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# Hydrolysis study of bis-1,2-(triethoxysilyl)ethane silane by NMR

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## ABSTRACT

The hydrolysis process of bis-1,2-(triethoxysilyl)ethane (BTSE) was studied in aqueous and methanol solutions at pH 4. Nuclear magnetic resonance (NMR) evaluation of different solutions was carried out for 7 days. Unlike other researches, methanol-rich solutions are proven inadequate to reach a complete hydrolysis process. In water-rich solutions, hydrolysis takes place for 3 days, 85% of the silane molecules being transformed into silanols; this amount continues increasing up to the seventh day of hydrolysis.

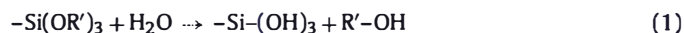
### Keywords:

Nuclear magnetic resonance  
Hydrolysis  
BTSE silane

## 1. Introduction

Functional silanes, with general formula  $R-(CH_2)_n-Si(OR')_3$ , are widely used as silane coupling agents. On one hand, their  $(OR')_3$  groups are capable of hydrolyzing, yielding silanols ( $Si-OH$ ) and therefore reacting with the inorganic substrate. On the other hand, their  $R$  group is capable of reacting with the monomers to be polymerized. Their  $R-(CH_2)_n$  group forms the non-hydrolyzable part of the molecule [1].

During the hydrolysis process, condensation reactions also take place, diminishing the amount of silanol groups and thus the effectiveness of bond formation. Hydrolysis must be maximum (high silanol formation) and condensation must be avoided as much as possible [2,3]. Thus, these are the two main reactions taking place during the hydrolysis process [4,5]:



Silanes are placed on surfaces using aqueous solutions also containing alcohol, due to their limited water solubility [6]. The main factors governing these reactions are solution pH and hydrolysis time [1]. Acidic conditions accelerate the hydrolysis rate and limit self-condensation reactions [7,8]. Moreover, these conditions seem to be the most efficient to form silane films on aluminium alloys [9]. Silane adsorption on the metal surface takes place through the reaction between the silanol groups of the hydrolyzed silane and the hydroxyl groups in the metallic surface. Bonds such as  $Si-O-Al$  on

aluminium substrates are formed [10], while water is a sub-product [11,12].

This study is focused on bridged silane coupling agents. These silanes lack the organofunctional group  $R$ , substituted by a second  $-Si-(OR')_3$  moiety, thus resulting in structures of the type  $(R'O)_3-Si-(CH_2)_n-Si(OR')_3$ . Literature includes scarce hydrolysis studies for bridged silane bis-1,2-(triethoxysilyl)ethane (BTSE) solutions for times over 1 h [2,3]. However, despite the lack of data, it is said that BTSE must be hydrolyzed for at least 24 h to maximize silanol formation [13–15]. BTSE has been used for dental applications [16], blending it with 3-acryloyloxypropyltrimethoxysilane [17].

These studies are focused on solutions with high BTSE and alcohols concentration. Alcohols are not recommended for industrial processes due to economic, environmental and health reasons [18]. Therefore, whether correct hydrolysis can be achieved in solutions without or with little amounts of alcohol—reaching a good compromise between hydrolysis and condensation—becomes an interesting research issue.

This paper studies the hydrolysis process in three solutions containing different amounts of water and methanol during a 7-day period, so as to investigate if the influence of methanol on reaction kinetics can be studied at longer hydrolysis times. NMR techniques were used, previously proven useful for the study of hydrolysis of other silanes [8,19–26], but it has not been applied to BTSE.

## 2. Experimental

### 2.1. Silane solution preparation

The silane, bis-1,2-(triethoxysilyl)ethane (BTSE), was provided by ABCR GmbH&Co. KG, with approximate purity of 97%

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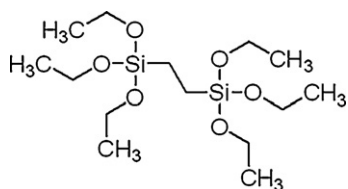


Fig. 1. Molecular structure of BTSE.

(batch number: 1004499). Its molecular structure is shown in Fig. 1.

Three 1% BTSE solutions were prepared with different amounts of water- $d_2$  and methanol- $d_4$ . *Solution 1* contains 6% of water- $d_2$  and 93% of methanol- $d_4$ , while these amounts are reversed in *Solution 2* (93% of water- $d_2$  and 6% of methanol- $d_4$ ). Finally, *Solution 3* only contains 99% of water- $d_2$ .

Water pH was adjusted to 4 with acetic acid 1 M [27] before adding the silane, as acid pHs are typically used for alkoxy silanes [1]. The solution was left to stand during the whole hydrolysis process and studied for 168 h (7 days).

## 2.2. NMR and HR/MAS spectroscopy

A Bruker Avance 500 MHz NMR spectrometer, operating at 500 MHz for  $^1\text{H}$  RMN, was used for *Solutions 1* and 2. *Solution 3*, due to its lack of homogeneity, was studied with the HR/MAS (*High Resolution/Magic Angle Spinning*) technique in a Bruker AMX 500 MHz NMR spectrometer operating at 500 MHz.

Measurements were carried out at 25 °C to prevent changes in the hydrolysis and condensation behaviour of the silane solution, since temperature increases or decreases may influence hydrolysis rates and, accordingly, condensation reactions [28].

## 3. Results

Fig. 2 shows the spectra obtained for methanol-rich *Solution 1* with different hydrolysis times. The initial spectrum shows a quartet–triplet at approx. 3.80 and 1.15 ppm related to the methylene and methyl protons of the ethoxy groups in the BTSE molecule, respectively [29] as shown in Fig. 1. Moreover, the singlet at 0.70 ppm corresponds to Si- $\text{CH}_2$  bonds [20,29], while the one at

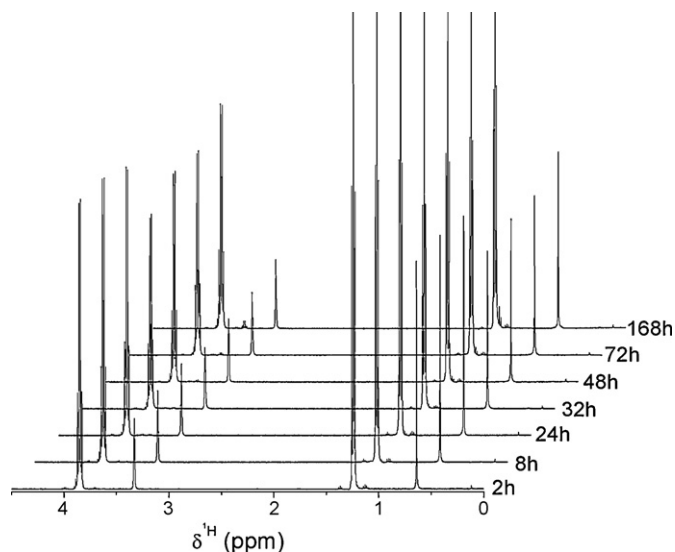


Fig. 2. NMR spectra of *Solution 1* (93% methanol + 6% water + 1% BTSE) for different hydrolysis times.

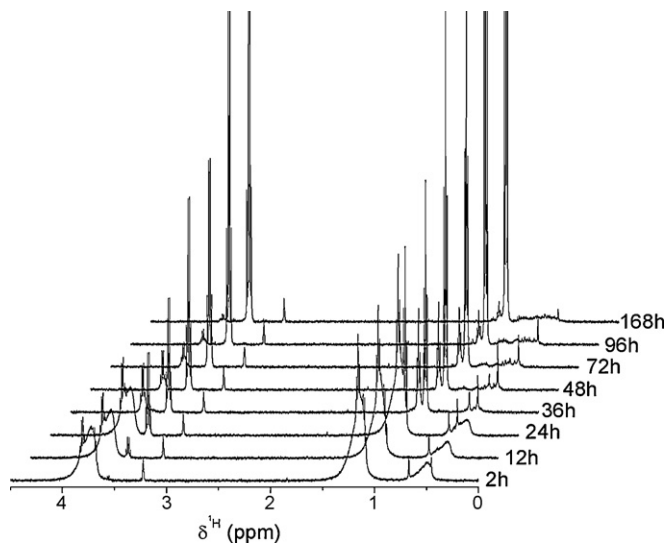


Fig. 3. NMR spectra of *Solution 2* (6% methanol + 93% water + 1% BTSE) for different hydrolysis times.

3.30 ppm corresponds to non-deuterated methanol and involves no practical importance.

Until 48 h of hydrolysis, the spectra show no significant changes. At this time, a quartet–triplet, associated to the methylene and methyl protons of the ethanol formed as a sub-product of the hydrolysis reaction, appears at 3.60 and 1.10 ppm [2,3,20].

The evolution of NMR spectra along the hydrolysis time for *Solution 2* is shown in Fig. 3. Resonances of BTSE ethoxy groups (assigned to the quartet–triplet at 3.8 and 1.15 ppm) constantly diminish since test onset and almost disappear after 72 h of hydrolysis. The increases observed in the signals of ethanol protons (assigned to the quartet–triplet at 3.60 and 1.10 ppm) are progressive and simultaneous.

When hydrolysis time increases, a singlet at 0.70 ppm begins to drop until disappearing after 72 h. At the same time, another singlet appears around 0.60 ppm.

The spectra obtained for *Solution 3* (Fig. 4) are very close to those obtained for *Solution 2*. Ethanol is formed since test onset and the intensity of its signals increases along with hydrolysis time. After 3 days, its signal shows no meaningful changes until the end of the test. Another singlet, shifted to 0.60 ppm, appears. Its inten-

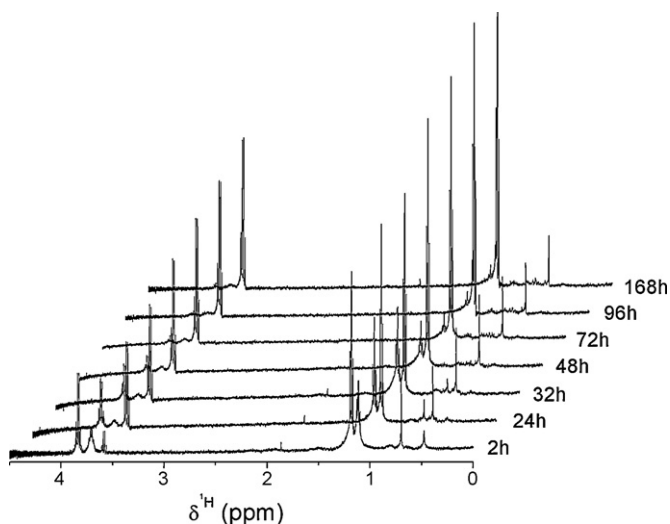


Fig. 4. NMR spectra of *Solution 3* (99% water + 1% BTSE) for different hydrolysis times.

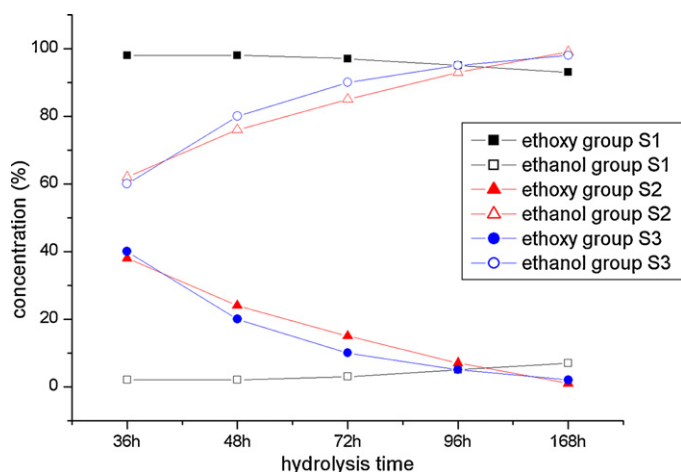


Fig. 5. Evolution of concentration of ethoxy and ethanol groups in studied solutions.

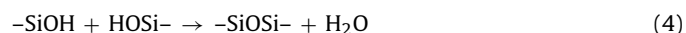
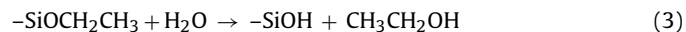
sity increases as the 0.70 ppm singlet diminishes, until its complete disappearance after 48 h.

The concentration of the individual type of protons in the solution can be obtained from the integral intensity of the corresponding peaks of the spectra [28]. Fig. 5 compares the change of the concentration of methyl protons in ethoxy groups (non-hydrolyzed silane molecule) and ethanol (reaction product) for different hydrolysis times and all the studied solutions. The spectra of Solutions 2 and 3 will be integrated from the moment those spectra are solved (i.e., after 36 h of hydrolysis).

In all cases, increased concentration of methyl protons of ethanol is observed, this increase not being noticeable for Solution 1. However, in Solutions 2 and 3, this growth is important, as well as the reduction of the concentration of methyl protons in the ethoxy groups of the BTSE molecule, which takes place at the same time. Meaningful concentration changes take place until 72 h of hydrolysis, being almost constant from that time onward. Moreover, concentrations are very similar for both solutions.

#### 4. Discussion

Upon time, the BTSE molecule in solution will undergo hydrolysis and condensation reactions according to:



Two features are studied to follow the hydrolysis process: on one hand, the reduction of the quartet–triplet associated to the methylene and methyl protons in the ethoxy groups of the non-hydrolyzed BTSE molecule (Fig. 1) and, on the other hand, the increase of the quartet–triplet (around 1.10 ppm) associated to the methylene and methyl protons of ethanol, formed as a sub-product of the hydrolysis reaction [2,3]. At the same time, changes in the pattern of Si–CH<sub>2</sub> bonds (singlet at 0.70 ppm) are observed, as shown by the changes observed in the symmetry of the molecule along the hydrolysis process [2,3]. Those assignments are valid for all the spectra and will therefore help us to follow the hydrolysis process of the studied solutions.

The methanol-rich solution (Solution 1) shows a very slow hydrolysis process. The quartet at 3.80 ppm and the triplet at 1.15 ppm, associated to the ethoxy groups of the non-hydrolyzed BTSE molecule, do not change with time, indicating that these groups are not hydrolyzed. Moreover, no changes are found in the singlet at 0.70 ppm, associated to the symmetry of the pure BTSE molecule (Fig. 1), thus proving that no hydrolysis takes place.

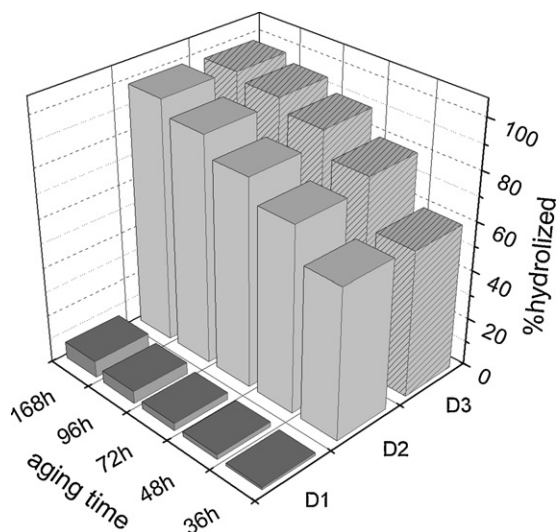


Fig. 6. Hydrolysis evolution for the three studied solutions.

The state of the hydrolysis process can be known at all times through the integration of signal data (Fig. 5) [30]. Fig. 6 shows the hydrolysis evolution between 36 and 168 h for the three considered solutions.

As previously indicated in a qualitative manner (Fig. 2), the hydrolysis process for Solution 1 is slow, only 7% is reached after 7 days (Fig. 6). Spectra changes appear at 48 h (Fig. 2), when hydrolysis begins and ethanol bands are observed. This result is contrary to the scarce existing literature on this issue, since most authors state that the complete hydrolysis process takes place quickly (i.e., within 24 h) for 10%-BTSE methanol-rich (80–90%) solutions. This difference in results may be due to the fact that reaction kinetics depends on BTSE content to a certain extent [18].

The short-time spectra of Solution 2 (Fig. 3) are not well resolved. Signals are broad and without multiplicity. As BTSE is slightly soluble in water, micelles are formed. The solution is then non-homogeneous and low-defined signals are obtained. Hydrolysis transforms the molecule's ethoxy groups (–OEt) into hydroxyl groups (–OH). Therefore, the molecule becomes more polar and hence more soluble in water, so signals are resolved. This process occurs after 36 h of hydrolysis.

The spectra obtained for Solution 3 (Fig. 4) are similar to those for Solution 2 (Fig. 3). In both solutions, signals of quartet (at 3.80 ppm) and triplet (overlapping with the methyl protons of ethanol at 1.15 ppm) disappear after approx. 36 h.

Solutions 2 and 3 present very similar hydrolysis rates, by far faster than those for Solution 1. The resonances of ethoxy groups of BTSE in Solutions 2 and 3 almost disappear after 72 h of hydrolysis (Fig. 3), when the process has reached 85 and 90%, respectively. Then, they stabilize and no meaningful changes are observed for longer times. Since test onset, a small hydrolyzed fraction (3.60 and 1.10 ppm signal) from ethanol protons is found (Fig. 3) [2].

The singlet at 0.70 ppm becomes a more complex multiplet as the molecule becomes more complex during the hydrolysis process. This is explained by the appearance of mono-, bi-, tri- or more hydrolyzed BTSE species, apart from non-hydrolyzed forms [30]. The formed species in this case may not be necessarily symmetric and protons from methylene groups (bonded to silicon atoms) would involve more complex resonance patterns [3]. Since the solution contains a reduced BTSE amount (1%), the signals produced by the protons of –SiCH<sub>2</sub> bonds shall be very small, thus hindering the observation of an increase of its multiplicity. However, the disappearance of the singlet at 0.70 ppm and the appearance of another singlet at 0.60 ppm indicate changes in molecule symme-

try. The singlet at 0.70 ppm corresponds to the symmetry given by the ethyl groups, while the new singlet at 0.60 ppm corresponds to the symmetry given by the hydroxyls once molecules have been hydrolyzed. Transforming –OEt into –OH modifies the chemical environment and, accordingly, a singlet disappears to give rise to a new one. When the former has almost disappeared, hydrolysis is nearly completed.

In *Solution 2*, the singlet at 0.70 ppm disappears at 72 h of hydrolysis. However, in *Solution 3*, it disappears after 48 h, when 80% of the hydrolysis process has already been completed (Fig. 6).

Both solutions are completely hydrolyzed after 3 days. However, De Graeve et al. [18] report that the main difference between water-based and methanol-based solutions is the amount of high molecular weight condensed species, being higher in the former.

A little change in the spectra of the silane solution is observed between 72 and 168 h of hydrolysis [2]. This may be the best hydrolysis time for the use of silane *Solutions 2* and *3*, but it must be confirmed by other studies.

## 5. Conclusions

The influence of the methanol amount in BTSE solutions, as well as the presence of silanols, was studied by NMR. Hydrolysis of BTSE in methanol-rich solutions is a very slow process: 7% is reached after 7 days (in a solution containing 93% methanol, 6% water and 1% BTSE). The increase of water favours the hydrolysis process. A solution with 6% methanol, 93% water and 1% BTSE completes the hydrolysis process after approx. 3 days.

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