



Kinetics and mechanisms of hydrolysis of tetraphenylporphyrins tethered to silicate glass via a primary or tertiary alcohol linker



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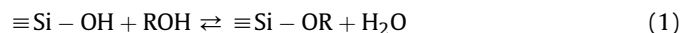
ABSTRACT

Tetraphenylporphyrins carrying primary or tertiary alcohols in a phenyl group were bonded to silicate glass by heat treatment. The rate of base catalyzed hydrolysis of tertiary ester was 20 times slower than that of primary ester, while the rate of acid catalyzed hydrolysis of tertiary ester was only 2.5 times slower than that of primary ester. Hydrolysis of tertiary alcohol bonded silica in $\text{HCl}/\text{H}_2^{18}\text{O}$ displayed that there is a covalent bond between alcohol oxygen and silicon, and the C–O bond is cleaved under acidic conditions, while the Si–O bond is cleaved under basic conditions.

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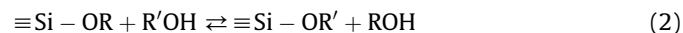
1. Introduction

The interconversion between silanols (hydroxysilanes) and alkoxy silanes (Eq. 1) is a key reaction in a number of practically important processes, such as sol–gel synthesis of ceramics,¹ surface modification of silicate glass or silica gel,² and silyl protection/deprotection of OH groups in organic synthesis.³



Surface reactions and adsorption on silicate or other metal oxides are applied to catalysis, separation science, microelectronics and composite materials. Elucidation of the stability of silyl ester bonds and the mechanism of their reactions can extend applicability of the thin film of alcohols on metal oxides to various fields of chemistry and materials science. In this paper, we focus on the reactions between surface silanols on solid silicon oxide and alcohols. In most studies on reactions of silanols on solid surface, primary alcohols have been used, such as methanol, ethanol, and butanol. There are a few reports employing tertiary alcohol.⁴ Lambert and Singer⁵ reported that chemisorption reactivity of pentanol isomers toward thermally activated silica decreases in the order: normal>iso>secondary>neo>tertiary.

Kitahara reported that the forward reaction of Eq. 1 proceeded sluggishly when *tert*-butyl alcohol was used: the number of alkoxy groups per 100 Å² of *n*-butyl alcohol bonded silica gel was 3.2 while that of *tert*-butyl alcohol was 0.7.⁶ Hasegawa and Sakka reported that transesterification shown in Eq. 2 proceeds in the presence of cation-exchange resin in the proton form for all isomers of butanol, and only *tert*-butanol unexpectedly gave a reactive silanol species.⁷



Peculiar reactivities of tertiary alcohols have been reported, while the molecular mechanisms behind the reactivities are not well known.

We report herein comparative studies on the forward and backward reactions of Eqs. 1 and 2 on silicate glass or silica gel employing primary alcohol and tertiary alcohol bearing a porphyrin chromophore. Both primary alcohol and tertiary alcohol reacted with silanol groups on silicate glass to afford alcohol bonded silicate glass. Tertiary alcohol bonded silicate glass was resistant against base catalyzed hydrolysis compared to primary alcohol bonded silicate glass. We found that the acid catalyzed solvolysis (Eqs. 1 and 2) of tertiary alcohol bonded silicate proceeded through C–O bond scission, while the base catalyzed solvolysis reaction of primary and tertiary alcohol bonded silicate as well as the acid catalyzed solvolysis reaction of primary alcohol bonded silicate all proceeded through Si–O bond scission.

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2. Results and discussion

2.1. Preparation of porphyrin alcohols

Three alcohols bearing a porphyrin chromophore **1**, **2**, and **3** were prepared to compare influence of the alcohol structures on the forward and backward reactions of Eq. 1. Monolayers of porphyrin on silicate glass can be easily detected with electronic absorption spectroscopy owing to the large molar absorptivity of porphyrin in the visible region, so that kinetic studies were feasible. Alcohol **1** was prepared by the Williamson ether synthesis reaction of 5-(4-hydroxyphenyl)-10,15,20-triphenylporphyrin with 5-bromopentyl acetate followed by alkaline hydrolysis of the ester.⁸ Alcohol **2** was obtained by the Williamson ether synthesis reaction of the same porphyrin with methyl 5-bromopentanoate, followed by the reaction with the methyl Grignard reagent. Alcohol **3** was prepared by the ether synthesis reaction of the same porphyrin with methyl 5-bromo-2-ethylpentanoate, followed by reduction with LiAlH₄. Alcohols **1**, **2**, and **3** were characterized with ¹H NMR and MALDI-TOF mass spectroscopy (Supplementary data) (Chart 1).

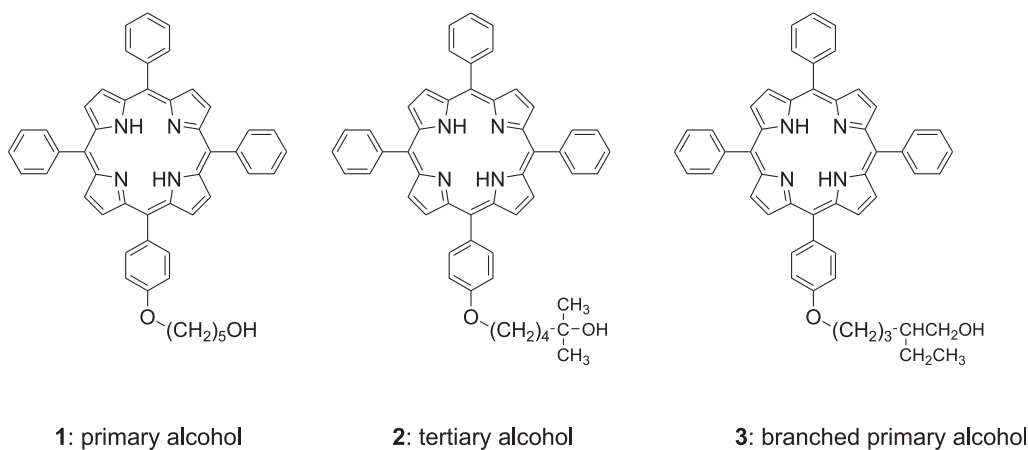


Chart 1.

2.2. Reaction of alcohols with silicate glass

Alcohols **1** and **2** were spin-coated on silicate glass and heated at 80–240 °C for up to 5 h. Washing with chloroform to remove unreacted alcohols afforded the alcohol bonded silicate glass. Figs. 1 and 2 show plots of absorbance at the Soret band of the glass against reaction time for various reaction temperatures. The

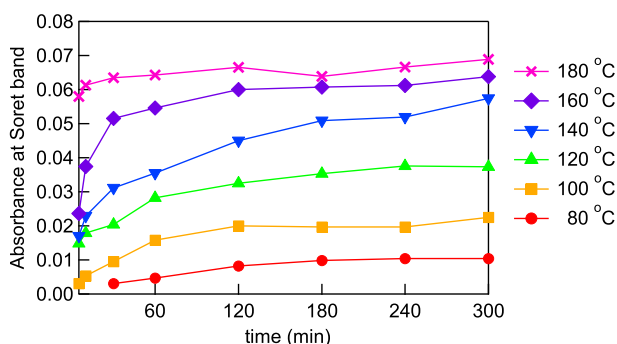


Fig. 1. Plots of absorbances at the Soret band of UV–visible spectra of **1** bonded silicate glass against time.

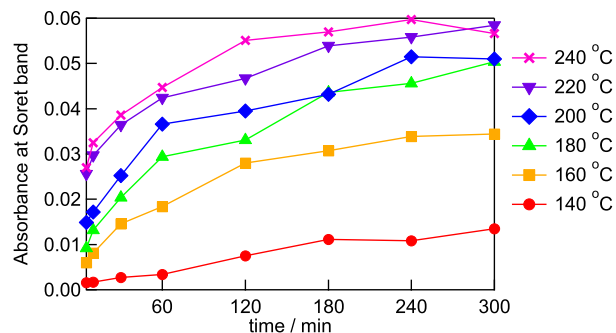


Fig. 2. Plots of absorbances at the Soret band of UV–visible spectra of **2** bonded silicate glass against time.

absorbances increased as the reaction time was longer and saturated when the temperature was high. The absorbances of **1** or **2** bonded glass were saturated at 0.07 and 0.06, respectively. The amounts of porphyrins bonded to silicate glass was determined by immersing the silicate glass in 0.1 M NaOH at 50 °C for 30 min, and

the amounts of desorbed porphyrin was spectrophotometrically determined.⁸ The amounts of porphyrins **1** and **2** adsorbed on silicate glass were 1.8×10^{14} and 1.4×10^{14} molecules/cm², respectively. Therefore, tertiary alcohol reacted slower than primary alcohol, while the adsorbed amount of tertiary alcohol was not much smaller than that of primary alcohol. The Langmuir rate constant⁹ at 180 °C for formation of **1** bonded silicate glass was 0.012 min⁻¹ while that for **2** was 0.0058 min⁻¹, indicating that tertiary alcohol **2** reacted ca. two times slower than primary alcohol **1**. The amount of bonded **2** was much smaller than **1** at temperatures below 160 °C, consistent with reported low reactivity of *tert*-alcohol at 55 °C toward thermally activated silica gel.⁵

2.3. Kinetic studies on hydrolysis of alcohol-bonded silica

Alcohol **1** and **2** bonded silicate glass was immersed in 1 M aq HCl at 50 °C or in 1 M aq NH₃ at 30 °C and progress of hydrolysis was monitored by recording UV–visible spectra of the glass after washing it with CHCl₃. The progress of hydrolysis under acidic conditions is shown in Fig. 3. Comparison of the half-life of the reaction showed that hydrolysis of **2** in HCl was ca. 2.5 times slower than that of **1**. It is interesting to note that the progress of acid-catalyzed hydrolysis did not follow a simple first-order kinetic model. There seem to be fast and slow fractions owing to

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