Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Reaction Mechanisms of Aqueous Monoethanolamine with Carbon Dioxide: A Combined Quantum Chemical and Molecular Dynamics Study

Gyeong S. Hwang[1,2,*], Haley M. Stowe[2], Eunsu Paek[1], and Dhivya Manogaran[3]

[1]Department of Chemical Engineering, [2]Materials Science and Engineering Program, and [3]Departments of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712, United States

*Author to whom correspondence should be addressed: email: gshwang@che.utexas.edu

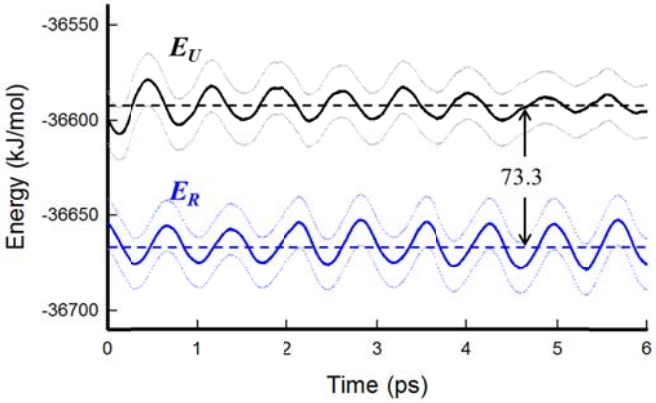

Figure S1. Total enegy variations from AIMD simulations for the unreacted (E_U) and reacted (E_R) systems consisting of (2 MEA, 1 CO_2, 16 H_2O) and (1 $MEACOO^-$, 1 $MEAH^+$, 16 H_2O), respectively, as discussed in Sec. III.A. For each case, the solid line represents the average of five simulations with different initial configurations.

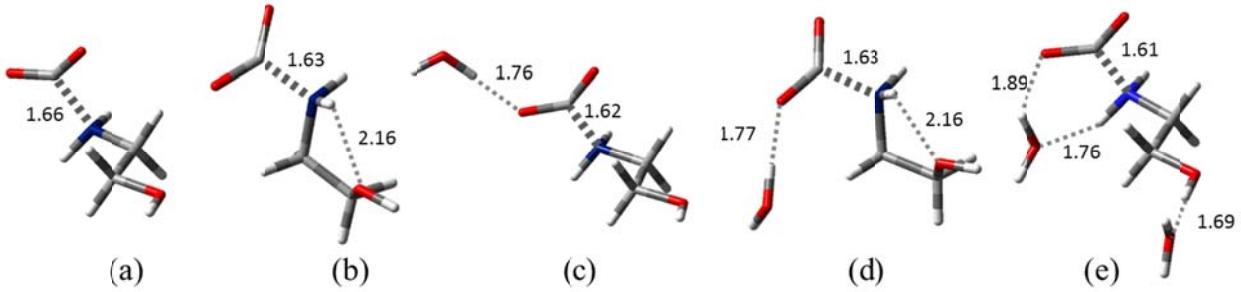

Figure S2. Various configurations employed for the calculation of $E_b(H^+)$ at different abstraction sites in Fig. 4.

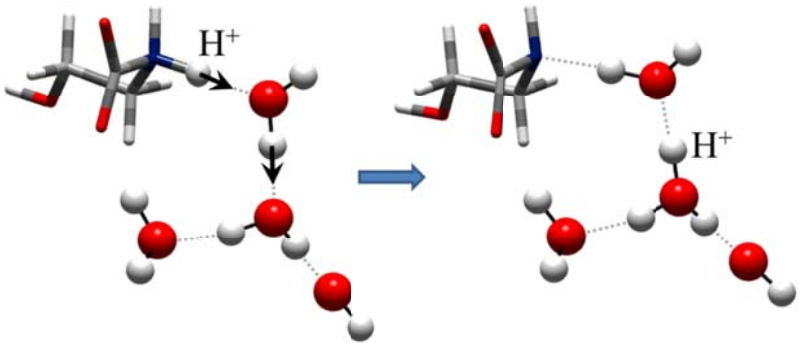

Figure S3. Predicted deprotonation process from a zwitterion (MEA^+COO^-) via a well-connected water network, giving a low barrier of 0.08 eV. The red, blue, and white indicate O, N, and H atoms, respectively.

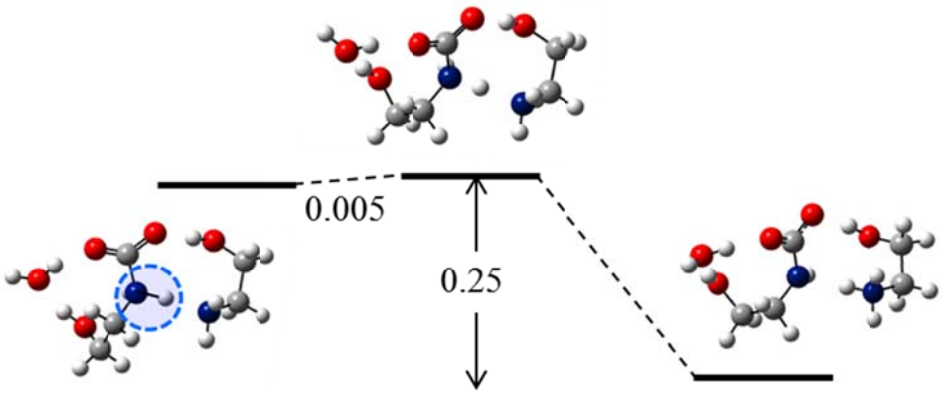

Figure S4. Predicted pathway and energetics (in eV) for proton transfer from a zwitterion (MEA^+COO^-) to a nearby MEA molecule. The white, grey, blue, and red balls represent H, C, N, and O atoms, respectively.

Force fields employed in this work

The total energy (E_{total}) is the sum of the bond (E_{bond}), angle (E_{angle}), torsion ($E_{torsion}$) and nonbonding energies ($E_{nonbond}$). The nonbonding energy for each pair includes Colulomb interaction and van der Waals interaction in the 12-6 Lennard-Jones form. Bond and angle energies were expressed in the harmonic form. Two different forms were used to express the torsion energies, depending on the dihedral type.

$$E_{total} = E_{bond} + E_{angle} + E_{torsion} + E_{nonbond}$$

$$E_{bond} = \sum_i k_{b,i}\left(r_i - r_{0,i}\right)^2$$

$$E_{angle} = \sum_i k_{\theta,i}(\theta_i - \theta_{0,i})^2$$

$$E_{torsion} = \sum_i K[1 + \cos(n\emptyset - d)]$$

or

$$E_{torsion} = \sum_i [C_1 + C_2\cos(\emptyset) + C_3(\cos(\emptyset))^2 + C_4(\cos(\emptyset))^3]$$

$$E_{nonbond} = \sum_i \sum_{j>i} \left\{ \frac{q_i q_j e^2}{r_{ij}} + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]\right\}$$

Here, $k_{b,i}$, $k_{\theta,i}$, represent the bond and angle force constants, respectively. K, C_1, C_2, C_3, and C_4 are torsion energy coefficients, n is the periodicity of the torsion, d is the phase offset, and $\emptyset$ is the dihedral angle. $r_{0,i}$ and $\theta_{0,i}$ are the bond distance and bond angle at equilibrium, respectively. For E_{bond}, q_i is the partial atomic charge, r_{ij} is the distance between atoms *i* and *j*, ε_{ij} and σ_{ij} are the Lennard-Jones parameters which refers to the depth of the potential well and the distance where the potential is zero, respectively. The Coulomb and L-J energies were calculated between atoms separated by three or more bonds. Although most force fields scale the 1-4 L-J and Coulomb energies, in this simulation, they were unscaled as recommended by a previous study to prevent overestimation of intramolecular hydrogen bonding in the amine species.[1] The Lorentz-Berthelot combination rule was applied for unlike atom pairs where $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_i}$ and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$.

Table S1. Nonbonded Force Field Parameters

Species	Atom	q_i	σ_i (Å)	ε_i (kcal/mol)	Reference (σ_i, ε_i)
MEA	H_N	0.297	1.069	0.0157	1
	N	-0.739	3.25	0.170	
	C_N	-0.113	3.3996	0.1094	
	C_O	-0.007	3.3996	0.1094	
	O_H	-0.662	3.0664	0.2104	
	H_O	0.383	0.0	0.0	
	H_C	0.136	2.4714	0.0157	
$MEACOO^-$	H_N	0.294	1.069	0.0157	
	N	-0.676	3.250	0.1700	
	C_N	-0.069	3.3996	0.1094	
	C_O	0.019	3.3996	0.1094	
	O_H	-0.663	3.0664	0.2104	
	H_O	0.379	0.0	0.0	
	H_C	0.131	2.4714	0.0157	
	C_{COO}	0.534	3.3996	0.0860	2
	O_{COO}	-0.671	2.9599	0.2100	
$MEAH^+$	H_N	0.438	1.069	0.0157	1
	N	-0.719	3.340	0.1700	2
	C_N	-0.141	3.3996	0.1094	1
	C_O	-0.020	3.3996	0.1094	
	O_H	-0.641	3.0664	0.2104	
	H_O	0.395	0.0	0.0	
	H_C	0.203	2.4714	0.0157	
MEA^+COO^-	H_N	0.390	1.069	0.0157	1
	N_H	-0.706	3.34	0.1700	2
	C_N	-0.098	3.3996	0.1094	1
	C_O	-0.027	3.3996	0.1094	
	O_H	-0.649	3.0664	0.2104	
	H_O	0.393	0.0	0.0	
	H_C	0.177	2.4714	0.0157	
	C_{COO}	0.587	3.3996	0.0860	2
	O_{COO}	-0.494	2.9599	0.2100	

Table S2. Bond Parameters

Species	Bond Type	k_b (kcal/mol/ Å^2)	r_0 (Å)	Reference
MEA $MEACOO^-$ $MEAH^+$ MEA^+COO^-	N - C_N	320.6	1.470	1
	C_N - C_O	303.1	1.535	
	N - H_N	394.1	1.018	
	C_O - O_H	314.1	1.426	
	O_H - H_O	369.6	0.974	
	$C_{N/O}$ - H_C	335.9	1.093	
$MEACOO^-$ MEA^+COO^-	N - C_{COO}	490.0	1.335	2
	C_{COO} - O_{COO}	570.0	1.229	

Table S3. Angle Parameters

Species	Angle Type	k_θ (kcal/mol/rad^2)	θ_0 (°)	Reference
MEA	C_N - N - H_N	46.0	116.78	1
MEA $MEAH^+$	H_N - N - H_N	35.0	109.5	
MEA $MEAH^+$ $MEACOO^-$	N - C_N - C_O	66.2	110.38	
MEA $MEAH^+$ $MEACOO^-$ MEA^+COO^-	H_C - $C_{N/O}$-$C_{N/O}$	46.4	110.07	
	C_N - C_O - O_H	67.7	109.43	
	C_O - O_H - H_O	47.1	108.16	
	H_C - C_N - N	50.0	109.5	2
	H_C - $C_{N/O}$ - H_C	35.0	109.5	
	H_C - C_O - O_H	50.0	109.5	
$MEACOO^-$	C_N - N - H_N	30.0	118.04	
$MEACOO^-$ MEA^+COO^-	C_N - N - C_{COO}	50.0	121.9	
	C_{COO} - N - H_N	30.0	120.0	
	N - C_{COO} - O_{COO}	80.0	122.90	
	O_{COO} - C_{COO} - O_{COO}	80.0	126.0	
$MEAH^+$ MEA^+COO^-	C_N - N - H_N	50.0	109.5	
MEA^+COO^-	N - C_N - C_O	66.2	111.2	
	H_N - N -H_N	35.0	109.5	

Table S4. Dihedral Parameters (Multi-Harmonic Form)[1]

Species	Dihedral Type	C_1 (kcal/mol)	C_2 (kcal/mol)	C_3 (kcal/mol)	C_4 (kcal/mol)
MEA $MEAH^+$ $MEACOO^-$ MEA^+COO^-	H_N - N - C_N - C_O	0.59	-3.75	-1.18	3.28
	O_H - C_O - C_N - N	0.08	-4.487	-0.16	4.6224
	C_N - C_O - O_H - H_O	0.0	-0.22	0.0	-0.28

Table S5. Dihedral Parameters (Amber Form)[2]

Species	Dihedral Type	K (kcal/mol)	n	d (°)
$MEACOO^-$	H_C - C_N - N - H_N/C_{COO}	0.0	2	0
$MEACOO^-$ MEA^+COO^-	H_N - N - C_{COO} - O_{COO}	2.0	1	0
	O_{COO} - C_{COO} - N - C_N	2.5	2	180
	H_C - C_O - O_H - H_O	0.167	3	0
	C_O - C_N - N - C_{COO}	0.530	1	0
	H_C/O_H/N - $C_{O/N}$ - $C_{N/O}$ - H_C	0.156	3	0
MEA^+COO^-	H_C - C_N - N - H_N/C_{COO}	0.156	3	0

REFERENCES

[1] E. F. da Silva, T. Kuznetsova, B. Kvamme, and K. M. Merz, *J. Phys. Chem. B*, 2007, **111**, 3695–3703.

[2] W. D. Cornell, P. Cieplak, C. I. Bayly, I. R. Gould, K. M. Merz Jr., D. M. Ferguson, D. C. Spellmeyer, T. Fox, J. W. Caldwell, and P. W. Kolmman, *J. Am. Chem. Soc.*, 1995, **117**, 5179-5197.