Theoretical study of the degradation mechanisms of substituted phenyltrimethylammonium cations

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Degradation mechanisms of substituted phenyltrimethylammonium cations were investigated through density functional theory (DFT) calculations performed at the B3LYP/6-311++G (2d, p) level. Several substituents and their positions on the benzene ring were changed in order to explore the relation between the orientation effect and the stability of the substituted phenyltrimethylammonium cations. The results of the DFT calculations indicated that the calculated energy barriers are raised when the electron-donating substituents are at the ortho and para positions of the benzene ring. Specifically, the calculations showed that the double-$(CH_3)_2$N-substituted phenylTMA+ is more stable than the double-$(CH_3)_2$N-substituted benzylTMA+. The highest increase in $\Delta G^{\neq}$ was 3.7 kcal/mol and resulted from the triple $(CH_3)_2$N-substitution of phenylTMA+. These results elucidate the effects of substituents on the degradation of model cations and provide a reference for their potential use in anion-exchange membranes.

1. Introduction

Substituted trimethylammonium (TMA) cations in alkaline anion-exchange membranes (AEMs) have received attention owing to the fact that they degrade and limit the lifetime of alkaline membrane fuel cells [1–21]. A number of experimental and theoretical studies have indicated that the substituted TMA cations can react with hydroxides through three pathways, namely, the S_N2 pathway, Hofmann elimination pathway, and ylide reaction. To improve the stability of TMA cation, a series of alkyltrimethylammonium (alkylTMA+) and aromatictrimethylammonium (aromaticTMA+) cations have been tested both experimentally and theoretically, including $N(CH_3)_4^+$, $N(CH_2CH_3)(CH_3)_3^+$, $N(C_6H_5)(CH_3)_3^+$, and $N(CH_2C_6H_5)(CH_3)_3^+$. In the case of alkylTMA+ cations, the theoretical results reported by Pivovar et al. [12–14] indicate that the ylide reaction is reversible and plays a minor role in the cation degradation process; the Hofmann elimination is the most favorable channel for cation degradation. In the case of aromaticTMA+, Einsla [15] experimentally found that benzylTMA+ cations are much more stable than phenylTMA+ cations in various concentrations of sodium hydroxide at 353 K. The calculations of Pivovar et al. [14] showed that in the S_N2 pathway for producing CH_3OH, the free-energy barrier, $\Delta G^{\neq}$, for the degradation of phenylTMA+ is 2.0 kcal/mol lower than that for

benzylTMA+. The methyl group of phenylTMA+ is attacked more readily, leading to the degradation of AEMs. A possible reason for this characteristic is that the electron-withdrawing effects of the phenyl group decrease the negative charge of the methyl group.

Although the stability of TMA cation has been increased steadily through experimental design, it still does not meet the actual engineering needs. Therefore, a number of cations need to be reconsidered and redesigned. Because the electronic effect and reactivity of phenyls can be changed by substituents on the benzene ring, benzylTMA+ and phenylTMA+ cations are potential modified object. It is obvious that benzylTMA+ would be a better choice owing to its stability being higher than that of phenylTMA+. Recently, Pivovar et al. [16] investigated the degradation channels of substituted benzyltrimethylammonium cations, and found that the degradation barrier can be increased by substituting an electron donor at a meta-position in the benzyl ring. However, the improvement is limited; the largest increase in the barrier is only 1.6 kcal/mol. If we consider the structure of benzyltrimethylammonium, it can be seen that there is a CH_2 group between the benzene ring and the nitrogen atom. This means that the effects of the electrons on the benzene ring are not transferred readily to the amino group.

Even though phenylTMA+ is unstable, it has recently been used in AEMs [22]. Thus, investigating the effects of substituents on the benzene ring can provide insights regarding the design of substituted trimethylammonium cations.

In this study, the degradation mechanisms of substituted phenyltrimethylammonium cations were investigated through density functional theory (DFT) calculations. The electron-donating substituents included RO– (R = H, CH_3) and R'_2N– (R′ = H, CH_3, CH_2CH_3).

2. Methods

All the calculations were performed using the Gaussian03 package [23]. The geometries of the transition states were optimized at the B3LYP/6-311++G (2d, p) level with the polarizable continuum solvation model (PCM) in water. For the model reaction $B^+ + OH^- \rightarrow [B–OH]^{\neq}$, the free-energy barrier, $\Delta G^{\neq}$, was calculated using the following formula: $\Delta G^{\neq} = \Delta G^{\neq}([B–OH]^{\neq}) - \Delta G^{\neq}(B^+) - \Delta G^{\neq}(OH^-)$. Because the operating temperature of AMFC is usually lower than 100 °C, a temperature of 80 °C was used in the calculations. Calculations were performed for 20 cations; their models are shown in Fig. 1.

3. Results and discussion

Because phenyl has no α-Hs, the ylide reaction does not take place. The β-Hs on the benzene ring are difficult to eliminate; therefore, the Hofmann eliminations can be ignored. Our discussions will center on the S_N2 pathway in the degradation of the substituted phenylTMA+ cations. The optimized geometries of the transition states are shown in Figs. 2–5. For conciseness, only some of the critical data for the transition-state geometries are shown in the figures. All the images were created using the program VMD [24]. The calculation results are listed in Tables 1 and 2.

3.1. Degradations of phenylTMA+

As shown in Fig. 2, phenylTMA+ has two types of methyl groups. The first type can be called the "planar methyl" group; in these, the carbon atom lies nearly in the same plane as the benzene ring. The other methyls are named the "nonplanar methyl". PhenylTMA+ can degrade through three S_N2 pathways. The products ($C_6H_5OH + N(CH_3)_3$) are obtained with a free-energy barrier of 27.0 kcal/mol. The other two channels produce $CH_3OH +$

$N(C_6H_5)(CH_3)_2$; the $\Delta G^{\neq}$ value for the planar methyl S_N2 is 22.2 kcal/mol, while that for the nonplanar methyl is 20.4 kcal/mol. The methyl S_N2 pathway is more favorable than the phenyl S_N2 one. Therefore, improving the stability of phenylTMA+ is necessary for increasing the barrier for the methyl S_N2 pathway.

3.2. Degradations of RO-phenylTMA+ (CH_3O-phenylTMA+, HO-phenylTMA+)

To generate a series of RO-phenylTMA+ cations, RO– (R = H, CH_3), an electron-donating group, has been used as a substituent at the ortho, meta, and para positions of the phenyl group. The degradation mechanisms of these cations have been studied using DFT calculations in order to investigate the effects of substituents on the stability of cations. All the transition states for the three types of methoxy-phenylTMA+ reactions are shown in Fig. 3.

In the degradations of o-CH_3O-phenylTMA+, $\Delta G^{\neq}$ for the planar methyl S_N2 is 22.1 kcal/mol, while that for the nonplanar methyl is 20.3 kcal/mol. These two barriers are lower by 0.1 kcal/mol than that for phenylTMA+. The $\Delta G^{\neq}$ value for the o-methoxy-phenyl S_N2 is 30.8 kcal/mol, which is 3.8 kcal/mol higher than that for the phenylTMA+ group. These results show that the o-methoxy group can improve the stability of the phenyl group but has a minimal effect on the methyl group in the substituted phenylTMA+.

For m-CH_3O-phenylTMA+, $\Delta G^{\neq}$ for the planar methyl S_N2 is 21.5 kcal/mol, while it is 19.9 kcal/mol for the nonplanar methyl S_N2. The $\Delta G^{\neq}$ value for the m-methoxy-phenyl S_N2 is 26.2 kcal/mol. In contrast to the case for phenylTMA+, the m-methoxy group has a negative effect on cation stability.

Similarly, there are three S_N2 pathways for the degradation of p-CH_3O-phenylTMA+. The first product channel involves the formation of p-CH_3O-C_6H_4–OH + $N(CH_3)_3$. This decomposition process requires overcoming a relatively higher barrier of 30.6 kcal/mol. The $\Delta G^{\neq}$ value of the channel for the planar methyl S_N2 is 22.3 kcal/mol, while it is 20.9 kcal/mol for the nonplanar methyl S_N2. Compared to free-energy barrier for phenylTMA+, these values are higher by 3.6, 0.5, and 0.1 kcal/mol, respectively.

As can be seen from the discussion above, when a methoxy group is at the ortho and para positions of the benzene ring, it can improve the stability of the phenyl group but has little effect on the methyl S_N2.

The hydroxyl group is a stronger electron-donating group than is the methoxy group. The placement of the hydroxyl group at different positions on the benzene ring can result in three different hydroxyl-phenylTMA+ entities.

Analogous to the degradation of CH_3O-phenylTMA+, every HO-phenylTMA+ can degrade through three S_N2 pathways. These transition states are shown in Fig. 3.

As shown in Table 1, the $\Delta G^{\neq}$ values for o-hydroxyl-phenyl and p-HO-phenylTMA+ S_N2 are higher than those for phenylTMA+ and CH_3O-phenylTMA+. This means that cation stability is improved when the hydroxyl group is at the ortho and para positions of the benzene ring, and the substituent effects of the hydroxyl group are stronger than that of the methoxy group.
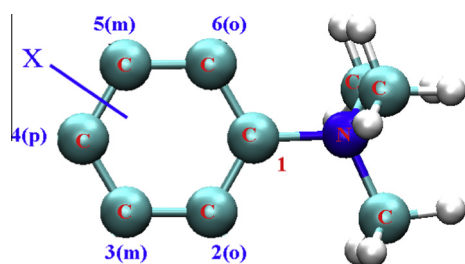

Fig. 1. Structure diagram for the substituted phenyltrimethylammonium cations. X = –OH, –OCH_3, –NH_2, –N(CH_3)_2, –N(CH_2CH_3)_2.
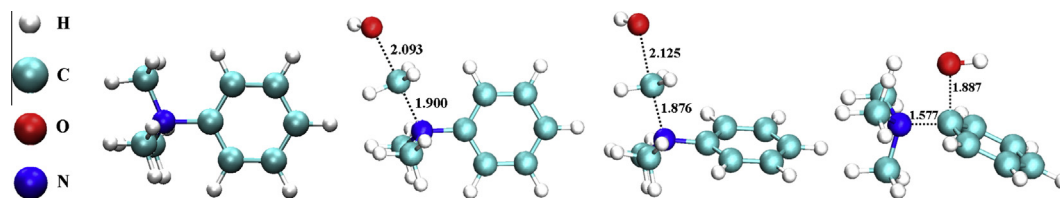

Fig. 2. Optimized structures of cation and transition states of planar-methyl, nonplanar-methyl S_N2 and phenyl S_N2 reactions for phenylTMA+.