Hydrolysis of Trialkoxysilanes Catalyzed by Fluoride Anion. Nucleophilic vs. Basic Catalysis

Marek Cypryk[1], Bartłomiej Gostyński[1], Mateusz Pokora[2]

[1]) Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, Lodz 90-363, Poland

[2]) Lodz University of Technology, Faculty of Chemistry, Żeromskiego 116, 90-924 Łódź, Poland

Electronic Supplementary Information

For New Journal of Chemistry

Additional calculated geometries and free energy profiles for the reactions are presented.

Due to large number of calculated structures, geometries (in Cartesian coordinates) of all discussed species are available from authors upon request.

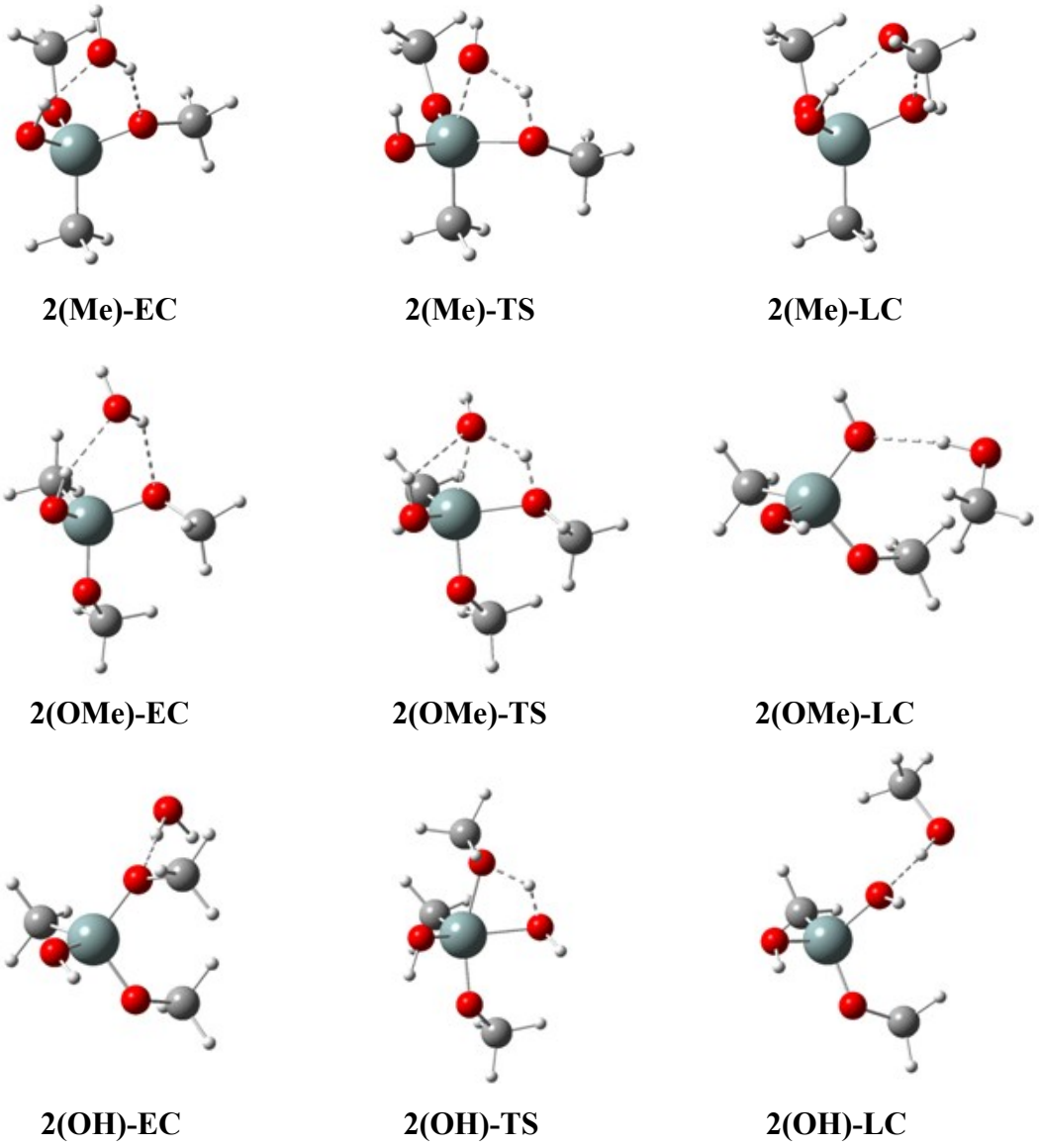


Fig. S1. Geometries of stationary points for non-catalyzed hydrolysis of $MeSi(OMe)_2(OH)$ (**2**) without fluoride ion (variant **I**); **2(Me)** - attack of a water molecule from the opposite direction to the methyl group; **2(OMe)** - attack of a water molecule from the opposite direction to the methoxy group; **2(OH)** - attack of a water molecule from the opposite direction to the hydroxy group; **EC** - early complex, **TS** - transition state, **LC** - late complex; predicted hydrogen bond interactions were marked with dashed lines.

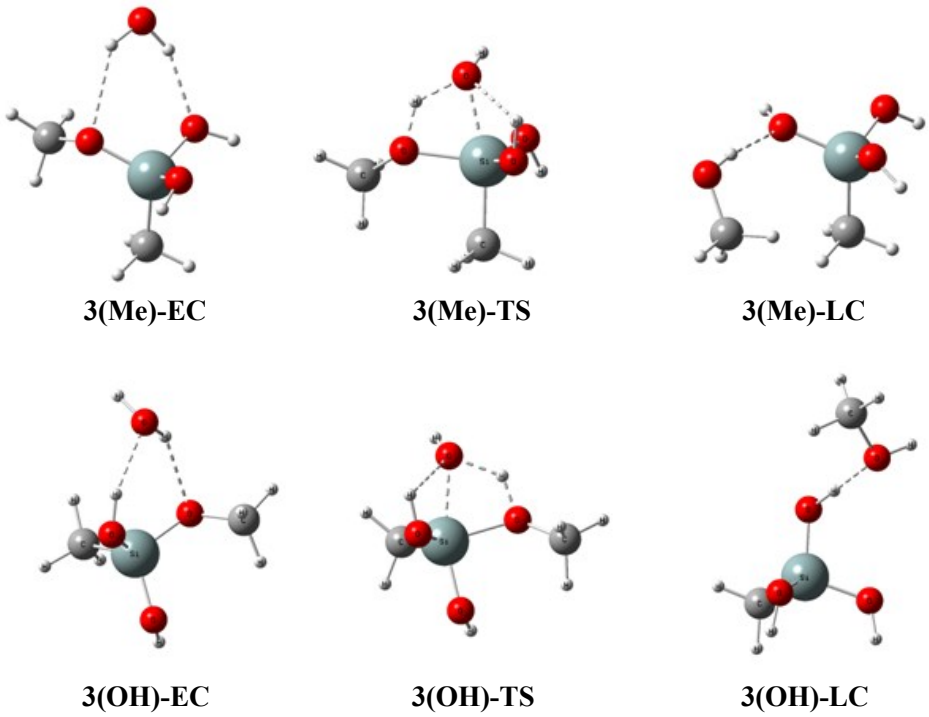


Fig. S2. Geometries of stationary points for non-catalyzed hydrolysis of $MeSi(OMe)(OH)_2$ (**3**) without fluoride ion; **3(Me)** - attack of a water molecule from the opposite direction to the methyl group; **3(OH)** - attack of a water molecule from the opposite direction to the hydroxy group; **EC** - early complex, **TS** - transition state, **LC** - late complex; predicted hydrogen bond interactions were marked with dashed lines.

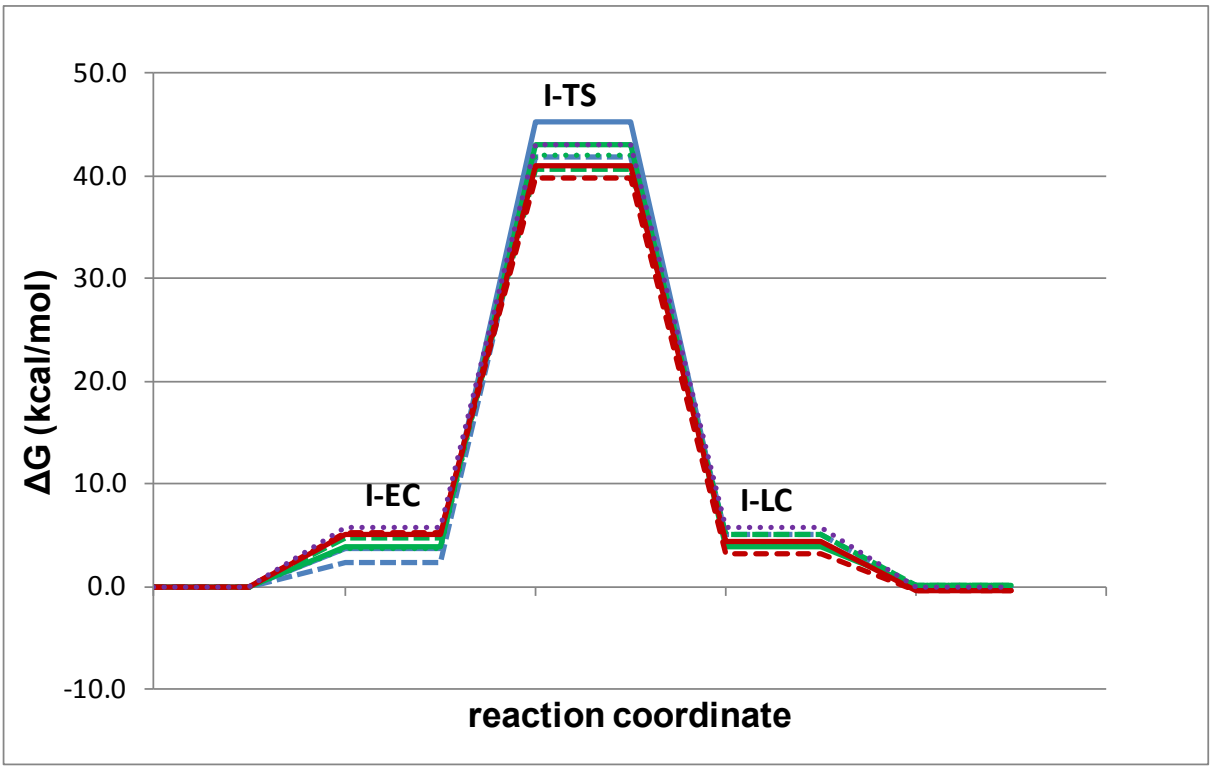
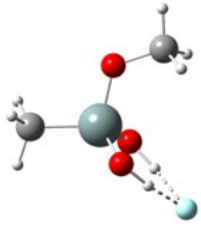
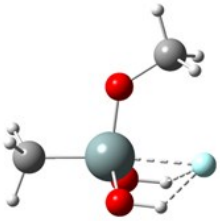


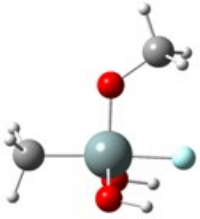
Fig. S3. Free energy profiles for non-catalyzed hydrolysis of $MeSi(OMe)_{3-n}(OH)_n$, n=0-3, with a single water molecule without fluoride anion (variant I); $MeSi(OMe)_3$ – blue, $MeSi(OMe)_2(OH)$ – green, $MeSi(OMe)(OH)_2$ – red, and $MeSi(OH)_3$ – violet; attack opposite to Si-Me - continuous line, opposite to Si-OMe - dashed line and opposite to the Si-OH group - dotted line.



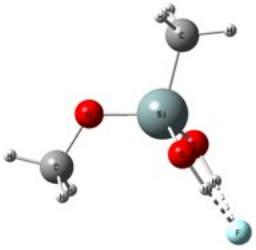
3(Me)(Si^{IV}···F$^-$)



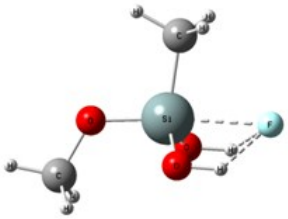
3(Me)(SiF)-TS



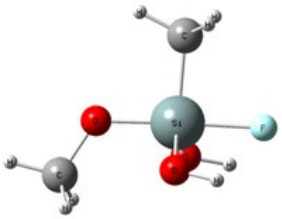
3(Me)(Si^{V}F$^-$)



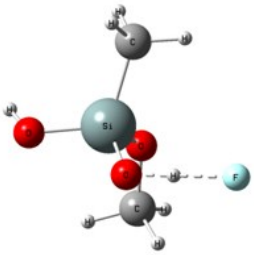
3(OMe)(Si^{IV}···F$^-$)



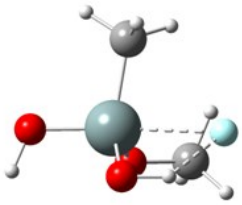
3(OMe)(SiF)-TS



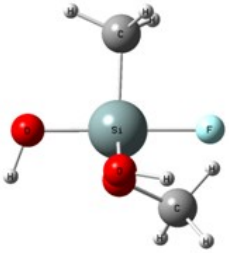
3(OMe)(Si^{V}F$^-$)



3(OH)(Si^{IV}···F$^-$)

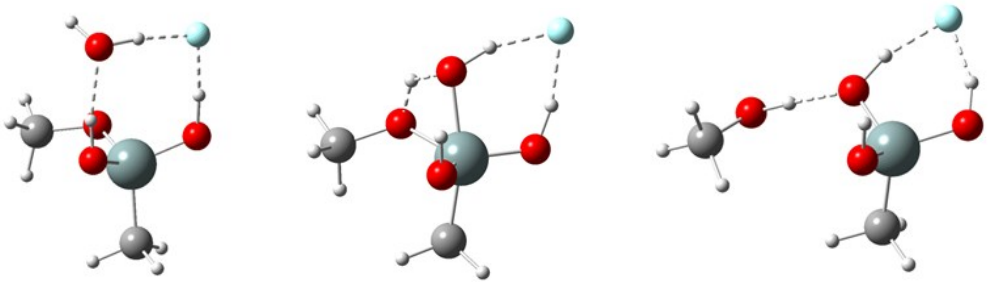


3(OH)(SiF)-TS

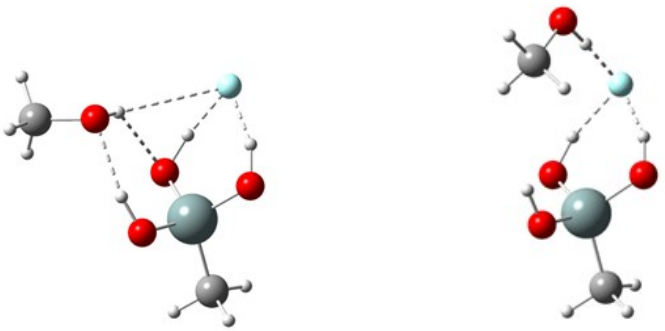


3(OH)(Si^{V}F$^-$)

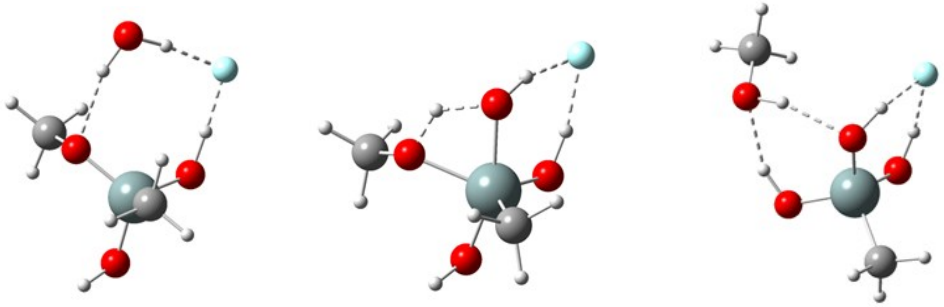
Fig. S4. Geometries of stationary points on the MeSi(OMe)(OH)$_2$ (**3**) + F$^-$ complex formation pathway; upper row - attack from the side opposite to Me, middle row - attack from the opposite to OMe, lower row - attack from the opposite to OH.



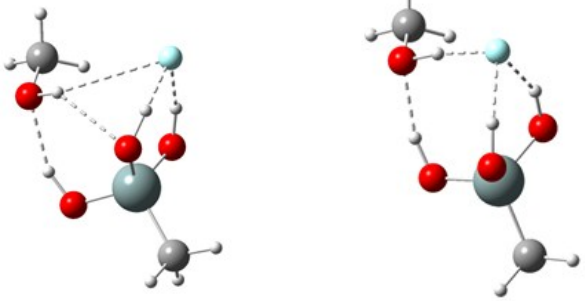
3(Me)-EC **3(Me)-TS1** **3(Me)-IC**



3(Me)-TS2 **3(Me)-LC**



3(OH)-EC **3(OH)-TS1** **3(OH)-IC**



3(OH)-TS2 **3(OH)-LC**

Fig. S5. Geometries of the stationary points for hydrolysis of $MeSi(OMe)(OH)_2 \cdots F^-$ (variant **II**); attack of a water molecule from the opposite direction to the hydroxy group; **EC** - early complex, **TS1** - transition state of the proton transfer, **IC** - intermediate complex, **TS2** – MeOH shift to F, **LC** – late complex; predicted hydrogen bond interactions were marked with dashed lines.

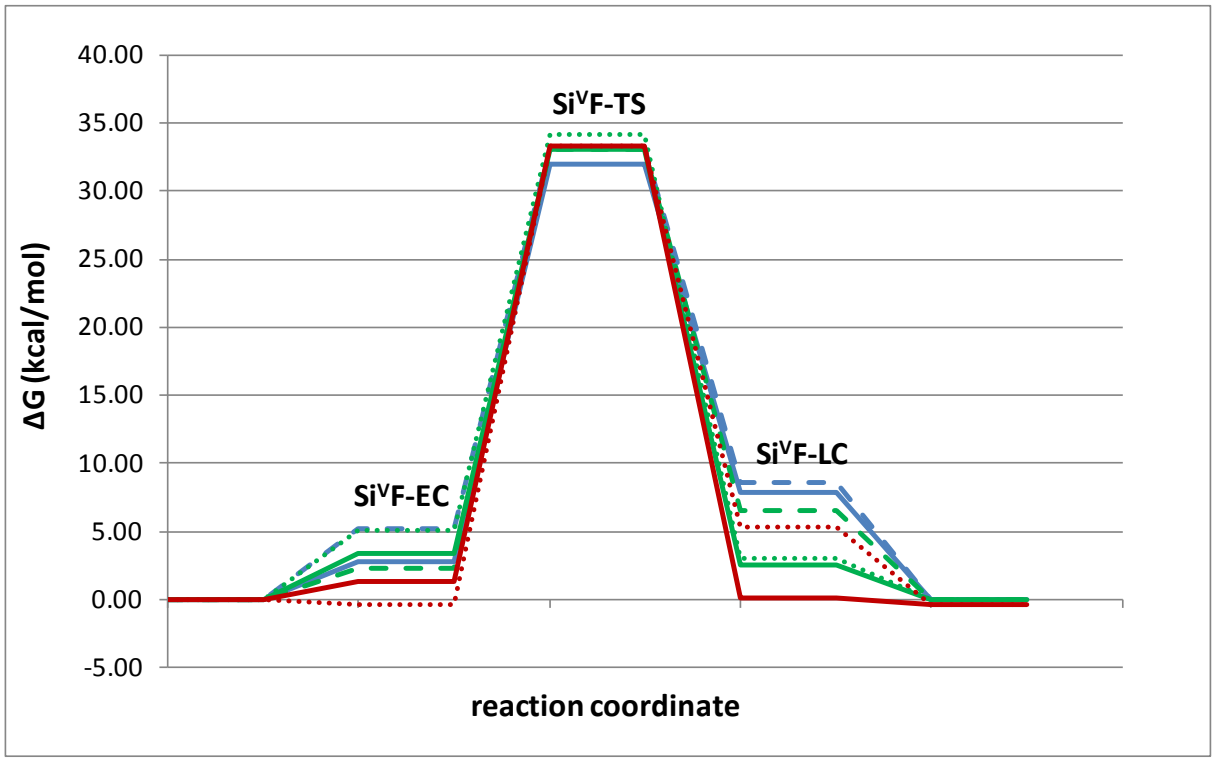


Fig. S6. Dependence of free energy as a function of the coordinate of water molecule attack on the hypervalent $MeSi(OMe)_n(OH)_{3-n}F^-$ intermediates; $MeSi^V(OMe)_3F^-$ – blue, $MeSi^V(OMe)_2(OH)F^-$ - green, $MeSi^V(OMe)(OH)_2F^-$ - red; attack from the opposite side to Si-Me - continuous line, opposite to Si-OMe - dashed line and opposite to Si-OH - dotted line