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Stereomutations in silicate oligomerization: Role of steric hindrance and intramolecular hydrogen bonding : Supplementary information†

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Effect of Exchange Correlation

B3LYP is a well-recognized hybrid exchange-correlation functional which had been incorporated to investigate a wide variety of reaction mechanisms. The only disadvantage associated with B3LYP is that it underestimates the H-Bond strength (as reported in previous literature by Wijst et. al.[1]) due to the absence of dispersion corrections. To identify the possible effects of dispersion corrections, some of the cases of stereomutations have been investigated using ωB97XD. The activation barrier and net change in free energy of different stereomutations calculated using ωB97XD have been provided in the table 1. Simultaneously, these values obtained from B3LYP have been mentioned within the parenthesis. The strength of intramolecular H-Bonds which govern E_a and ΔG have been listed in table 2 which demonstrates the low strength being predicted by B3LYP. In spite of this factor, the overall conclusion drawn from B3LYP calculation regarding the effects of intramolecular H-Bonds on the E_a and ΔG also holds for ωB97XD.

Table 1 Comparison of activation barrier (E_a) and net change in free energy (ΔG) for different stereomutations calculated using ωB97XD and B3LYP(given in parenthesis)

Oligomer	Process (Transition state fig in the main file)	E_a (kcal/mol)	ΔG (kcal/mol)
Dimer	M1 (fig. 1b)	9.8 (10.5)	7.2 (9.4)
Dimer	M1 (fig. 2b)	6.0 (5.3)	2.9 (2.1)
Dimer	M1 (fig. 2d)	5.5 (5.5)	2.1 (2.0)
Dimer	M1 (fig. 3b)	8.2 (9.2)	7.1 (8.0)
Dimer	M3 (fig. 3d)	8.7 (9.6)	1.0 (2.3)
Trimer	M1 (fig. 8b)	6.1 (5.9)	3.8 (3.1)
Trimer	M3 (fig. 8e)	10.7 (10.8)	0.9 (1.8)

Table 2 Comparison of H-bond strength for different H-bonds calculated using ωB97XD and B3LYP(given in parenthesis)

Oligomer	H-bonds	E_{stb} (kcal/mol)
Dimer (from anionic-I) (fig. 1a)	O2-H1···O6	14.2 (12.0)
Dimer (from anionic-II) (fig. 3a)	O2-H1···O6	14.9 (12.4)
Trimer (fig. 5a)	O7-H5···O3	12.5 (11.1)
Trimer (fig. 5a)	O6-H4···O5	11.7 (10.9)

Pseudorotation in trimer silicate ring

Fig. 1 shows the M1 and $M3_{alt}$ mechanism of pseudorotation in a 3-member silicate ring resulting from anionic-II condensation. Here Si2-O1 is the bridging bond formed by the nucleophilic attack of O1 on Si2 atom (fig. 1d). The anionic-II mechanism can be characterized by the hydroxyl groups O4-H2 pointing towards

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‡ Additional footnotes to the title and authors can be included *e.g.* 'Present address:' or 'These authors contributed equally to this work' as above using the symbols: ‡, §, and ¶. Please place the appropriate symbol next to the author's name and include a `\footnotetext` entry in the the correct place in the list.

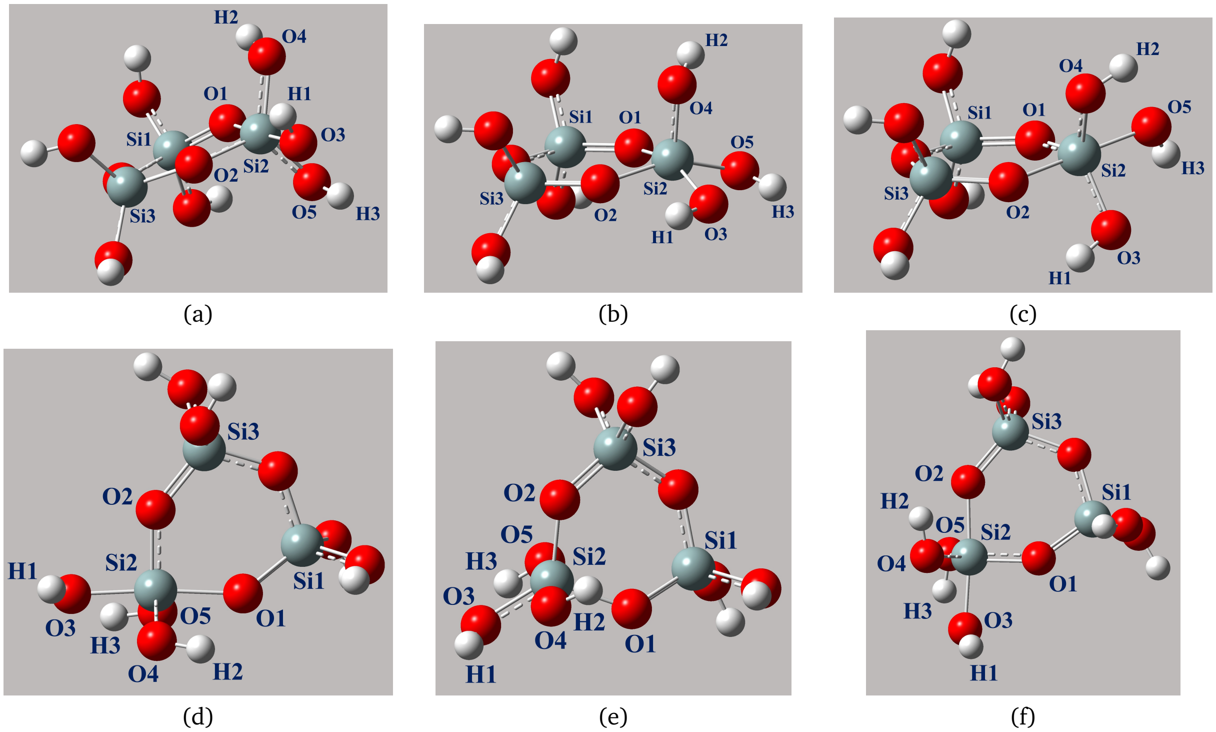

Fig. 1 M1 pseudorotation about Si2-O4 bond as a pivot in 3-member silicate ring. (a) Reactant ([Si2-O4, Si2-O2, Si2-O5] → equatorial and [Si2-O1, Si2-O3] → apical) (b) Transition state and (c) Product ([Si2-O2, Si2-O5] → apical and [Si2-O1, Si2-O3, Si2-O4] → equatorial); $M3_{alt}$ mechanism of rearrangement about bridging Si2-O2 bond as a pivot in 3-member silicate ring (d) Reactant ([Si2-O4, Si2-O2, Si2-O5] → equatorial and [Si2-O1, Si2-O3] → apical) (e) Transition state and (f) Product ([Si2-O2, Si2-O3] → apical and [Si2-O1, Si2-O4, Si2-O5] → equatorial) (color in web version: Si-grey, H-white, O-red)

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the nucleophile O1 atom and O5-H3 directing in the opposite direction. The M1 pseudorotation takes place about pivot Si2-O4 as the corresponding initial reactant has been shown in fig. 1a. Fig. 1b demonstrates the transition state with the hydroxyl group attached to pivot O4-H2 rotating towards Si2-O5. The bond angles O1-Si2-O3 and O2-Si2-O5 are measured as 154.84° and 153.99° respectively at transition state. The process accomplishes with bond angle O1-Si2-O3 reducing to 116.12° and O2-Si2-O5 rising to 175.03° in the final product. The activation barrier(E_a) and net change in free energy(ΔG) of this process are determined as 5.42 kcal/mol and 0.23 kcal/mol respectively.

The bridging Si2-O2 bond acts as a pivot in the $M3_{alt}$ mechanism. Fig. 1e shows the transition state for this process which resembles trigonal bipyramidal geometry (TBP). The bond angles primarily involved in reaction coordinate are O1-Si2-O3 and O4-Si2-O5. These are measured as 127.24° and 173.48° respectively at the transition state. This is quite similar to the transition state for $M3_{alt}$ mechanism for silicate ring-I as shown in fig. 11e in the main file. The E_a and ΔG is determined as 8.93 kcal/mol and 0.16 kcal/mol respectively. The process concludes with O1-Si2-O3 reducing to 92.78° and O4-Si2-O5 rising to 126.02° in the final product. The $M3_{alt}$ mechanism in dimer silicate resulting from anionic-II condensation has been shown in fig. 3 of the main file. The absence of a hydroxyl group at O2 facilitates this process. The possibility of $M3_{alt}$ mechanism persists even if O2 would be a part of hydroxyl group O2-H. During pseudorotation O2-H would rotate towards either Si2-O4 or Si2-O5. Rotation of O2-H towards Si2-O5 would lead to $M3_{alt}$ process. However, rotation of O2-H towards Si2-O4 would prevent the rotation of O4-H2 by steric hindrance which would ultimately result in M1 pseudorotation.

Notes and references

1 T. van der Wijst, C. F. Guerra, M. Swart and F. M. Bickelhaupt, *Chemical Physics Letters*, 2006, **426**, 415–421.