$ clusters (where n= 1, 3 and 6).