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On the Interactions of Alkyl 2-Hydroxycarboxylic Acids with Alkoxysilanes: Selective Esterification of Simple 2-Hydroxycarboxylic Acids

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Abstract: The interactions of a range of monocarboxylic acids with tetramethoxysilane $Si(OMe)_4$ (TMOS), in methanol (MeOH), have been investigated by using ^{1}H, ^{13}C and ^{29}Si solution-phase NMR spectroscopy and electrospray mass spectrometry (ESMS). $Si(OMe)_4$ acts as a catalyst/reagent in the selective methylation of 2-hydroxycarboxylic acids (2HOAs) in MeOH at room temperature: glycolic acid, lactic acid and 2-hydroxybutyric acid are esterified more than a hundred times faster in MeOH and $Si(OMe)_4$ than in MeOH alone. No acceleration of methylation is observed for carboxylic acids lacking the 2-hydroxy group. Methylation of the 2HOAs is associated with the condensation of individual siloxane units to form oligomers. A mechanism is proposed in which 2HOAs attach to silicon via the alkoxy group, then subsequently via the carboxyl group in an intramolecular rearrangement to form an unstable and reactive cyclic intermediate. This intermediate may lead to accelerated methylation of the carboxylic acid via nucleophilic attack of MeOH at the carbonyl group, while a separate reaction pathway leads to condensation of silanols and/or alkoxysilanes leading to oligosiloxanes. The mechanism has implications for the use of 2HOAs as templates in sol–gel silica preparation.

Keywords: homogeneous catalysis · mass spectrometry · NMR spectroscopy · silicates · siloxanes

Introduction

Esterification of carboxylic acids is one of the most widely used and best understood reactions in synthetic chemistry.[1] Nonetheless, new catalysts or reagents capable of regio-, stereo- or chemoselectively esterifying acids are of continuing interest. For example, in 2004 Houston et al.[2] reported that boric acid ($B(OH)_3$, 10–20 mol%) was effective as a catalyst for the chemoselective esterification of 2-hydroxycarboxylic acids (2HOAs) with excess alcohol as solvent. Glycolic, lactic and tartaric acids were methylated in 80, 65 and 98% yields after 18 h at room temperature, whilst succinic acid was methylated $<5\%$. The authors proposed a mechanism involving a five-membered intermediate with both the carboxy and alkoxy oxygen atoms bonded to boron. The following year, Yamamoto et al.[3] reported improved yields in the same reaction by replacing boric acid with *N*-methyl-4-boropyridinium iodide.

It is shown here that tetramethoxysilane, TMOS or $Si(OMe)_4$, is capable of methylating 2HOAs in MeOH with similar selectivity and efficiency to boric acid (Table 1). This work focuses particularly on the mechanism of this reaction, which is associated with the condensation of monomeric siloxane units to form oligosiloxanes. Alkoxysilanes $Si(OR)_4$ are commonly used as precursors in the sol–gel process and their complicated chemistry has been the subject of extensive investigations.[4] The generation of silica from mixtures of alkoxysilane, alcohol, acid and water has been the subject of numerous studies.[5] 2HOAs have been widely used in such mixtures as templates or structure-directing agents,[6] with some interaction with the polymerising siloxane centres assumed but not well understood. Understanding the chemistry of siloxanes, silanols or silicates with small organic ligands is also important in bioinorganic chemistry[7] and theories of the chemical origins of life.[8]

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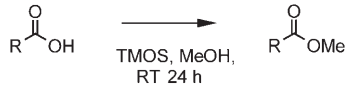
Table 1. Results for mixtures of acids (0.45 M) with TMOS (0.53 M) left in CD_3OD at room temperature for 24 h. Yields calculated from ^1H NMR spectra as described in the Results section.



Acid	R =	Yield [%]
acetic (AA)		1
(*R*)-(−)-β-hydroxybutyric (3HBA)		0
glycolic (GA)		71
(*S*)-(+)-lactic (LA)		84
(*S*)-(+)-α-hydroxybutyric (2HBA)		81

Although the reaction of carboxylic acids with alkoxysilanes has been known to produce carboxylate esters, as well as causing siloxane oligomerisation, dependent on the conditions, for many years,[9,10] there has been no report of the selectivity of this reaction for 2HOAs. In fact the production of carboxylate esters has been observed not only in this reaction, but also in those of carboxylic anhydrides with alkoxysilanes,[11] alcohols with acyloxysilanes[12,13] and ternary reactions of carboxylic acids with chlorosilanes and alcohols;[14] however, in each case, the literature is divided over the actual mechanisms. The chemistry of alkoxy and acyloxysilanes can be broadly understood in terms of a reactivity series Si−Cl > Si−OOCR > Si−OR > Si−OH > Si−O−Si. Thus, acyloxysilanes are susceptible to alcoholysis and hydrolysis, whilst the substitution of an alkoxy ligand by an acyloxy one is difficult. The reaction of carboxylic acids with alkoxysilanes is generally believed to include (at least) two steps, carboxylation (step 1a), followed by reaction of the acyloxysilane group with alcohol (step 1b) and/or an alkoxysilane group (step 1c) to give the ester.[5,13]

$$L_3SiOR^1 + R^2COOH \rightarrow L_3SiOOCR^2 + R^1OH \quad (1a)$$

$$L_3SiOOCR^2 + R^1OH \rightarrow L_3SiOH + R^2COOR^1 \quad (1b)$$

$$L_3SiOOCR^2 + L_3SiOR^1 \rightarrow L_3SiOSiL_3 + R^2COOR^1 \quad (1c)$$

These reactions generally proceed in rigorously dry conditions and at a high temperature.[15,16] Driving off the alcohol created in step 1a promotes the formation of acyloxysilanes, rather than esters and oligosiloxanes/siloxane gels.

In the course of studying the action of 2HOAs in the sol–gel process, we found that these acids readily undergo esterification in dilute solutions of $Si(OMe)_4$ in MeOH, at room temperature and without rigorous exclusion of water. The acids compared in this work are shown in Table 1. The rate of esterification for GA, LA and 2HBA is accelerated to 100–10000 times the background rate in MeOH alone, whilst for AA and 3HBA (carboxylic acids without a 2-hydroxy group) the acceleration due to $Si(OMe)_4$ is minimal or zero. This selectivity suggests direct involvement of the hydroxy group, probably as a ligand to the silicon, which for the 2HOAs but not for 3HBA serves to accelerate steps 1a, 1b or 1c.

2HOAs are known to form stable complexes in aqueous solution with a range of metals,[17] but their complexes with silicon are apparently less stable. Mehrotra et al. in the 1960's reacted salicyclic, mandelic and lactic acids with $Si(OEt)_4$ in benzene with distillation of the EtOH/benzene isotrope and isolated products that contained residual alkoxy ligands together with salicylate, mandelate or lactate ligands, either divalent (via both carboxy and hydroxy) or monovalent (via the hydroxy), depending on the exact conditions.[16] However, structures were assigned purely on the basis of the measured quantity of alcohol eliminated and elemental analysis of the residue. Tacke et al. isolated a series of penta- and hexavalent silicon-HOA complexes with SiO_5 or SiO_6 cores by treating $Si(OMe)_4$ with BA, GA, citric acid or malic acid in MeCN or THF and recrystallising the precipitated product.[18] For most of these complexes, crystal structures have been obtained which show that the 2HOA ligands chelate the silicon via both the carboxyl and hydroxyl groups. By using alkylalkoxysilanes instead of $Si(OMe)_4$, similar complexes were isolated incorporating one Si–C bond, which in some cases were reported to be water stable.[19]

When 2HOAs have been used as templates or structure-directing agents in the sol–gel synthesis of silica from alkoxysilanes it has usually been in alcohol/water cosolvent systems.[6] Hence, the question arises whether under these conditions the 2HOAs and Si centre only interact via "outer sphere" interactions, such as hydrogen bonding to the alkoxy ligands, or whether "inner sphere" interactions occur via covalent complexation. Moreover, if such complexes can form in protic solvents, do they include coordinating interactions via both the hydroxyl and carboxyl groups, or single point interactions? In an attempt to shed light on these issues and to investigate further the mechanism of the carboxylic acid–alkoxysilane reaction we applied a range of modern analytical methods to the reactions of different carboxylic acids with $Si(OMe)_4$ in MeOH.

Results

^{13}C and ^1H NMR spectroscopy of acid/TMOS mixtures in [D_4]methanol—the acid and ester signals: When carboxylic acids are added to $Si(OMe)_4$ in CD_3OD, ligand exchange (L_3SiOCD_3 for L_3SiOCH_3) is accelerated, as well as the hydrolysis and condensation reactions of L_3SiOMe (the initial steps of the sol–gel process), leading to changes in the siloxane signals of the ^1H and ^{13}C spectra and the growth of signals due to CH_3OD. For certain carboxylic acids investigated, the rapid conversion of the acid into the methyl ester was observed (step 2a).

$$R^2COOD + R^3OC(D_3/H_3) \leftrightarrow R^2COOC(D_3/H_3) + R^3OD \quad (2a)$$

Assuming complete exchange of the acidic protons for the more abundant deuteriums of the solvent. The methoxy group transferred to the acid may come from free solvent ($R^3 = D$), or from the methoxy side chains of the siloxane species ($R^3 = L_3Si$)). Figure 1 shows selected regions of the ^1H and ^{13}C spectra after mixing TMOS + GA for 7 h,

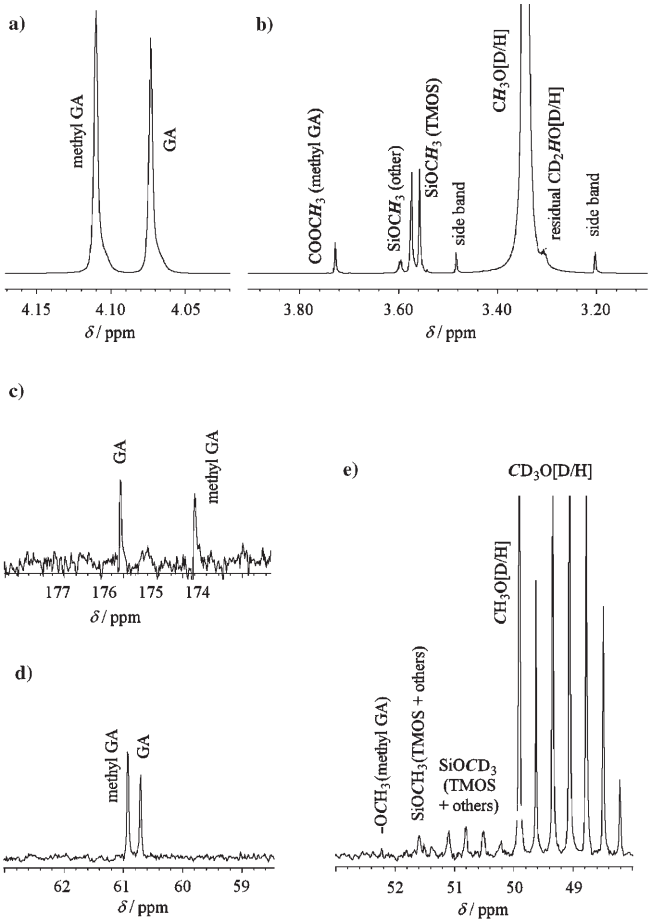


Figure 1. Selected regions of the ^1H and ^{13}C spectra after mixing TMOS + GA for 7 h. a) C*H*O(D/H) region, b) OC*H*$_3$ region, c) *C*OOMe region, d) *C*HOH region and e) O*C*H$_3$ region.

whence approximately 50 % of the GA has been esterified. The C*H*O(D/H), *C*OOMe and *C*HOH peaks due to the ester are clearly seen (the COOC*H*$_3$ and COO*C*H$_3$ peaks, however, are very small because most of the ester created is in the form $-COOCD_3$). Signals attributed to methyl GA were confirmed by spiking the mixture with pure ester.

Esterification occurs when carboxylic acids are incubated in CD_3OD even in the absence of TMOS, but usually at an extremely slow rate. The rate of esterification was measured for a series of acids in CD_3OD in the presence or absence of TMOS (either TMOS or CH_3OH added, Figure 2). For GA, LA and 2HBA, the extent of esterification was quantified

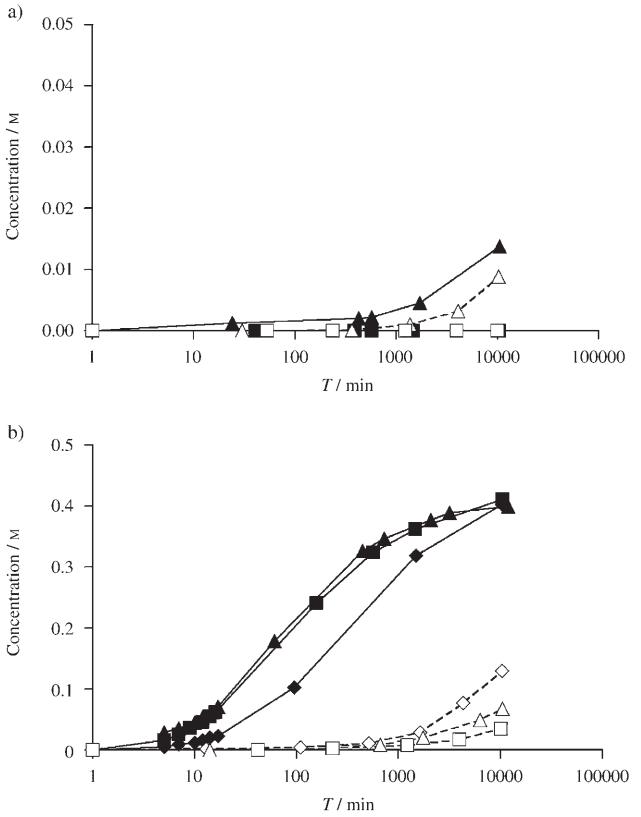


Figure 2. Concentrations of product esters versus time for the mixtures of acids (0.45 M) with TMOS (0.53 M, filled symbols and bold lines) or CH_3OH (2.1 M, open symbols and dotted lines) in CD_3OD, determined from ^1H NMR spectra as outlined in text. a) AA (▲, △), 3HBA (■, □). b) GA (◆, ◇), LA (▲, △), 2HBA (■, □). Note different scales are used in a) and b).

by comparing the integrals of the C*H*O(H/D) signals for the free acid and ester. This calculation was easiest for GA and LA, in which the C*H*O(H/D) is a singlet (Figure 1a), but more complicated for 2HBA, for which it required the measurement of overlapping multiplets. For 3HBA, the signals do not change as there is no ester produced. For AA, the integrals of the C*H*$_3$–C signal for the free acid and ester were measured, and, being singlets, the calculation was again simple. Signals attributed to the esters were confirmed by spiking the reactions after one week with authentic samples of the esters which were commercially available. Assignments of all the observed signals are given in Table 2.

In the absence of TMOS, the rate of esterification increases in the order 3HBA < AA < 2HBA < LA < GA, suggesting this process is governed by a combination of acid pK_a and steric accessibility. When the acids are mixed with TMOS in CD_3OD, only minor changes to the background esterification rate are observed for the non-2HOAs. The rate remains insignificant for 3HBA + TMOS and is accelerated < 10 fold for AA + TMOS. For all of the 2HOAs, when added to TMOS in CD_3OD, dramatic acceleration of esterification is observed. The rate enhancements are ≈100-fold over the background rate for GA, ≈1000-fold for LA and >10000-

Table 2. Assignment of signals in ^{1}H and ^{13}C spectra. Chemical shifts (δ) are measured in ppm and coupling constants (J, shown in parentheses) in Hz.

Acid	Form	α *H*	β *H*	γ *H*	Ester C*H*$_3$	α *C*	β *C*	Carboxy *C*	γ *C*	Ester *C*H$_3$
AA	free	1.99, s	–	–	–	20.76	–	175.25	–	–
3HBA	free	2.44, dd (15.24, 7.08) 2.38, dd (15.36, 5.92)	4.15, dqd, (ca. 6) merged	1.21, t (6.50)	–	44.56	65.54	175.37	23.25	–
GA	free	4.08, s	–	–	–	60.71	–	176.13	–	–
	ester	4.11, s	–	–	3.73, s	60.92	–	174.79	–	51.59
LA	free	4.22, q (6.95)	1.377, d (7.00)	–	–	67.60	20.71	178.34	–	–
	ester	4.25, q (7.00)	1.36 d, (6.90)	–	3.72, s	67.83	20.56	176.83	–	51.60
2HBA	free	4.060, dd (7.07, 4.72)	1.674, dqd (14.21, 7.10, 7.08) 1.806, dqd (13.99, 7.55, 4.63)	0.98, t (7.35)	–	72.60	28.47	177.74	9.69	–
	ester	4.09, dd (7.25, 4.75)	1.66, dqd (14.31, 7.19, 7.16) 1.78, dqd (14.44, 7.20, 4.76)	0.95, t (7.50)	3.72, s	72.89	28.47	176.35	9.69	51.60

fold for 2HBA. Thus, TMOS appears to act as either reagent or catalyst in the methylation of 2HOAs, whilst being less effective, or ineffective, in the methylation of carboxylic acids lacking 2-hydroxy groups.

The observed selectivity suggests that a covalently bound intermediate, either via the 2HOA hydroxyl ligand, carboxyl group or both, may be involved in the mechanism, although no signals were ever identified in the ^{1}H and ^{13}C NMR spectra that could be assigned to such intermediates. This does not preclude their existence, as they may be short-lived on the NMR timescale and their nuclei may possess chemical shifts only slightly different from the free acid.

^{13}C and ^{1}H NMR spectroscopy of acid/TMOS mixtures in [D$_4$]methanol—the siloxane signals: When Si(OMe)$_4$ is incubated alone in CD_3OD, slow processes of ligand exchange (step 3a) and hydrolysis (step 3b) are observed.

$$L_3SiOCH_3 + CD_3OD \rightarrow L_3SiOCD_3 + CH_3OD \quad (3a)$$

$$(L_3SiOCH_3 \text{ or } L_3SiOCD_3) + D_2O \rightarrow L_3SiOD + (CH_3OD \text{ or } CD_3OD) \quad (3b)$$

D_2O is derived from H_2O, which is initially present or which ingresses into the tube and exchanges its protons with the more abundant CD_3OD. Both processes lead to the loss of the L_3SiOCH_3 ($\delta = 3.56$ ppm, singlet; Figure 1b) and L_3SiOCH_3 ($\delta = 51.6$ ppm, singlet; Figure 1e) signals, but the growth of new CH_3OD ($\delta = 3.35$ ppm, singlet) and CH_3OD ($\delta = 49.9$ ppm, singlet) signals, almost overlaying the CHD_2OD and CD_3OD signals. The ligand exchange process (step 3a) also leads to a L_3SiOCD_3 signal ($\delta = 50.8$ ppm, septet). In the presence of added H_2O, these processes are accelerated and, because L_3SiOD is formed in larger quantities, condensation reactions to form $L_3SiOSiL_3$ also become significant (steps 3c and 3d).

$$(L_3SiOCH_3 \text{ or } L_3SiOCD_3) + L_3SiOD \rightarrow L_3SiOSiL_3 + (CH_3OD \text{ or } CD_3OD) \quad (3c)$$

$$L_3SiOD + L_3SiOD \rightarrow L_3SiOSiL_3 + D_2O \quad (3d)$$

Each of these processes leads to further signals due to L_3SiOCH_3 or L_3SiOCD_3 within hydrolysed or oligomeric species which can also be seen in Figure 1b and e.

Figure 3 shows how the concentrations of L_3SiOCH_3, L_3SiOCD_3 and CH_3OD change after adding TMOS to LA or H_2O in CD_3OD. Changes occur $\approx$1000 fold faster with LA than with H_2O. TMOS+AA and TMOS+3HBA behaved essentially identically to TMOS+H_2O, whilst mixtures of TMOS with GA or 2HBA behaved essentially identically to TMOS+LA. Initial growth of the CH_3OD and

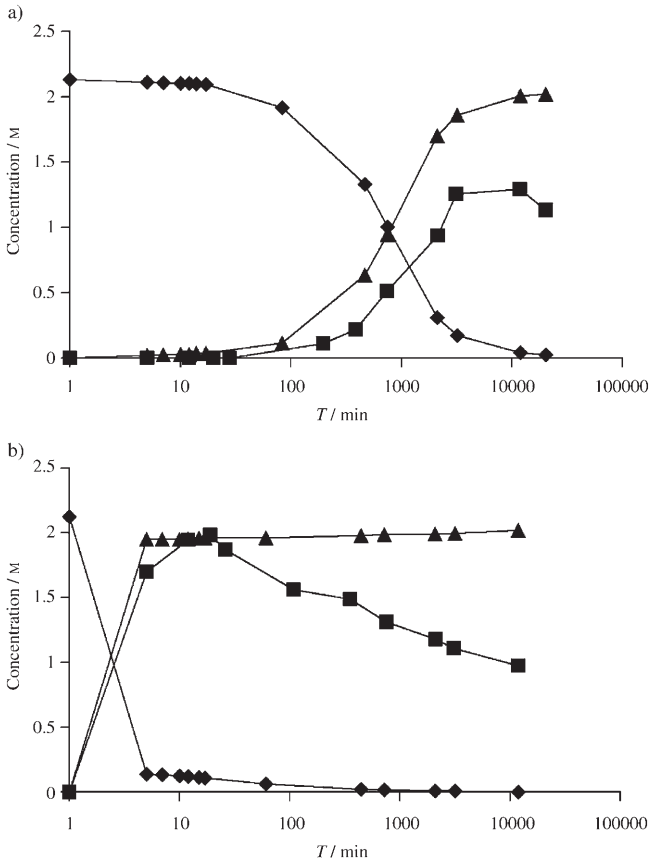


Figure 3. Changes in the concentration of TMOS L_3SiOCH_3 (♦), L_3SiOCD_3 (■) and CH_3O(D/H) (▲) after TMOS (0.53 M) is added to CD_3OD containing a) H_2O (0.90 M) and b) LA (0.45 M).

L_3SiOCD_3 signals due to ligand exchange is followed by a slow decrease of the L_3SiOCD_3 signal due to processes 3b and 3c. The time at which the L_3SiOCD_3 concentration reaches a maximum can be taken as a measure of the rates of processes 3a to 3d combined: this time is approximately one week for TMOS with H_2O, AA or 3HBA, and $\approx$10 min for TMOS with GA, LA or 2HBA.

FTIR analysis of 2HOA + TMOS mixtures in [D_4]methanol: Short-lived species may be resolved more easily by FTIR than by NMR spectroscopy. Thus, FTIR was used to study the reactions of the acids with TMOS in CD_3OD. However, the results were complicated by the similar frequencies of absorbances due to groups in CD_3OD and L_3SiOCD_3, and in CH_3OD and L_3SiOCH_3. The data confirmed the ^1H and ^{13}C NMR findings that $SiOCD_3$ groups were more abundant after one week in the mixtures of TMOS with AA and 3HBA than in mixtures of TMOS with the 2HOAs. No evidence was found for transient siloxane–acid complexes (see the Supporting Information).

^{29}Si NMR of 2HOA + TMOS mixtures in [D_4]methanol: ^{29}Si NMR was also used to probe the species present after mixing the acids with TMOS in CD_3OD (Figure 4). The assignments shown are based on reported studies of the hydrolysis of alkoxysilanes by using ^{29}Si NMR spectroscopy.[20,21] Q^0 corresponds to silicon with four OC or OD ligands, Q^1 to silicon with one of these ligands replaced by OSi and Q^2 to silicon with two ligands replaced with OSi.

The major Q^0 peak is in each case a singlet at $\delta = -78.2$ ppm, which by comparison with the spectrum of pure TMOS and with the literature can be assigned to $Si(OCH_3$ or $OCD_3)_4$. For the mixture of TMOS + AA and TMOS + 3HBA, an additional Q^0 peak appears at $\delta = -76.0$ ppm which can be assigned to $(CH_3O$ or $CD_3O)_3SiOD$.[21] This peak also appears after 24 h, for TMOS + H_2O. However, the spectra observed for TMOS with the 2HOAs are quite different: the only Q^0 peak observed is that due to $Si(OCH_3$ or $OCD_3)_4$, and this is observed to diminish over time while Q^1 and Q^2 signals grow. The Q^1 species present are chain-end $L_3SiOSi(OR_3)$, and the Q^2 species are mid-chain $L_3SiOSi(OR)_2OSiL_3$. Different length chains and cycles, as well as different combinations of OH and (OCH_3 or OCD_3) ligands split the Q^1 and Q^2 signals. In the spectrum of GA + TMOS one hour after mixing, there are just two Q^1 signals at $\delta = -85.6$ and -85.8 ppm, but after 16 h these are joined by two Q^2 signals at $\delta = -93.5$ and -93.8 ppm, indicating the evolution of a more complex array of oligosiloxane products. Similar spectra are observed with TMOS + LA and TMOS + 2HBA.

^{29}Si NMR spectra thus show a clear difference between the initial stages of the AA + TMOS and 3HBA + TMOS reactions (which lead to slow production of L_3SiOD) and the 2HOA + TMOS reactions (which lead to no measurable L_3SiOD, but relatively fast production of $L_3SiOSiL_3$). It could be conjectured that the signals assigned as Q^1 and Q^2 species actually correspond to complexes, that is, siloxanes

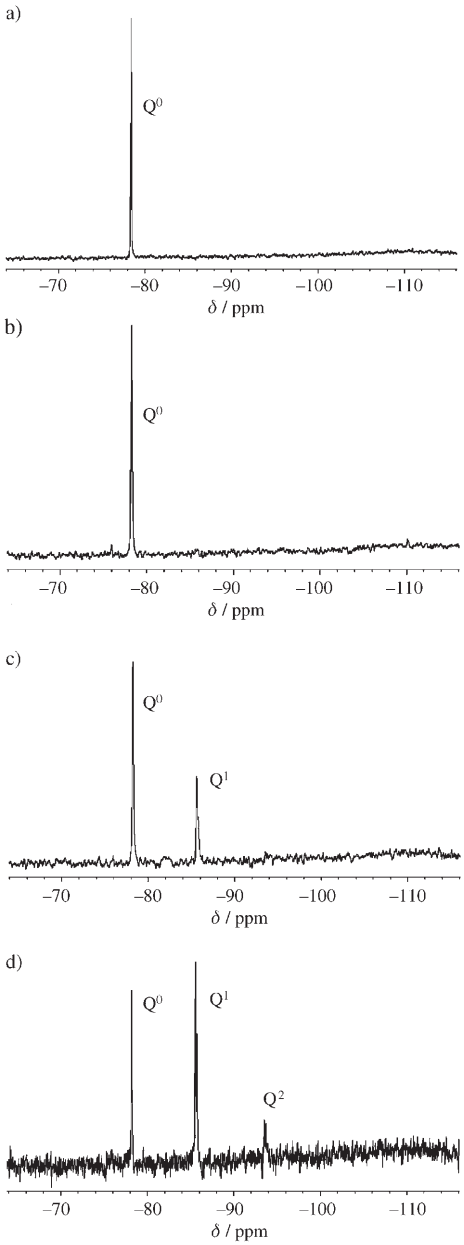


Figure 4. ^{29}Si NMR spectra of TMOS (0.53 M) in CD_3OD, mixed with a) H_2O (0.90 M), b) AA (0.44 M) and c) and d) GA (0.45 M). a) recorded 7 h after mixing, b) and c) 1 h after mixing and d) 16 h after mixing. Number of scans for d) was reduced to 128.

substituted with 2HOAs. Substitution of an alcohol with an acyl group can lead to large changes in the ^{29}Si chemical shift, but in the opposite direction to that observed here.[22] Substitution via the 2HOA hydroxyl group would lead to much smaller changes[23] and so might account for the observed splitting of the Q^1 and Q^2 signals.

MS analysis of 2HOA + TMOS mixtures in methanol: GCMS has been used previously to identify intermediates in the sol–gel process of TEOS.[24] It is by no means obvious, however, that ions identified under these conditions truly re-

flect the species present in solution at a given stage. A more accurate picture of the inherent ions might be expected by using electrospray ionisation. Thus, Cooney et al.[25] used electrospray with a quadrupole mass analyser to obtain a spectrum for TEOS in EtOH in positive-ion mode (dominated by $Na(Si(OEt)_4)_2^+$), but could only obtain spectra in negative-ion mode by using an inherently ionisable siloxane, 3-sulfanylpropyl-triethoxysilane ($HS(CH_2)_3Si(OEt)_3$). Schüth et al.[26] used a similar setup to study solutions of silica dissolved in tetraethylammonium hydroxide in $MeOH/H_2O$. Under these alkaline conditions, they identified a range of oligomeric species with various levels of OH/OCH_3 exchange. Marshall et al.[27] used electrospray with a Fourier transform ion-cyclotron resonance mass analyser to characterise alkaline $TEOS/EtOH/H_2O$ mixtures, and used the accurate mass resolution of their instrument to assign the oligosiloxane structures present with confidence. The limitations of their approach, however, are that the solution was diluted in acetonitrile prior to electrospraying, which may have altered the equilibria between different species present, and the instrument was operated in positive-ion mode, with species being identified as cationic metal–siloxane complexes. Subsequently Woenckhaus et al.[28] employed electrospray with a quadrupole analyser to characterise acidic TMOS/water and TEOS/water mixtures. They directly injected the unadulterated reaction mixtures and compared positive and negative-mode ionisation; only the latter gave useful spectra, enabling them to assign peaks to anionic silicate chains (5 min after mixing) cylcles and polyhedra (after longer intervals). As the quadrupole instrument used had limited mass resolution, they identified the various ions on the basis of integral m/z ratios and with the use of H/D exchange.

In the current work, unadulterated samples were directly injected into a TOF instrument. They were ionised by negative electrospray and the structures of the resulting ions were assigned on the basis of accurate masses. Spectra are shown in Figure 5 and assignments of selected peaks in Table 3 (for more complete assignments see the Supporting Information). The first spectrum shown is for $TMOS+H_2O$ in CH_3OH and was recorded 26 hours after mixing. The same mixture analysed immediately after mixing gave only a very weak spectrum, confirming the observation via ^{29}Si NMR spectroscopy that only TMOS itself is present in the early stages. The sample after 26 hours contains oligomeric ions of one to seven silicon atoms, which can be assigned as shown to either chains in which some of the silicon atoms are 3-coordinate with one $L_2Si{=}O$ group, or to cycles and polyhedra. The ions are similar to those observed by Schuth et al.[26] and by Woenckhaus et al.,[28] except that the ions in our spectrum, recorded with a 56:1 (v/v) ratio of $MeOH/H_2O$, are more extensively methylated. 3-Coordinate silicon species containing $L_2Si{=}O$ groups are certainly not expected to be present in the actual solution. Woenckhaus et al. proposed that these arose due to dehydration of oligomers containing $-Si(OH)_2-$ during the electrospray process, in the current work, they might also arise from de-

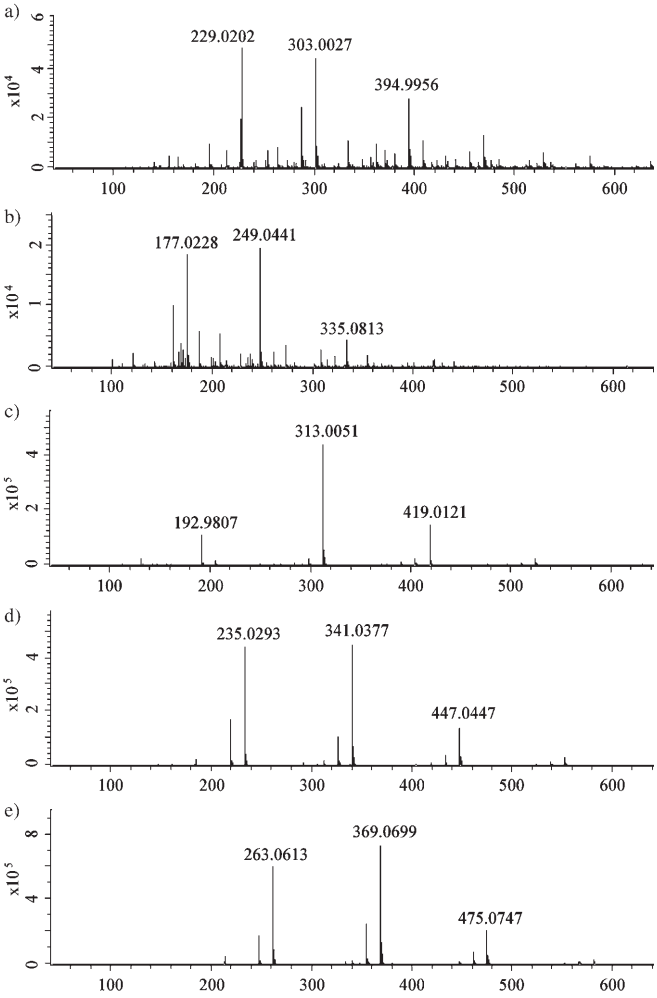


Figure 5. ES-MS spectra obtained in negative-ion mode with direct infusion of samples. TMOS (0.53 M) in CH_3OH mixed with a) H_2O (0.90 M), b) 3HBA (0.45 M), c) GA (0.45 M), d) LA (0.45 M), e) 2HBA (0.45 M).

methoxylation of oligomers containing $-Si(OH)(OMe)-$. Thus included in Table 3 are the "parent ion" linear, saturated oligomers which could yield the observed ions by loss of one or more CH_3OH.

The remaining spectra were recorded approximately two hours after mixing. The spectrum for TMOS+AA in MeOH was extremely weak with no signals above 10^4 (not shown). ^1H, ^{13}C and ^{29}Si NMR spectroscopy has shown that L_3SiOH is formed in the TMOS+AA reaction, as in $TMOS+H_2O$; however, the acid presumably suppresses the ionisation of the silanols under electrospray conditions.

All of the hydroxy acids studied when mixed with TMOS in MeOH generated spectra containing peaks that could be assigned to complexes between monomeric or oligomerised siloxanes and the acids. However, the spectra for TMOS with the 2HOAs, GA, LA and 2HBA, were very similar (Figure 5c–e), and quite different to that for TMOS+3HBA (Figure 5b). The peaks in the spectrum for TMOS+3HBA are of comparable intensity to those in the spectrum for

Table 3. Selected ions observed in ESI-TOF MS experiments (for more complete assignments see the Supporting Information).

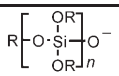
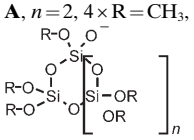
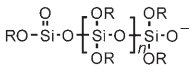
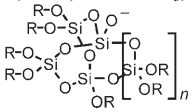
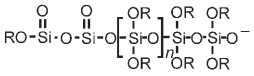
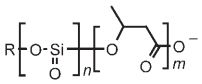
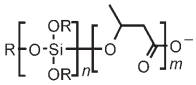
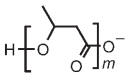
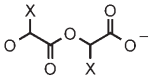
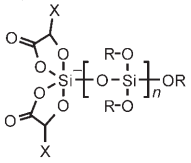
Sample	Observed ions	Assigned	Calcd *m*/*z* (difference [ppm^{-1}])	Possible structure	Suggested parent ion
H_2O + TMOS, 1568 min	229.0202	$Si_2C_4H_{13}O_7^-$	229.0205 (+1.3)	 **A**, $n=2$, 4 × R = CH_3, 1 × R = H	
	303.0027	$Si_3C_5H_{15}O_9^-$	303.0029 (+0.8)	 or  **B**, $n=1$, 5 × R = CH_3	**A**, $n=3$, 6 × R = CH_3, 1 × R = H
	394.9956	$Si_4C_6H_{19}O_{12}^-$	394.9959 (+0.8)	**B**, $n=2$, 6 × R = CH_3, 1 × R = H	**A**, $n=4$, 7 × R = CH_3, 2 × R = H
	468.9788	$Si_5C_7H_{21}O_{14}^-$	468.9783 (−1.1)	 or  **C**, $n=1$, 7 × R = CH_3	**A**, $n=5$, 9 × R = CH_3, 2 × R = H
3HBA + TMOS, 122 min	177.0228	$SiC_5H_9O_5^-$	177.0225 (−1.6)	 **E**, $n=1$, $m=1$, R = H	 **F**, $n=1$, $m=1$, 1 × R = CH_3, 2 × R = H
	189.0768	$C_8H_{13}O_5^-$	189.0768 (+0.1)	 **G**, $m=2$	
	249.0441	$SiC_8H_{13}O_7^-$	249.0436 (−2.2)	**E**, $n=1$, $m=2$, R = H	**F**, $n=1$, $m=2$, 1 × R = CH_3, 2 × R = H
	275.1146	$C_{12}H_{19}O_7^-$	275.1136 (−3.6)	**G**, m = 3	
	335.0813	$SiC_{12}H_{19}O_9^-$	335.0804 (−2.6)	**E**, $n=1$, $m=3$, R = H	**F**, $n=1$, $m=3$, 1 × R = CH_3, 2 × R = H
	421.1184	$SiC_{16}H_{25}O_{11}^-$	421.1172 (−3.0)	**E**, $n=1$, $m=4$, R = H	**F**, $n=1$, $m=4$, 1 × R = CH_3, 2 × R = H
GA + TMOS,146 min	133.0142	$C_4H_5O_5^-$	133.0142 (+0.1)	 **H**, all X = H	
	192.9807	$SiC_4H_5O_7^-$	192.9810 (+1.6)	 **I**, $n=0$, all X = H, 1 × R = H	
	313.0051	$Si_2C_7H_{13}O_{10}^-$	313.0053 (+0.5)	**I**, $n=1$, all X = H, 3 × R = CH_3	
	419.0121	$Si_3C_9H_{19}O_{13}^-$	419.0139 (+4.3)	**I**, $n=2$, all X = H, 5 × R = CH_3	
LA + TMOS, 129 min	221.0123	$SiC_6H_9O_7^-$	221.0123 (−0.2)	**I**, $n=0$, all X = CH_3, 1 × R = H	
	235.0293	$SiC_7H_{11}O_7^-$	235.0280 (−5.9)	**I**, $n=0$, all X = CH_3, 1 × R = CH_3	
	327.0208	$Si_2C_8H_{15}O_{10}^-$	327.0209 (+0.3)	**I**, $n=1$, all X = CH_3, 2 × R = CH_3, 1 × R = H	
	341.0377	$Si_2C_9H_{17}O_{10}^-$	341.0366 (−3.4)	**I**, $n=1$, all X = CH_3, 3 × R = CH_3	
	433.0299	$Si_3C_{10}H_{21}O_{13}^-$	433.0295 (−0.8)	**I**, $n=2$, all X = CH_3, 4 × R = CH_3, 1 × R = H	
	447.0447	$Si_3C_{11}H_{23}O_{13}^-$	447.0452 (+1.2)	**I**, $n=2$, all X = CH_3, 5 × R = CH_3	

Table 3. (Continued)

Sample	Observed ions	Assigned	Calcd m/z (difference [ppm^{-1}])	Possible structure	Suggested parent ion
2HBA+TMOS, 136 min	249.0429	$SiC_8H_{13}O_7^-$	249.0436 (+2.8)	**I**, $n=0$, all X = CH_2CH_3, 1×R = H	
	263.0613	$SiC_9H_{15}O_7^-$	263.0593 (−7.7)	**I**, $n=0$, all X = CH_2CH_3, 1×R = CH_3	
	355.0512	$Si_2C_{10}H_{19}O_{10}^-$	355.0522 (+2.8)	**I**, $n=1$, all X = CH_2CH_3, 2×R = CH_3, 1×R = H	
	369.0699	$Si_2C_{11}H_{21}O_{10}^-$	369.0679 (−5.4)	**I**, $n=1$, all X = CH_2CH_3, 3×R = CH_3	
	461.0600	$Si_3C_{12}H_{25}O_{13}^-$	461.0608 (+1.9)	**I**, $n=2$, all X = CH_2CH_3, 4×R = CH_3, 1×R = H	
	475.0747	$Si_3C_{13}H_{27}O_{13}^-$	475.0765 (+3.8)	**I**, $n=2$, all X = CH_2CH_3, 5×R = CH_3	

TMOS+H_2O after 26 hours, and can be assigned to dimers and trimers of 3HBA, and to mono- and disiloxanes with varying levels of OH/OCH_3 exchange and between one and four 3HBAs attached. The peak at m/z: 189.0768 could be the 3HBA anhydride with a deprotonated hydroxyl, but given the existence of the peak at m/z: 275.1146, the homoester structures shown seem more probable. These ions also appear in the spectrum of 3HBA+CH_3OH in the absence of TMOS, so must form spontaneously in solution. Various structures might account for the acid–siloxane complexes. It has been assumed that as the ionisation of SiOH is suppressed for the AA+TMOS mixture, the same is true here and ions must be due to ionised carboxylate groups. Complexes in which silicon is multiply substituted with single 3HBA ligands might appear more probable than those singly substituted with oligomeric 3HBA as illustrated by structures **E** or **F**. However, the ion with m/z: 421.1172 shows that some of the ligands must indeed be oligomeric. This ion cannot result from a complex with only monomeric ligands.

The spectra for each of the 2HOAs with TMOS are different from that for 3HBA+TMOS in several ways: the peaks are ≈20 times more intense; a dimer is observed for GA but only weakly for LA, and not at all for 2HBA, there are no trimers for any of the 2HOAs and the silicon complexes present can all be assigned with monomeric ligands only; the oligosiloxanes are larger with up to four silicon atoms; and however many silicon atoms are present, there are always exactly two 2HOA ligands. The greater extent of oligomerisation is in agreement with the ^{29}Si spectra. The fact that all of the silicon complexes in these three spectra can be assigned with a general structure I, with exactly two 2HOA ligands, has implications for the mechanisms of complex formation and esterification as discussed below.

Discussion

The reaction of carboxylic acids with alkoxysilanes has been studied since at least 1928[9] and been suggested as a method for the preparation of esters since 1956,[10] but the mechanism was for a long time unclear. Mechanisms involving acid–siloxane complexes as intermediates, such as that outlined in the introduction (steps 1a–1c), originate with Andrianov et al. who, in the 1950's, proposed that during the reaction of $Et_2Si(OEt)_2$ with AcOH (or other acids) in toluene,[29] the acid displaced an alkoxy ligand giving $Et_2Si(OEt)(OAc)$. A second cycle gave $Et_2Si(OAc)_2$, which was the final product if EtOH was removed by distillation, but otherwise might react with EtOH to give EtOAc, and, by condensation, polydiethylsiloxanes. Andrianov's reactions took place under water-free conditions at an elevated temperature, and the only alcohol present was that produced in step 1a. Also, the alkylsiloxane groups should stabilise the resulting complex with the less electron-donating carboxyl ligand. Sanchez and Livage et al. showed later by using NMR spectroscopy that acetic acid will displace ethoxy groups from $Si(OEt)_4$, although they only observed this to occur for the 2-component mixture under reflux.[30] Thus, it is unclear whether the mechanism in steps 1a–1c (outlined more fully by Sharp[13]) could actually apply for acids reacting with tetraalkoxysilanes, such as TEOS, at room temperature.

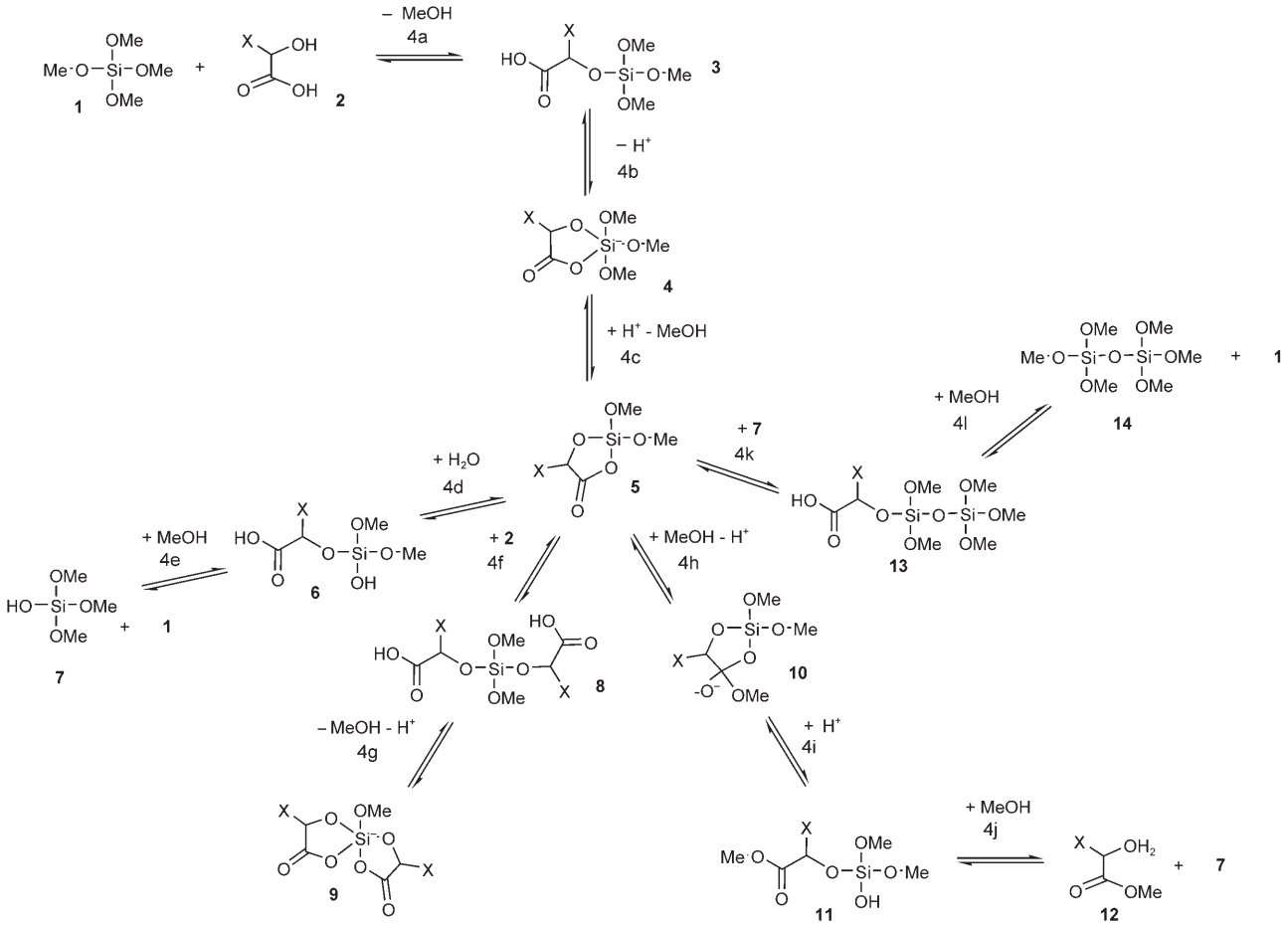
In our studies, we observed esterification of AA (very slow) in CD_3OD in the absence of TMOS. For AA+TMOS in CD_3OD, only very slight acceleration of esterification was observed, perhaps because in the presence of excess alcohol and at temperatures less than reflux, the reaction in step 1a is unfavourable. NMR spectroscopy and MS both failed to identify any complexes of silicon with AA.

For 3HBA no esterification was observed at all, which may be attributed to steric hindrance (the pK_a for 3HBA is almost identical to that for AA), even in the presence of TMOS. Consideration of the CH_3OD, $SiOCD_3$ and *Si* signals suggests that the processes in steps 3a–3d occur at a similarly slow rate for 3HBA+TMOS as for AA+TMOS. However, MS shows a clear difference between AA+TMOS and 3HBA+TMOS: in the latter case, a series of complexes are observed involving one or two siloxane units with some or all of the methoxy ligands hydrolysed or replaced with 3HBA (in its mono-, di- or trimeric form). It is proposed that these complexes involve 3HBA complexing the silicon centre via the alkoxy group as in structure **F**. Such complexes can arise by simple alkoxy exchange as in step 4a.

$$Si(OCH_3)_4 + HO{-}Y{-}COOH \leftrightarrow (CH_3O)_3SiO{-}Y{-}COOH + CH_3OH \quad (4a)$$

In the case of 3HBA (Y = $(CH_2)_3$)), the ligand is proposed to have no effect on the reactions of the other three groups, which can subsequently undergo the reactions in steps 3a–3d (or in step 4a again). The 3HBA-siloxane complexes are present in very small amounts, such that they are not detected in the NMR spectra, and the MS signals are very weak. Even smaller amounts of complexes with two siloxane units are formed (the two peaks in the MS spectrum are yet smaller, and no Q^1 signal is detected in the ^{29}Si NMR spectrum). With the 2HOAs, GA, LA and 2HBA, however, the situation is quite different. ^{1}H and ^{13}C NMR spectroscopy confirm esterification is hugely accelerated, as are processes in steps 3a–3d. MS indicates that complexes with silicon form and they are present at higher concentrations and/or more readily ionised than those with 3HBA. To explain these observations, it is proposed that the complexes with 2HOAs can cyclise and eliminate MeOH as in steps 4b and 4c in Scheme 1 below, whereas complexes with 3HBA do not. The initial complex **3** would again be in equilibrium with the starting materials and present in very small amounts. The complexes **4** and **5** may be unstable and short-lived, so not detected by NMR spectroscopy. If **5** forms, however, it could react with nucleophiles, either at the silicon centre (which is more electropositive than in TMOS) or at the carbonyl carbon atom. Attack by MeOH at the silicon, would lead, by steps 4c, 4b and 4a in reverse, to the rapid exchange of OCD_3 and OCH_3 groups observed in CD_3OD. Attack by H_2O (or D_2O) at the silicon would cause hydrolysis, by steps 4d and 4e, as observed by the rapid loss of $SiOCD_3$ in the ^{13}C NMR spectra. As **7** does not appear in the ^{29}Si NMR spectra, it is proposed that it reacts rapidly, probably with **5** as shown in steps 4k and 4l, leading to the acceleration of condensation, and Q^1 species, such as **14**, observed soon after mixing in the ^{29}Si spectra. There is also the possibility of **5** reacting with another molecule of 2HOA as in 4f, by means of acid-catalysed alkoxy exchange, to form the 2:1 complex **8**. Compound **8** could undergo elimination to form **9**, which may happen particularly under ES conditions such that **9** is detected in the spectra of TMOS with all of the 2HOAs. Compound **9** is reminiscent of the stable structures isolated from solution by Tacke et al.[18,19] and is presumably stabilised by the exactly sufficient amount of electron donation from the five ligands to the silicon.

It is proposed that for the 2HOAs mixed with TMOS, esterification occurs via the attack of MeOH at the carbonyl carbon of **5**, forming a tetrahedral intermediate **10** as shown

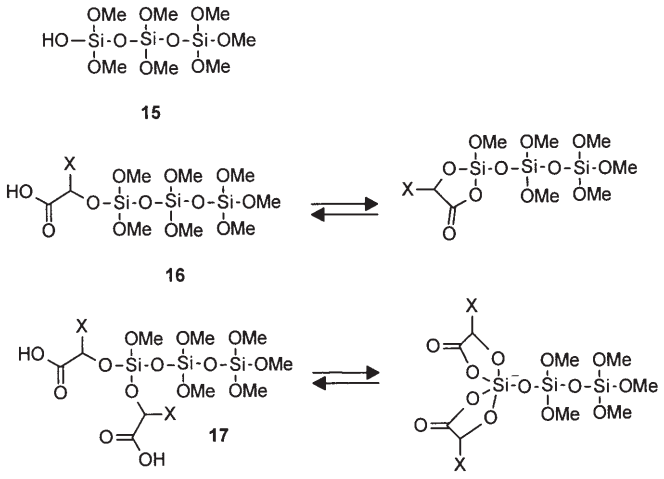


Scheme 1. Proposed mechanism for reaction of 2HOAs + TMOS in MeOH.

in step 4h. This may be accelerated relative to the equivalent attack on free **2** for two reasons: firstly, the inductive effect of the silicon and secondly, L_3SiO^- is a much better leaving group than OH^-.

Alternative mechanisms might equally account for our observations. Thus, esterification and SiOSi bond formation could be concerted as in Sharp's mechanism for non-2-hydroxy-carboxylic acids.[13] This is particularly appealing since, for GA for example, the concentration of SiOSi linkages (estimated from the integrals of Q^1 and Q^2 species in Figure 4c and d) appears to increase in line with the concentration of ester (in Figure 2b). However, such a mechanism would be necessarily more complex. Scheme 1 is sufficient to explain the simultaneous production of SiOSi and ester, if monomeric **7** (a byproduct of esterification) reacts faster with **5** (or similar oligomers) due to the increased electrophilic nature of the silicon, than it would with TMOS or a silicon with four other alkoxy or hydroxy ligands. The scheme does not yet, however, explain the details of the MS spectra observed. Why, unlike the complexes with 3HBA, do all the siloxane complexes with 2HOAs in the MS include exactly two 2HOA moieties and between one and four siloxane units?

Repeated cycles of the hydrolysis, esterification and condensation steps can rapidly lead to a diverse array of oligosiloxane species—some examples are indicated in Scheme 2. It can be explained why no 1:1 (siloxane:2HOA) complexes are observed. Under the vacuum conditions of the electrospray source, complexes **3** and **4** undergo elimination of MeOH forming **5**, which is uncharged. This route is less favourable for TMOS+3HBA, as it would require formation of a six-membered cycle, hence 1:1 complexes are observed with 3HBA. Further, although oligomeric species, such as **16**, are postulated to form under ES conditions they also eliminate MeOH forming cyclic species as shown, which also do not ionise. Only when two 2HOA moieties have attached to the same silicon atom, as in **17**, will the ES conditions result in an ionic pentavalent species, which is stabilised in the same way as **9** as discussed above.



Scheme 2. Examples of some of the oligomeric species that may be formed in the reactions of 2HOAs with TMOS by repeated hydrolysis, esterification and condensation steps, and the "daughter species" that may arise under ES conditions.

As species, such as **15**, are postulated to form, it is necessary to explain why these do not ionise, even though the equivalent species do give peaks in the MS for the mixture of TMOS+H_2O in CH_3OH (Figure 5, Table 3). Firstly, these compounds may ionise more easily in the mixture including H_2O than in the less-polar CH_3OH-based solution. Secondly, the peaks in the spectrum for TMOS+H_2O are in any case very much weaker than the major peaks observed for the mixtures of TMOS+2HOAs.

Conclusion

It has been shown that 2HOAs are methylated selectively by TMOS in MeOH at room temperature, and a mechanism consistent with data obtained by means of ^1H, ^{13}C and ^{29}Si NMR spectroscopy as well as FTIR spectroscopy and ESMS has been proposed. The reaction may form a useful route for the preparation of 2-methoxy carboxylic acids, as it proceeds at room temperature, without rigorous exclusion of water, and the reagent TMOS is very inexpensive.

In the proposed mechanism, 2HOAs attach to silicon centres via the alkoxy group, forming $L_3Si(OCHXCOOH)$. Such species are not detected in NMR spectra because they are present at low concentrations in equilibrium with $L_3Si(OCH_3)$ and the chemical shifts for the silicon, α-carbon and α-hydrogen may scarcely change from those in the starting materials. Subsequently the bound 2HOA also interacts with the silicon via the carboxyl group in an intramolecular rearrangement to form an unstable and reactive cyclic intermediate. This intermediate may lead to accelerated methylation of the carboxylic acid via the nucleophilic attack of methanol at the carbonyl group, while a separate reaction pathway leads to condensation of silicon centres leading to oligosiloxanes. The cyclic intermediate is considered to be short-lived, such that it cannot be detected spectroscopically, but its existence is supported by the presence of 1:1 siloxane:acid complexes in the MS of TMOS+3HBA, but not the MS of TMOS+2HOAs. The existence of ions in the MS spectra for TMOS+2HOAs with always two 2HOA moieties is considered to be due to the stabilisation of pentavalent silicon with two chelating 2HOAs. These are probably present only at low concentration in solution, but other complexes do not ionise.

The existence of the five-membered cyclic intermediates, even transiently, may have implications for the use of 2HOAs as templates in the sol–gel synthesis of structured silica. Further work is being conducted on the interactions of TMOS with di- and tricarboxylic acids containing the 2HOA group.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker Avance 500 spectrometer operating at 500 MHz. Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer operating at 75.5 MHz. Proton-decoupled ^{29}Si NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 99.4 MHz, an aquisition time of 0.43 s with a delay of 5 s was used and the number of scans was 256, unless otherwise stated. Acid (0.375 mmol) was dissolved completely in [D_4]methanol (0.75 mL), and ^{1}H and ^{13}C spectra were recorded. Subsequently $Si(OMe)_4$ (0.442 mmol) was added immediately before placing the sample into the magnet and further spectra of the acid + $Si(OMe)_4$ mixtures recorded at increasing intervals. ^{1}H and ^{13}C spectra were recorded in 0.5 × 18 cm borosilicate glass tubes. Amounts for ^{29}Si NMR spectra are four times the quantities above and spectra were recorded in 1.0 × 21 cm teflon tubes. ^{29}Si NMR spectra were recorded only after mixing acid + $Si(OMe)_4$ and were compared to a $Si(OMe)_4$ only control. All shifts are reported relative to $SiMe_4$ as internal standard. NMR spectra were recorded in a laboratory maintained at 18 °C. Between measurements, samples were left at RT in a laboratory without temperature control (15–25 °C).

Mass spectra were recorded on a Bruker micrOTOF instrument by using direct injection electrospray introduction in negative-ion mode with a total capillary voltage of 4500 V and a capillary exit voltage of −100 V. Prior to injecting the sample, LiOOCH (10 mM) in MeOH/*i*PrOH (9:1 v/v) was injected at 9 μL min^{-1} to provide a calibration signal. The capillary was then flushed with H_2O/MeCN (1:1 v/v) at 0.3 mL min^{-1} before the sample was introduced at 4 μL min^{-1}. Data were collected for at least 2 min or until a constant signal was obtained. Mass spectra were recorded in a laboratory maintained at 18 °C. Prior to measurements, samples were left at RT in a laboratory without temperature control (15–25 °C).

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