Functionalized Tertiary Amines as SO$_2$ Absorbents

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Abstract - Nitrile-functionalized amines, including 3-($N, N$-diethylamino)propionitrile, 3-($N, N$-dibutylamino)propionitrile, and $N$-methyl-$N, N$-dipropionitrile amine were synthesized, and their interaction behaviours with SO$_2$ were compared with those of hydroxyl-functionalized amines by experimental, spectroscopic, and computational methods.

Keywords: SO$_2$; Absorbent; Amine; Nitrile; Recycle

1. Introduction

The absorption of SO$_2$ in a liquid absorbent is mostly governed by the interaction between acidic SO$_2$ and the basic absorbent [1, 2]. In this context, high SO$_2$ absorption capacity can be easily achieved simply by employing a basic primary or secondary amine as an absorbent [3, 4]. However, the primary and secondary amines with a N-H bond or bonds tend to strongly interact with SO$_2$, forming sulfamite and/or bisulfite species, which are hard to desorb SO$_2$ even at elevated temperatures. Moreover, the desorption of SO$_2$ at elevated temperatures often results in the irreversible decomposition of amines. For this reason, the aqueous solutions of tertiary amines without possessing a N-H bond have been employed as SO$_2$ absorbents. The most commonly used tertiary amines for this purpose are the tertiary alkanolamines with two or three N-bound hydroxyethyl groups such as $N$-methyl-$N, N$-diethanolamine (MDEA) and $N, N, N$-triethanolamine (TEA). In spite of their high thermal stability toward the degradation, tertiary alkanolamines, however, are also found to exhibit poor recyclability (cyclic capacity) similar to those of primary and secondary amines at temperature around 100 °C. Computational calculation with $N, N$-dibutyl-$N$-ethanolamine (DBEA), conducted in this study, suggests that the poor cyclic capacity of tertiary alkanolamines can be ascribed to the interaction of SO$_2$ with the hydroxyl groups, resulting in the formation of thermally stable zwitterionic species with a tethered sulfite anion (-OSO$_2^-$) (vide infra).

As a means of improving the regenerability of tertiary alkanolamines, a hydroxyl group or groups of alkanolamines have been replaced by an electron-withdrawing nitrile group or groups. With this approach, it is expected that the higher cyclic capacity could be achieved because the additional interaction between SO$_2$ and the hydroxyl group is not available.

Herein, we report the synthesis of several nitrile-functionalized tertiary amines, including 3-($N, N$-diethy lamino)propionitrile (DEAPN), 3-($N, N$-dibutylamino)propionitrile (DBAPN), and $N$-methyl-$N, N$-dipropionitrile amine (MADPN) as well as their performances as SO$_2$ absorbents. The different absorption behaviors of nitrile-functionalized tertiary amines from those of tertiary alkanolamines are also discussed on the basis of experimental and computational calculation results.

2. Results and Discussion

The nitrile-functionalized tertiary amines (DEAPN, DBAPN, and MADPN) were synthesized as shown in Scheme 1, and their gravimetric and molar SO$_2$ absorption capacities were compared with those of hydroxyl-functionalized tertiary amines ($t$-alkanolamines). As can be seen in Fig. 1, $t$-alkanolamines exhibit higher gravimetric SO$_2$ absorption capacities (g SO$_2$/g amine) than the nitrile-functionalized tertiary amines at 30 °C. The gravimetric SO$_2$ absorption at saturation were measured at 0.897 (1.77), 0.730 (2.08), 0.655 (1.39), 1.517 (2.78), 1.084 (2.94), and 1.183 (2.20) for DEAPN, DBAPN, MADPN, DEEA, DBEA, and MDEA, respectively.
Scheme 1. Synthetic route for the nitrile-functionalized amines.

The numbers in parentheses are the molar absorption capacities (mole SO$_2$/mole amine). It is worthwhile to note that the molar absorption capacities of $t$-alkanolamines are in the range 2.20 – 2.94. If SO$_2$ is absorbed in $t$-alkanolamines only through the chemical interaction, the molar SO$_2$ absorption capacities of $t$-alkanolamines cannot exceed 1. In this context, it is assumed that physical interaction is also involved in the absorption of SO$_2$ in $t$-alkanolamines. As zwitterionic species with a tethered sulfite anion (-OSO$_2$-) are expected to produce from the interaction of SO$_2$ with $t$-alkanolamines [30], it is conceivable that substantial amounts of SO$_2$ are absorbed in $t$-alkanolamines through the physical interaction between acidic SO$_2$ and the basic sulfite anion. In contrast to the $t$-alkanolamines, nitrile-functionalized tertiary amines do not possess an additional functional group to chemically interact with SO$_2$. Moreover, their basicities are also too weak to form stable charge transfer complexes with SO$_2$ due to the presence of an electron-withdrawing nitrile group. Therefore, it is considered that the absorption of SO$_2$ in nitrile-functionalized tertiary amines is mostly governed by the physical interactions via hydrogen bonding between SO$_2$ and CH$_2$ groups (vide infra). This is probably one of the reasons why nitrile-functionalized tertiary amines exhibited lower absorption capacities than the corresponding $t$-alkanolamines. Nonetheless, the absorption capacities of nitrile-functionalized tertiary amines are still sufficiently high enough to remove SO$_2$ present in small quantities in flue gases.

Interestingly, the nitrile-functionalized tertiary amines exhibited higher absorption rates than the corresponding $t$-alkanolamines. It is well recognized that the viscosity of a physical sorbent for SO$_2$ capture decreases with the increase of the SO$_2$ absorption in the solvent, whereas the viscosity of a chemical sorbent increases rapidly with increasing absorption of SO$_2$ [5,6]. In this context, the higher rates of absorption for the nitrile-functionalized tertiary amines could be ascribed in part to their lower viscosities, resulting in the faster mass transfer (see vide infra).

To examine the reversibility of SO$_2$ absorption, SO$_2$ was absorbed in a tertiary amine at 30 °C for 2 h at a rate of 20 mL min$^{-1}$ and desorbed at 80 °C for 2 h by bubbling N$_2$ at a rate of 20 mL min$^{-1}$ at atmospheric pressure. As can be seen in Fig. 2, the recycle experiments with DEAPN, DBAPN, and MADPN clearly demonstrate that the absorbed SO$_2$ can be completely desorbed at 80 °C, allowing all the nitrile-functionalized tertiary amines to be recyclable without any loss of initial performances. On the contrary, $t$-alkanolamines, DEEA, DBEA, and MDEA exhibited extremely poor recyclability.

As can be seen in Fig. 3, after the first absorption-desorption cycles, it was observed that approximately 40-45% of SO$_2$ absorbed in the $t$-alkanolamines remained undesorbed. The same amounts of desorbed SO$_2$ in the first cycle were found to be re-absorbed and easily desorbed in the following cycles. This is a strong indication that the absorption of SO$_2$ in $t$-alkanolamines proceeds through both chemical and physical interactions. Considering the amounts of undesorbed SO$_2$ in the first cycle, it is likely that SO$_2$ interacts with a $t$-alkanolamine approximately in a 1:1 molar ratio.

To elucidate the role of functional group on the SO$_2$ absorption in tertiary amines, theoretical investigation was conducted at the B3LYP level of the theory (6-31+G* for C, H, N, O, and S) using the Gaussian 03 program. Fig. 4 is the optimized structure showing the interaction of SO$_2$ with DBAPN. As can be seen in the optimized structure, there is a weak interaction between the sulfur atom of SO$_2$ and the amino nitrogen atom. The oxygen atoms of SO$_2$ are also found to weakly interact with each of the hydrogen atoms of methylene groups bonded to the nitrile and amino groups. The interaction enthalpy ($\Delta H$) was calculated as -8.1 kcal mol$^{-1}$, suggesting that the SO$_2$ absorption in DBAPN is a favorable process.
Fig. 1: Gravimetric $\text{SO}_2$ absorption capacity of (a) DEAPN, (b) DBAPN, (c) MADPN, (d) DEEA, (e) DBEA, (f) MDEA, and (g) TBA at 30 °C.

Fig. 2: $\text{SO}_2$ absorption-desorption cycles of DEAPN (●), DBAPN (○), and MADPN (▲). In each cycle, $\text{SO}_2$ is absorbed at 30 °C and at atmosphere pressure, and desorbed at 80 °C.

Fig. 3: $\text{SO}_2$ absorption-desorption cycles of DEEA (■), DBEA (▽), and MDEA (△). In each cycle, $\text{SO}_2$ was absorbed at 30 °C and at atmosphere pressure, and desorbed at 80 °C.
Fig. 4: Optimized structure showing the interaction of SO\(_2\) with DBAPN (\(\Delta H = -8.1\) kcal mol\(^{-1}\)).

For comparison, the interaction of SO\(_2\) with DBEA was also calculated. In order to better reflect the absorption behavior of SO\(_2\) in DBEA, two DBEA molecules were included in the calculation. Fig. 5a, 5b, 5c, and 5d are the optimized structures of the reactant, transition state, intermediate species, and the product for the interaction of SO\(_2\) with DBEA, respectively. The numbers in the parentheses are energies relative to that of the reactant. As can be seen in the optimized structure of the transition state (Fig. 5b), there is a strong intermolecular hydrogen bonding interaction between the hydroxyl group of the first DBEA molecule and the nitrogen atom of the second DBEA molecule. Such a hydrogen bonding interaction seems to be a driving force for the interaction of SO\(_2\) with the first DBEA molecule through the sulfur atom. The interaction distances of O···H, N···H, and S···O(H) were calculated as 1.21, 1.32, and 2.15 Å, respectively. The transition state energy was calculated as only +2.5 kcal mol\(^{-1}\), suggesting that there is practically no activation barrier for the interaction of SO\(_2\) with the hydroxyl group. As can be seen in Fig. 5c, strong intermolecular interactions among three molecules result in the formation of an ionic intermediate species consisting of [DBEAH]\(^+\) and [Bu\(_2\)NCH\(_2\)CH\(_2\)O-SO\(_2\)]\(^-\) anion with a covalently bound -OSO\(_2^–\) group, which interacts with two protic hydrogen atoms of the hydroxyl and N-H groups of [DBEAH]\(^+\). Gibbs free energy of formation (\(\Delta G\)) for the intermediate species was calculated as -0.6 kcal mol\(^{-1}\). The intermediate species seems to transform immediately into the final product, a zwitterionic compound having a structure of Bu\(_2\)N\(^+\)(H)CH\(_2\)CH\(_2\)O-SO\(_2^–\), via a proton transfer from [DBEAH]\(^+\) to [Bu\(_2\)NCH\(_2\)CH\(_2\)O-SO\(_2\)]. Gibbs free energy of formation (\(\Delta G\)) for the final product was calculated as -4.6 kcal mol\(^{-1}\). Thus generated DBEA molecule is capable of interacting with SO\(_2\), leading to the formation of Bu\(_2\)N\(^+\)(H)CH\(_2\)CH\(_2\)O-SO\(_2^–\). As a result such consecutive interactions of DBEA with SO\(_2\), 1:1 adduct of DBEA and SO\(_2\) is produced.

To support the computational results on the nature of SO\(_2\) absorption in the functionalized tertiary amines, the interactions of SO\(_2\) with DBAPN and DBEA were investigated by \(^1\)H and \(^13\)C NMR spectroscopy in DMSO-\(d_6\) using a high
pressure NMR tube. As can be seen in Fig. 6a and 6b, the peak corresponding to the OH group of DBEA at 4.22 ppm completely disappeared when the NMR tube containing a solution of DBEA in DMSO-$d_6$ was pressurized with 2 bar of SO$_2$. Instead, a new peak appeared at 9.89 ppm, which could be assigned to the hydrogen atom bonded to the nitrogen atom of [DBEAH]$^+$ [30]. In addition, all the peaks associated with the CH$_2$ groups bonded to the nitrogen and oxygen atoms were found to shift downfield by 0.424-0.644 ppm. Considering the disappearance of the peak for the hydroxyl group of DBEA along with the appearance of the peak at 9.89 ppm and the relatively large peak shifts for the methylene groups, it is evident that SO$_2$ interacts chemically with DBEA through the hydroxyl group, forming an ionic species with a covalently bound -OSO$_2^-$ [7,8]. The involvement of the hydroxyl group during the chemical absorption of SO$_2$ in DBEA was further demonstrated by $^{13}$C NMR experiments. As can be seen in Fig. 7a and 7b, the chemical shifts of the carbon atoms of the hydroxyethyl group bound to the nitrogen atom were found to move upfield by 5.2 (C-O) and 4.7 ppm (C-N), respectively.

Fig. 6: $^1$H NMR spectra showing the interactions of amines with SO$_2$ in DMSO-$d_6$: (a) DBEA, (b) DBEA under pressure of 1 bar of SO$_2$, (c) DBAPN, (d) DBAPN under pressure of 1 bar of SO$_2$, and (e) N$_2$ flowed (d) at 80°C.

In contrast, the peak corresponding to the methylene carbons of the butyl groups adjacent to the nitrogen atom moved upfield by only 1.6 ppm from 53.9 to 52.3 ppm, implying that the change in electronic environment is greater for the hydroxyethyl group than for the butyl groups. In consideration of this, it is likely that SO$_2$ prefers interacting with the hydroxyl group to the interaction with the nitrogen atom. Similar bonding mode was also suggested for interaction of between SO$_2$ and diethylaminoundecanol [7].

Fig. 6c and 6d show the $^1$H NMR spectra for the interaction of DBAPN with SO$_2$. Contrary to the interaction of SO$_2$ with DBEA, the peaks associated with the CH$_2$ groups shifted downfield, and the degree of peak shift in the range 0.116-0.192 ppm was considerably smaller than that observed for the interaction of SO$_2$ with DBEA, indicating that physical interaction is predominant. Such downfield shifts were also observed in the $^{13}$C NMR spectra. As can be seen in Fig. 7c and 7d, the peaks associated with the CH$_2$ groups bonded to the nitrogen atom and nitrile group shifted downfield by only 0.192, 0.116, and 0.129 ppm from 2.648, 2.529, and 2.392 to 2.840, 2.645, and 2.521 ppm, respectively. Fig. 7c and 7d are the $^{13}$C NMR spectra showing the interaction of SO$_2$ with TBAPN. Similar to $^1$H NMR results, the degree of peak shift for the CH$_2$ groups of CH$_2$CH$_2$CN moiety is much less pronounced than that for the CH$_2$ groups of CH$_2$CH$_2$OH moiety. In consideration of the smaller degree of peak shifts and the computational results, it is reasonable to assume that SO$_2$ interacts physically with DBAPN.

3. Conclusion

We have demonstrated that the tertiary amines bearing a nitrile functional group are highly efficient for the rapid and reversible absorption of SO$_2$. The saturation capacity of SO$_2$ in the nitrile-functionalized tertiary amines are approximately 2 moles per mole of amine. The physically absorbed SO$_2$ in the nitrile-functionalized tertiary amines can be readily and completely desorbed by heating at 80 °C under N$_2$ gas flow, thereby allowing the tertiary amines to be reused without any loss in their initial capacities. In contrast to the nitrile-functionalized tertiary amines, the hydroxy-functionalized tertiary amines interact chemically with SO$_2$, forming irreversible 1:1 zwitterionic species bearing a
covalently bound-OSO$_2^-$ group, which are hard to evolve SO$_2$ even at the elevated temperature of 120 °C.

**Acknowledgements**

This work was supported by the Fusion Research Program for Green Technologies (NRF-2012M3C1A1054497)” through the National Research Foundation of Korea (NRF) funded by Ministry of Education, Science and Technology.

**References**


