Correlation of the Frontier Orbital Properties of Alkanolamines with the Experimental CO_2 Loading

Taiichiro Suda,* Yan Zhang,†† Toru Iwaki,† and Masakatsu Nomura††
General Office of Plantsiting and Environmental, The Kansai Electric Power Co. Inc.,
3-22 Nakanoshima 3 chome, Kita-ku, Osaka 530-70
†*Hiroshima Research & Development Center, Mitsubishi Heavy Industries, Ltd., 4-6-22, Kan-on-shin-machi, Nishi-ku, Hiroshima 733*
††*Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565*

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The HOMO energy and the superdelocalizability for the most stable conformation of 18 kinds of alkanolamines plotted against experimentally measured absorption loading of CO_2 in an aqueous amine solution showed a good linear relationship for the usual secondary and tertiary amines, indicating that the frontier orbital properties of these amines appear to be predominant for the amine-CO_2 reaction.

The removal of acid gas components such as H_2S and CO_2 from natural gas, the synthesis gas for ammonia production and waste gas from power plants, is one of the most important objectives in the process industry. This separation technique is usually accomplished by applying chemical absorbents such as alkanolamines due to the easy regeneration of the large amount of absorbents used. Therefore, a high performance absorbent has been required for use in the CO_2 recovery plants at a power station especially for limiting global warming.[1]

Up to now, the studies about CO_2 absorbents were almost limited to studying the reaction kinetics between CO_2 and alkanolamines[2] and relatively little data have been developed for a fundamental understanding of the molecular chemistry of these systems.[3] The non-bonding orbital on the N atom of amine molecules exerting the electrophilic attack is remarkably affected by the alkyl substituents neighboring N atom. The Frontier Molecular Orbital theory by Fukui[4] provided a very convenient framework for the prediction of chemical reactivity. Namely, the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) are considered as the principal factors governing the easiness of a chemical reaction.

The present study was undertaken to explore correlation between the CO_2 absorption ability of an alkanolamine solution and the molecular orbital properties of alkanolamine molecules of a basic structure of N-C-C-O with different kinds of substituents. We have characterized the most stable conformation for 18 kinds of alkanolamines along with the HOMO energy, E_{HOMO}, and the electrophilic superdelocalizability of the N atom, $Sr^{(E)}_N$, by use of semi-empirical PM3 method and its partial charge, σ_N, by AM1 one. These alkanolamines are, as shown in Table 1, three primary (A-C), nine secondary (D-L) and six tertiary amines (M-R).

All absorption experiments were carried out as follows. At the start of the experiment, a 50 cm^3 of alkanolamine solution (30 wt% of amine concentration) was poured into a glass cell (35 mm inner diameter and 300 mm high). All alkanolamines used as received were at least 99% pure. The temperature of the alkanolamine solutions was thermostated to 40 ± 0.5 ℃ using a temperature regulated water bath outside the cell. The gas mixture of 10% CO_2, 3% O_2 and 87% N_2 was then passed through the cell after keeping the flow rate of CO_2 to 100 ± 3 cm^3/min (20 ℃, 101 kPa) using a mass-flow-controller (KOFLOK MODEL 3620), then adjusting the flow rate of O_2 and N_2 using another flowmeter (KOFLOK RK-1250). The CO_2 concentration at the entrance of the reaction cell and at the outlet was continuously monitored by means of a CO_2 IR-analyzer (VIA-510). The experiment is stopped when the concentration of CO_2 at the outlet is equal to that at the entrance. At the end of the experiment, the total amount of CO_2 absorbed was directly obtained by determining the CO_2 gas evolved from the amine solution with NDIR (TOC 5000, SHIMADZU. Co., Ltd.). Based on this experimental condition, the CO_2 molar loading was determined by evaluating the total amount of CO_2 absorbed and

Table 1. The molecular orbital properties of the most stable conformations of 18 alkanolamines

	Alkanolamine	Hf / kJ mol^{-1}	Dihedral angle (NC-CO) / deg	E_{HOMO} / eV	$Sr^{(E)}_N$	σ_N / au	CO_2 molar loading	pKa[6] (20 ℃)	pKa[6] (40 ℃)
A	2-aminoethanol	-222.21	61.87	-9.528	1.434	-0.328	0.56	9. 65	9. 07
B	1-amino-2-propanol	-251.51	59.78	-9.488	1.459	-0.329	0.53	9. 5[a]	
C	2-amino-2-methyl-1-propanol	-273.88	58.52	-9.533	1.479	-0.319	0.72	9. 88	9. 20
D	2-(methylamino)ethanol	-230.20	61.89	-9.264	1.584	-0.294	0.63	9. 95	9. 35
E	2-(ethylamino)ethanol	-259.73	64.39	-9.278	1.591	-0.296	0.68	9. 95[a]	
F	2-(n-propylamino)ethanol	-282.62	64.01	-9.264	1.597	-0.296	0.62		9. 4[a]
G	2-(isopropylamino)ethanol	-283.79	63.69	-9.266	1.622	-0.299	0.73	10. 1[a]	
H	2-(n-buthylamino)ethanol	-305.28	64.05	-9.268	1.595	-0.292	0.63	10. 0[a]	
I	2-(*tert*-buthylamino)ethanol	-306.72	52.98	-9.231	1.657	-0.291	0.70	10. 29	9. 64
J	2-methylamino-2-methyl-1-propanol	-275.52	68.21	-9.464	1.432	-0.306	0.88	9. 9[a]	
K	2-ethylamino-2-methyl-1-propanol	-304.18	66.56	-9.478	1.451	-0.307	0.90	9. 8[a]	
L	2-isopropylamino-2-methyl-1-propanol	-328.95	63.67	-9.481	1.469	-0.312	0.86	9. 7[a]	
M	2-(dimethylamino)ethanol	-238.58	76.26	-9.313	1.511	-0.270	0.56	9. 23	8. 69
N	N-ethyl-N-methyl-ethanolamine	-262.65	76.00	-9.259	1.555	-0.273	0.61		8. 95[a]
O	2-(diethylamino)ethanol	-288.56	71.83	-9.222	1.638	-0.274	0.75	9. 76	9. 16
P	N-methyl-2,2'-iminodiethanol	-431.57	60.63	-9.537	1.327	-0.274	0.29	8. 76	8. 28
Q	N-*tert*-buthyl-2,2'-iminodiethanol	-496.23	73.26	-9.391	1.463	-0.270	0.44		8. 7[a]
R	2-dimethylamino-2-methyl-1-propanol	-277.57	65.62	-9.246	1.576	-0.267	0.80	9. 4[a]	

[a] Estimated from the data in M. M. Sharma, *Trans. Faraday. Soc.*, **60**, 681 (1964) and in our experiments.

the concentration of amine solution.

All calculation procedures were carried out by MOPAC 94 in the CAChe system. All of the geometrical isomers were obtained as a local energy minimum on the energy maps which were constructed by rotating the principle bond axis such as the C-C, N-C and C-O bonds, clockwise and counterclockwise, respectively. For each conformation, the heat of formation, *Hf*, E_{HOMO}, $Sr^{(E)}_{N}$ and σ_N were evaluated stringently using the extra-keyword GNORM=0.01; $Sr^{(E)}$ was calculated by assuming the reagent energy of CO_2 to be -8.00 eV which is between the HOMO and LUMO energies of all the alkanolamines.

A large number of stable conformations obtained for all the alkanolamine sample can be classified into two groups: trans and gauche about the NC-CO bond. The most stable conformational structure having the lowest heat of formation shows the gauche type - an intramolecular NH--O or N--HO hydrogen bonded structure. These gauche conformations have been certified to be predominantly present in an aqueous state by the laser Raman study on some alkanolamine molecules.[5] The principle axis conformation and molecular properties for the most stable structure, which are characterized as the gauche type are presented in Table 1 along with the experimental CO_2 molar loading and p*Ka* values. With an increase in the steric hindrance of the alkyl substituents bonded to the N atom against a nonbonding orbital of the N atom, $Sr^{(E)}_{N}$ increases along with E_{HOMO} beside primary amines (Sample A and B) and sterically hindered amines having a N-C(C)$_2$-C-O structure (Sample C, J, K and L), which have the lower HOMO energy and the larger negative partial charge of the N atom, compared to other amines.

The values of both E_{HOMO} and $Sr^{(E)}_{N}$ of the 18 alkanolamines are plotted against the experimental CO_2 loading as shown in Figure 1(a) and (b), respectively. It is noted that these amines are divided into two groups in both plots; one is characterized by a close straight-line correlation for the usual secondary and tertiary alkanolamines and the other by a large nonlinear interaction with CO_2. The former indicates that frontier orbital properties, especially the $Sr^{(E)}_{N}$ of the tertiary alkanolamines appear to be predominant for the amine-CO_2 reactions. This is the same tendency as the case of the kinetics for the tertiary amine-CO_2 reaction that depends on the p*Ka* values of the amines including diethanol groups.[7] This relationship did not hold at a high CO_2 pressure such as one atmosphere, indicating that the chemical absorption rather than physical one occurs at these low CO_2 pressure. In this study, the p*Ka* value of the amines does not correlate well to the experimental CO_2 molar loading and any other calculated values such as σ_N, suggesting that the CO_2 molar loading may not be specified by the acid-base interaction alone.[8]

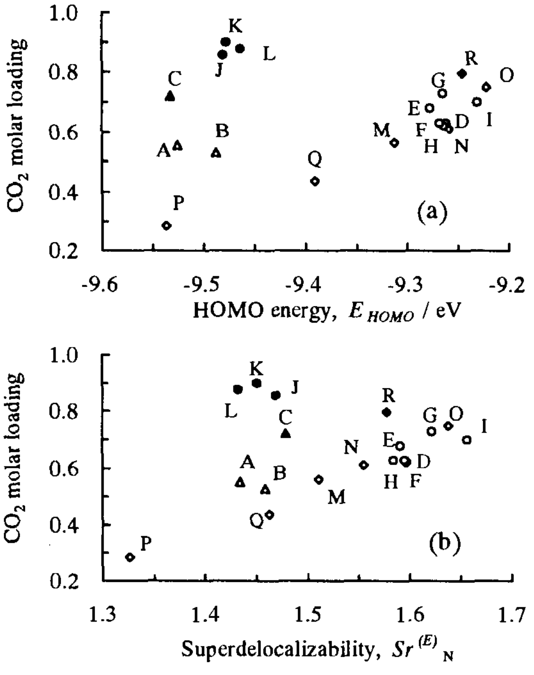

Figure 1. Plot of experimental CO_2 loading against the HOMO energy (a) and the superdelocalizability (b) of the most stable conformations of 18 alkanolamines.

Though the superdelocalizability has usually been used to evaluate the easiness for electrophilic attack of atoms within a molecule, we have obtained the same tendency that $Sr^{(E)}_{N}$ reflects the reactivity of CO_2 among the different kinds of secondary and tertiary amine molecules because these amines have the same reactive site - the N atom reacts with CO_2. Furthermore, the results obtained in this calculation strongly suggest that the most stable conformation of these usual alkanolamines significantly participates in the amine-CO_2 reaction, for example, experimentally performed CO_2 loading.

The reason, as is seen in Figure 1, why primary (A and B) and, in particular, sterically hindered amines (C, J, K, L) have a large drift interaction with CO_2 is not clear from the results of this experiment but may be ascribed to the larger negative charge on the N atom. These results may come from the difference in the reaction path of CO_2 between the primary and tertiary amines, the former being the direct reaction between two molecules forming the stable carbamate species accompanied by the formation of a protonated amine and the latter indirectly producing bicarbonate species with the incorporation of water, respectively, and the secondary amines between them.[9] On the other hand, the sterically hindered amines with larger negative charge may form the most labile carbamate species resulting in the easy formation of bicarbonate species and giving rise to higher CO_2 loading. The most sterically hindered amine (Sample R) also interacts considerably with CO_2 though its structural stability is fairly low.

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