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

Supporting information (SI)

Why does 2-(2-aminoethylamino)ethanol (AEEA) have superior CO_2 separation performance to monoethanolamine (MEA)? A computational study

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SI 1. Changes in orbital hybridization around the carbon atom of CO_2

The bond length between the carbon atom of CO_2 (C) and the nitrogen atom of primary amine (N), as well as the angle of CO_2 (C-O-C), were studied to confirm the change in the orbital hybridization (see Fig. S1). The primary amine in AEEA ($AEEA_p$) forms a single bond of length 1.59 Å in intermediate INT 1. After that, the C-N length slightly changes from INT 1 to INT 2. Finally, the bond is further strengthened through the transition state (TS) 3, and the product complex (PC) forms a 1.5-fold bond with length 1.35 Å as the result. Similarly, the secondary amine in AEEA ($AEEA_s$) forms a single bond of length 1.60 Å in INT that strengthens to a 1.5-fold bond with length 1.36 Å in the PC. This indicates that N and CO_2 form stronger bonds in the PC than the intermediate states for both $AEEA_p$ and $AEEA_s$. The C-O-C angle also changes in the same way between $AEEA_p$ and $AEEA_s$, from 180° in the reactant complex (RC), to about 135° in the INTs, to about 120° in the PC. These results indicate that the orbital hybridization around C changes from *sp* in the RC, to incomplete sp^2 in INTs, to complete sp^2 in the PC.

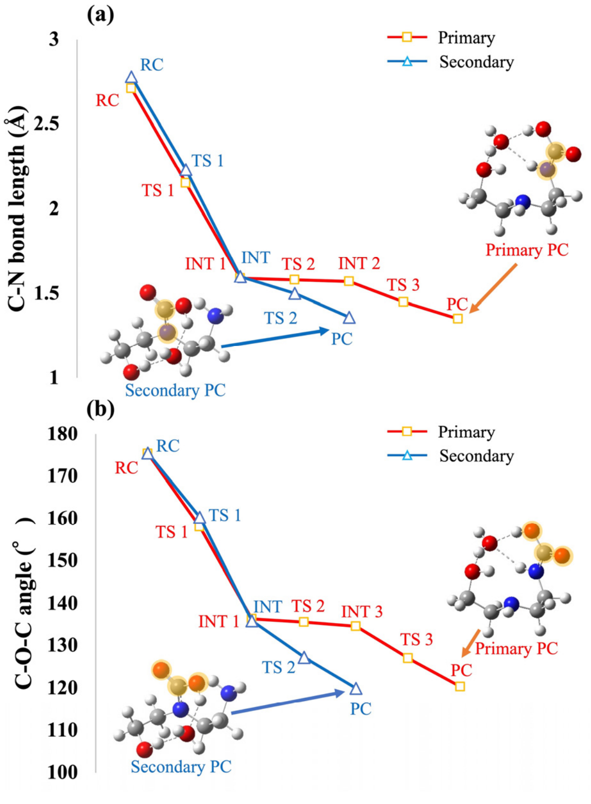


Fig. S1 Changes along the reaction coordinate from RC to PC for primary and secondary PCs. (a) Bond length between C and N. (b) C-O-C angle.

SI 2. Reactions with CO_2 interaction with the primary amine

This study investigated the total energy profile, which is a component of the Gibbs free energy (corresponding to Fig. 2), as shown in Fig. S2. This shows the reaction pathway of the primary amine with CO_2. Here, TS 2 is more unstable than INT 1. However, INT 1, TS 2, and INT 2 have very similar energy values, and thus the INT 1 and TS 2 energies can be reversed when the energy is corrected for temperature and pressure (as can be seen in Fig. 2). Additionally, the third step is the rate-limiting reaction that dominates the entire process; therefore, the energy reverse does not affect discussions and conclusions in this study. The activation energy (ΔG) in the third step is decreased by 3.78 (= 10.07 – 6.29) kcal/mol by correcting the temperature and pressure. Based on this result, we expect that ΔG can be changed from ΔE by several kcal/mol due to thermal correction. These facts explain the negative value of ΔG in Fig. 2.

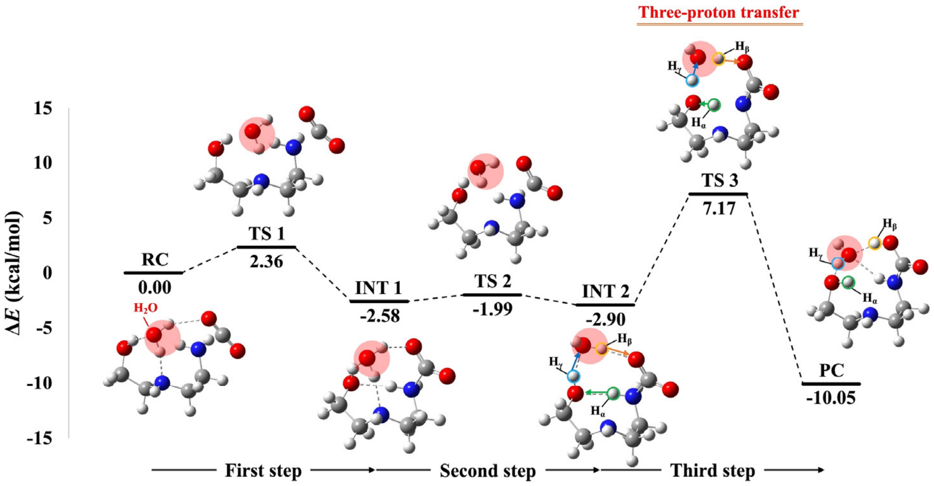


Fig. S2 Energy profile along the reaction coordinate for the CO_2 interaction with the primary amine in AEEA (total energy, ΔE) at the M06-2X/6-31+G(d,p) level within the IEF-PCM.

SI 3. Natural bond orbital (NBO) charge of hydrogen atoms in the TS structure for the three/two-proton transfer.

In order to investigate the charge of the hydrogen atoms in the three/two-proton transfer, the natural bond orbital (NBO) net charge was investigated (see Table S1). The definition of H_α, H_β, and H_γ are given by Figs. 2 and 3. Table S1 shows that the hydrogen atoms involved in the proton transfer are positively charged. Based on these results, the hydrogen atoms are referred to as protons in this study.

Table S1 The NBO net charge of hydrogen atoms in TS involved in the three/two-proton transfer.

	H_α	H_β	H_γ
Primary amine	+0.547	+0.559	+0.573
Secondary amine	+0.528	+0.565	-

SI 4. Comparison of the reaction pathway of the CO_2 interaction with the primary and secondary amines in AEEA.

Fig. S3 compares the profiles of Gibbs free energies during the reaction pathway of CO_2 interaction with the AEEA$_p$ and AEEA$_s$.

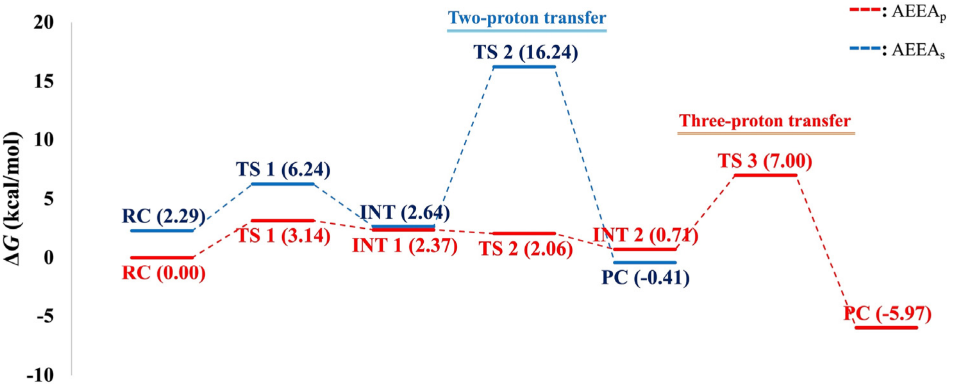


Fig. S3 Comparison of the reaction pathway of the CO_2 interaction with the AEEA$_p$ and AEEA$_s$. The number in parentheses is the relative energy to the RC in primary amine reaction.

SI 5. Change in NBO charge during CO_2 interaction process.

To investigate the polarity in the system, NBO net charges were examined for the "bases" (oxygen atoms of CO_2, hydroxyl group, and H_2O) in the three/two-proton transfer in the rate-limiting reactions of $AEEA_p$ and $AEEA_s$ (see Fig. S4). It can be seen that the charge of the primary amine is more negative than that of the secondary amine in the TS for oxygen atoms of CO_2 and hydroxyl group. According to the study by Nguyen *et al.*,[1] the base is more stable as its charge increases negatively. This supports results stating that the TS of primary amine with more negatively charged bases is more stable than that of secondary amine.

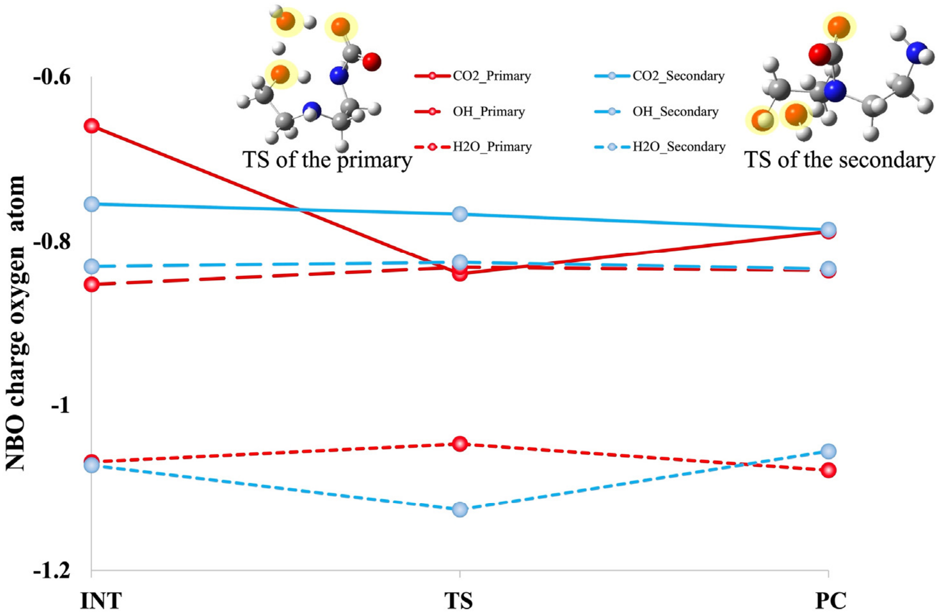


Fig. S4 NBO charge at the M06-2X/6-31+G(d,p) level within the IEF-PCM. The red lines are the primary amine, and blue lines are the secondary amine. The solid, dashed, dotted lines represent the oxygen atoms of CO_2, hydroxyl group, and H_2O, respectively.

SI 6. Geometric parameters between oxygen and hydrogen atoms in the PC.

To describe the stability of the PC structure (AEEACOO$_p$H/AEEACOO$_s$H), the geometric parameters regarding oxygen and hydrogen atoms were investigated (see Fig. S5). The difference in the PC stability can be described as follows. It is known that a cooperative proton transfer occurs when the H_2O chain (O-H---O-H---O-H---…) is formed, and this strengthens the hydrogen bonds and stabilizes the structure.[2] The PC in the primary amine reaction (AEEACOO$_p$H) has such a chain structure (see Fig. S5(a)). Conversely, the PC in the secondary amine reaction (AEEACOO$_s$H) has a mismatch in the chain that breaks the order (O-H---O---H-O) (see Fig. S5(b)). This mismatch can make the structure less stable. The hydrogen bonds formed in the PC structure are 2.75 Å and 2.77 Å in AEEACOO$_p$H, whereas they are 2.90 Å and 2.99 Å in AEEACOO$_s$H. Based on the bond lengths, AEEACOO$_p$H has stronger hydrogen bonds than AEEACOO$_s$H. In addition, the orbital hybridization of the nitrogen atom bonded to CO_2 changes from sp^3 to sp^2 during the RC→PC process for both the primary and secondary amine cases.

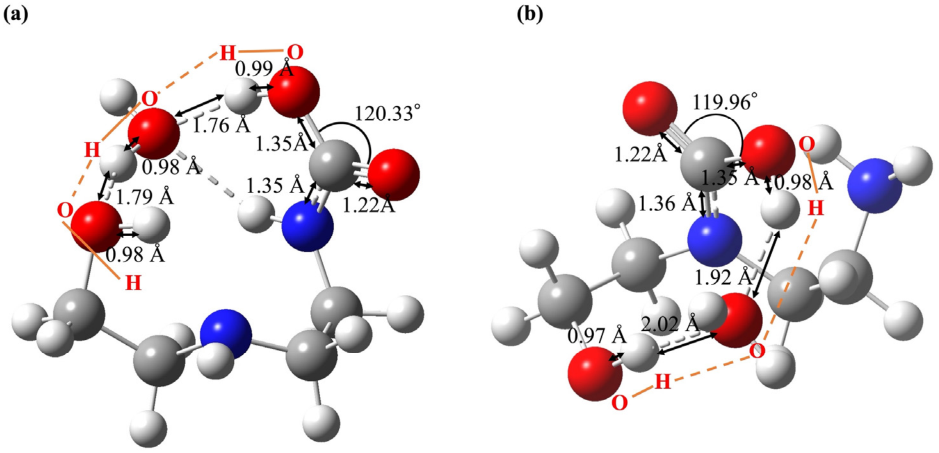


Fig. S5 Geometric parameters between oxygen and hydrogen atoms in the PC structures at the M06-2X/6-31+G(d,p) level within the IEF-PCM for (a) primary and (b) secondary amines reactions.

SI 7. Geometric parameters of the TS structure in the rate-limiting step of AEEA$_\text{p}$ and MEA reactions.

To describe the TS stability in the rate-limiting step of the AEEA$_\text{p}$ reaction compared with that of the MEA reaction, the geometric parameters of the TS structures were investigated (see Fig. S6). The length of the hydrogen bonds between the hydroxyl group and H_2O is 2.41 Å for AEEA$_\text{p}$ and 2.49 Å for MEA. Meanwhile, the length of the hydrogen bonds between H_2O and COOH is 2.46 Å for AEEA$_\text{p}$ and 2.62 Å for MEA. Based on bond lengths, we can consider that AEEA has stronger hydrogen bonds than MEA. Between the primary amine and hydroxyl group, bond lengths are 2.60 Å for AEEA$_\text{p}$ and 2.55 Å for MEA, indicating that AEEA in the AEEA$_\text{p}$ reaction has a slightly shorter hydrogen bond than MEA. In addition, H_α in AEEA in the AEEA$_\text{p}$ reaction also forms hydrogen bonds with the secondary amine at the same time as shown in Fig. S6(a). These strong hydrogen bonds in AEEA qualitatively explains the stability of the TS in the rate-limiting step of the AEEA$_\text{p}$ reaction compared with that of the MEA reaction.

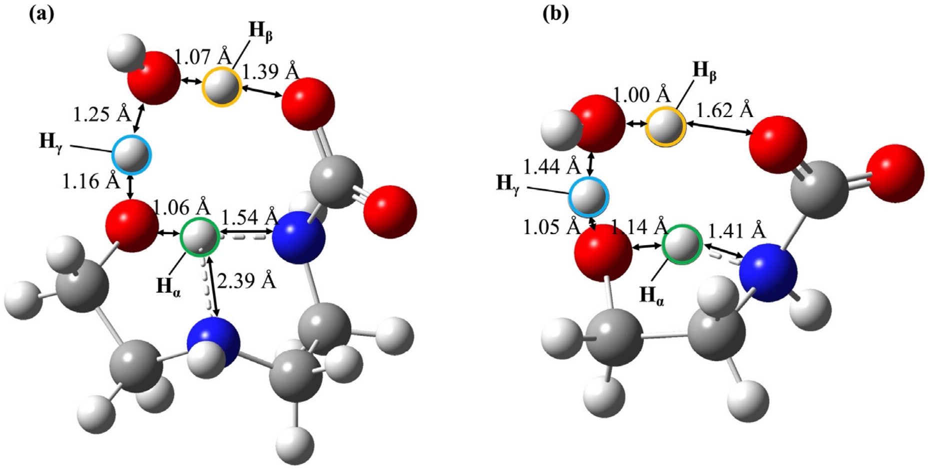


Fig. S6 Geometric parameters of AEEA and MEA in the TS structures (rate-limiting step) at the M06-2X/6-31+G(d,p) level within the IEF-PCM for the (a) AEEA$_\text{p}$ and (b) MEA reactions.

SI 8. Energy change for forming RC from separated reactants.

Table S2 shows the energy change for forming reactant complex (RC) from separated reactants for $AEEA_p$ (primary amine, AEEA), $AEEA_s$ (secondary amine, AEEA), and MEA reaction paths. Gibbs free energy of separated reactants was calculated by summing energies of twisted-form amine, CO_2 and H_2O isolated molecules. In $AEEA_p$ reaction path, enthalpy change was negative (-10.31 kcal/mol) when making RC due to the attractive interaction like hydrogen bonds. On the other hand, entropy change was positive (16.66 kcal/mol) due to the reduction of the degree of randomness by forming RC. By cancelling their changes, the change in Gibbs free energy for making the RC was positive (6.35 kcal/mol). Total energies before adopting thermal and zero-point energy corrections showed negative change (-13.99 kcal/mol) for the reactants→RC transition.

Table S2 Energy change for making reactant complex (RC).

		Reactants[c] (Hartree)	RC (Hartree)	Diff.[d] (kcal/mol)
Primary amine (AEEA)	Free energy[a]	-609.024524	-609.014407	6.35
	Enthalpy[a]	-608.925242	-608.941675	-10.31
	Entropy[a]	-0.099282	-0.072732	16.66
	Total energy[b]	-609.154098	-609.176389	-13.99
Secondary amine (AEEA)	Free energy	-609.024524	-609.010757	8.64
	Enthalpy	-608.925242	-608.934766	-5.98
	Entropy	-0.099282	-0.075991	14.62
	Total energy	-609.154098	-609.169235	-9.50
Primary amine (MEA)	Free energy	-475.172318	-475.160094	7.67
	Enthalpy	-475.086067	-475.095401	-5.86
	Entropy	-0.086251	-0.064693	13.53
	Total energy	-475.234477	-475.249568	-9.47

[a] Gibbs free energy (G = H − TS) and its components, enthalpy (H) and entropy (−TS), obtained at 358.15 K and 2.4 MPa. [b] Total energy before thermal and zero-point energy corrections. [c] Energy of separated reactants obtained by summing the energies of twisted-form amine, CO_2 and H_2O isolated molecules. [d] Energy difference between reactants and RC, that is, Diff. = G(RC) − G(reactants) for the free energy, for example.

Thus, the thermal corrections cause the destabilization for forming RC. The same trend was also found for $AEEA_s$ and MEA cases.

Table S3 shows the relative stability of product complex (PC) in each reaction path for predicting CO_2 desorption ability. Two different reference states, separated reactants and RC, were used to estimate the relative stability. From the table, free energies of PC relative to reactants showed positive values in all the paths, and the order of relative stability of PC was found to be $AEEA_p$ > MEA > $AEEA_s$. On the other hand, energies of PC relative to RC showed negative values for all the paths, but the same stability order of PC with $AEEA_p$ > MEA > $AEEA_s$ was obtained. These two reference states qualitatively result in the same conclusion on the expected order of CO_2 desorption ability with $AEEA_s$ > MEA > $AEEA_p$.

Table S3 Relative stability of product complex (PC).

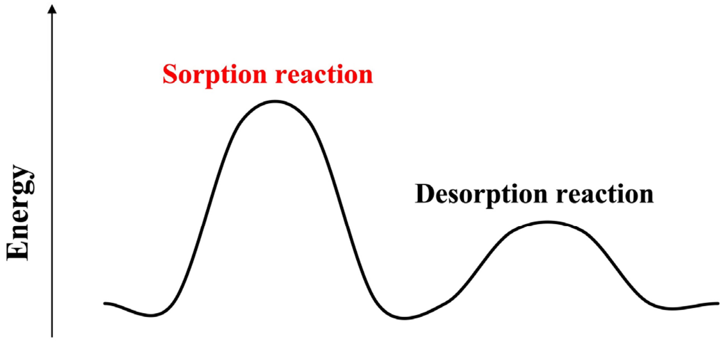
	Free energy[a] of PC relative to reactants[b] (kcal/mol)	Free energy of PC relative to RC (kcal/mol)
Primary amine (AEEA)	0.38	-5.97
Secondary amine (AEEA)	5.94	-2.70
Primary amine (MEA)	3.33	-4.34

[a] Gibbs free energy obtained at 358.15 K and 2.4 MPa. [b] Sum of energies of amine (twisted form), CO_2 and H_2O isolated molecules.

SI 9. Schematic diagram of the reaction pathways for CO_2 separation: assumable two cases.

For CO_2 separation by membranes, the rate-limiting step (sorption or desorption) depends on the experimental conditions. Fig. S7(a) shows a schematic diagram of the CO_2 separation reaction in which sorption is rate-limiting. Fig. S7(b) is a schematic for when desorption is rate-limiting.

(a) Sorption is rate-limiting



(b) Desorption is rate-limiting

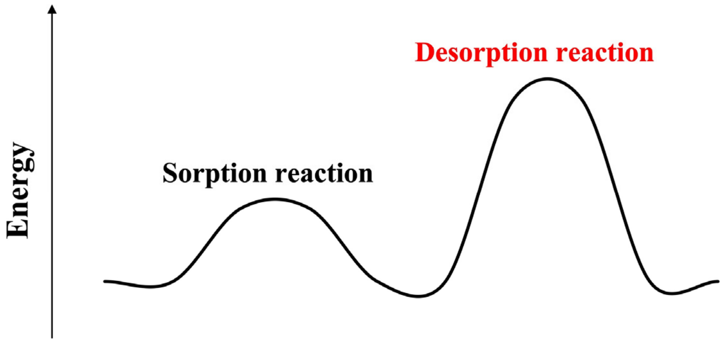


Fig. S7. Schematic diagrams of the reaction pathways in which the rate-limiting step are (a) sorption and (b) desorption, respectively.

SI 10. References

1. M. T. Nguyen, G. Raspoet, L. G. Vanquickenborne and P. T. Van Duijnen, J. Phys. Chem. A, 1997, 101, 40, 7379-7388.
2. J. E. H. Koehler, W. Saenger and B. Lesyng, J. Comput. Chem., 1987, 8, 8, 1090-1098.