Hydrosilane cleavage reactions accelerated by tartaric acid and dimethyl sulphoxide [1]

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Abstract

Tartaric acid reacts spontaneously with triethoxysilane (HTES) liberating hydrogen gas, but alkyl- or arylhydrosilanes are essentially inert under these conditions. Other α-hydroxyacids reacted similarly with HTES. The reaction of tartaric acid in tetrahydrofuran is a second order process, consistent with a reaction pathway involving first transesterification of HTES by tartaric acid and subsequent Si-H cleavage. In dimethyl sulphoxide (DMSO) the reaction is much faster, and has a more complex rate profile. The initial stages of the reaction follow second order kinetics. It is proposed that the reaction proceeds via extracoordinate intermediates involving DMSO. This has the consequence of facilitating transesterification to produce many different Si-H-containing intermediates, such as 3-7, and increasing the nucleophilicity of the silicon hydride. The reaction products are amorphous solids. Examination by ^{29}Si NMR spectroscopy of the organically modified sol-gel oligomer obtained from these condensations, shows the presence of sharp peaks compatible with extracoordinate species which, in time, change to broad signals consistent with Q^4 (SiO_2) species.

Keywords: Silicon; Hydrosilanes; Tartaric acid; Dimethyl sulphoxide; Kinetics; Oxidation

1. Introduction

Hydrosilanes are arguably the most efficient functional groups for the introduction of silicon moieties into organic or inorganic residues. This results in particular from the relatively weak Si-H bond [1]; hydrosilanes may be considered to be metal hydrides of low reactivity. The reducing capacity of hydrosilanes can be exploited through their addition to multiply-bonded species such as alkenes, alkynes [2] and carbonyl compounds (Scheme 1) [3,4]. Hydrosilanes, furthermore, behave as hydrides towards relatively acidic ROH compounds leading to alkoxysilanes and H_2 gas (Scheme 1A).

In spite of the low bond strength, the rate of reaction of Si-H compounds is low in the absence of catalysts [5,6]. For example, in the reaction (Scheme 1A) of triethylsilane with boiling anhydrous ethanol no evolution of H_2 was observed in 24 h [7]. Similarly, reacting triethoxysilane (HTES) and ethanol in a sealed tube at 100 °C for 125 h resulted in only a 50% conversion of HTES to tetraethoxysilane (TEOS) [7]. Catalysts such as potassium and sodium hydroxides, organic bases, hydrogen chloride and metal complexes have been used to assist the Si-H cleavage in the alcoholysis [5,8].

The work described below was prompted by the observation of effervescence of H_2 during the reaction of tartaric acid 1 with HTES 2 in tetrahydrofuran (THF) in the absence of catalysts, conditions under which one would normally expect a reaction to occur slowly or not at all [9,10]. The reaction was observed to proceed much more rapidly in dimethyl sulphoxide (DMSO). We have examined the rate of H_2 evolution while systematically varying the reaction components and, on the basis of the results, propose mechanistic pathways for the alcoholysis.

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[1] Dedicated to Professor R.J.P. Corriu. It is a profound pleasure to dedicate this paper to Robert Corriu. It is amazing, irrespective of which area of silicon chemistry one begins to explore, always to discover that Robert was there first. His creativity, especially in the area of mechanistic silicon chemistry, has been inspirational.
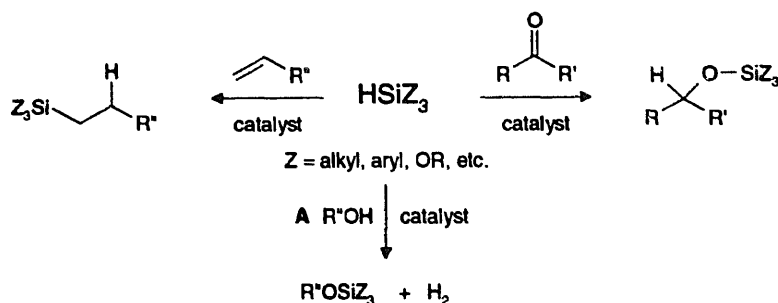
Scheme 1.

2. Experimental section

2.1. Materials

THF (99.5% BDH), hexanes (Caledon) and diethyl ether (Caledon) were freshly distilled from benzophenone (Aldrich)–sodium (BDH) under N_2 just prior to use. DMSO (400 ml, Caledon) was dried under N_2 over sodium hydroxide pellets (15 g, BDH) and then distilled at reduced pressure (b.p. 85–86 °C, 19 mmHg). NMR solvents, chloroform-d and dimethyl sulphoxide-d_6, both from Isotec Inc., were used as-received.

HTES (95% Aldrich) was distilled under reduced pressure prior to use. (+) = Tartaric acid (Aldrich), acetic anhydride (Aldrich), chromium acetylacetonate ($Cr(acac)_3$, Aldrich) Ph_3SiH (Aldrich), Et_3SiH (Aldrich), $HSiMe_2Ph$ (Aldrich), Et_3SiH (Aldrich), H_2SiPh_2 (Aldrich), $HSiMePh_2$ (Aldrich) and $MeHSi(OEt)_2$ (Aldrich) were used without further purification.

2.2. Stock solutions

A stock DMSO solution (0.02 M $Cr(acac)_3$), used in ^{29}Si NMR experiments, was prepared by dissolving chromium(III) acetylacetonate (0.94 g, 2.7 mmol) in freshly distilled DMSO (135 ml). $Cr(acac)_3$ (0.95 g, 2.7 mmol) was added to THF (135.7 ml) to give a 0.02 M mixture for ^{29}Si NMR spectroscopy. $Cr(acac)_3$ (0.47 g, 1.3 mmol) was added to a fresh bottle of $CDCl_3$ (66.7 ml) to give a 0.02 M mixture for ^{29}Si NMR spectroscopy.

2.3. Instrumentation

^1H NMR spectra were recorded on either Bruker AC 200 (200.1 MHz) or a Bruker AM-300 (300 MHz) spectrometers. Preliminary ^1H qualitative checks were performed with a Varian EM-390 (90 MHz) continuous wave instrument. ^{13}C NMR spectra were recorded on either Bruker AM-200 (50.3 MHz) or Bruker AM-300 (75.5 MHz) spectrometers. Samples were dissolved in chloroform-d ($CDCl_3$) or DMSO-d_6 with chemical shifts (ppm, δ) reported relative to tetramethylsilane (TMS)

or residual solvent peaks as internal references. Coupling constants J were recorded in hertz. The abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet are used in reporting the spectra. Solution ^{29}Si NMR spectra were obtained using a Bruker AM-300 (59.6 MHz) spectrometer at 300 K. Chemical shifts were determined relative to external TMS (^{29}Si, δ 0). $Cr(acac)_3$, 0.02 M in $CDCl_3$, DMSO or THF, was used to enhance the ^{29}Si relaxation and reduce nOes. Solid-state ^{13}C cross polarised-magic angle spinning (CP-MAS) NMR spectra were carried out on a Bruker MSL-100 (^{13}C 25.2 MHz, ^{29}Si 19.9 MHz) with a spinning rate of 4 kHz. Samples were packed into 7 mm zirconia rotors (Z5791, Bruker Spectrospin).

Infrared (IR) spectra were recorded with a Bio-Rad FTS-40 FTIR spectrometer equipped with an SPC 3200 data station. Samples were examined as either neat films with NaCl windows or as KBr pellets. Peaks are reported in wavenumbers.

Electron impact (EI) mass spectra were recorded at 70 eV with a source temperature ca. 200 °C on a VG analytical ZAB-E mass spectrometer equipped with a VG 11-250 data system.

2.4. Experimental procedures

All experimental work was performed under dry nitrogen, using syringe techniques or in a glove-bag which was continuously purged with nitrogen and dried with solid phosphorus pentoxide. Glassware was either

Table 1
Reactivity of various acids with HTES

Unreactive alcohols	Unreactive acids	Reactive acids [a]
Ethanol	acetic	glycolic
Ethylene glycol [b]	trichloroacetic	tartaric
Ethanol/acetic	oxalic	citric
	salicylic	malic
	malonic	mandelic
	succinic	

[a] Vigorous bubbling and reaction completion within 30 min was considered a positive result. [b] Bubbled very slowly for several hours.

Table 2
H$_2$ volume data: tartaric acid and HTES

Entry	Solvent	HTES (mmol)	HTES (molar equivalents)	Tartaric (molar equivalents)	H$_2$ (ml) expected [a]	H$_2$ (ml) produced	Produced (%)	k_{2obs}(l mol^{-1} s^{-1}) [b]
1	DMSO	0.843	1	1	20.4	19.9	97.4	8.10
2	DMSO	1.439	2	1	34.9	34.5	98.4	6.38
3	DMSO	1.699	3	1	41.4	38.7	93.5	7.07
4	DMSO	1.439	4	1	34.9	30.4	92.0	7.52
5	DMSO	2.198	10	1	11.7 [a]	10.5	89.6	ND [c]
6	DMSO	0.756	1	2	18.4	19.6	106.4	7.92
7	DMSO	0.644	1	3	15.7	15.8	100.7	6.15
8	DMSO	0.763	1	4	18.5	17.5	94.6	0.75
9	THF	0.933	1	1	22.6	21.8	96.0	0.049

[a] Based on 1 mol H$_2$ produced/mol HTES injected. However, no more than 4 equivalents of H$_2$ can be produced per equivalent of tartaric acid. In entry 5, only 4 of 10 equivalents HTES were consumed. [b] For the purposes of calculating the initial rates, the concentration used was the 2 × [tartaric acid] as both OH groups can participate initially: σ = 0.746 (entries 1–8). [c] Not determined.

flame-dried under a stream of nitrogen just prior to use or kept overnight in an oven at 120 °C.

2.5. Acetoxytriethoxysilane 15

Into a 50 ml round-bottom flask fitted with a condenser, N$_2$ line, and stir bar, were introduced TEOS (20 ml, 0.09 mol) and acetic anhydride (10.25 ml, 0.10 mol). The solution was heated at 180 °C for 10 h. Two fractional distillations at reduced pressure afforded the desired product in 9% yield (1.66 g).

B.p. 92 °C, 20 mmHg, (192–197 °C, 760 mmHg Ref. [11]); ^{1}H NMR (CDCl$_3$, 200 MHz): δ(ppm) = 1.20 (t, J = 4.7 Hz, 9H), 2.08 (s, 3H), 3.88 (q, J = 4.7 Hz, 6H); ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ(ppm) = 17.79, 22.38, 59.84, 169.55; ^{29}Si NMR (THF, 59.6 MHz): δ(ppm) = −86.6; MS (m/z): 222 (2), 177 (100), 163 (8), 45 (7), 43 (21); IR (neat): ν = 464, 597, 768, 951, 971, 1022, 1088, 1107, 1169, 1255, 1294, 1372, 1391, 1443, 1484, 1742, 2898, 2931, 2979, 3451 cm^{-1}.

2.6. Measuring H$_2$ evolution: HTES and tartaric acid

In a typical procedure for a 1:1 molar ratio of tartaric acid to HTES, tartaric acid (0.127 g, 0.843 mmol) was weighed into a flame dried test tube under N$_2$. A small

Teflon stirring bar was added and the test tube sealed with a rubber septum. The test tube was equipped with a small Teflon tube leading to an inverted burette (50 ml) containing light paraffin oil to enable measurement of the volume of H$_2$ evolved. The entire system was kept at room temperature. DMSO (1.67 ml) was injected from a syringe. After the acid had dissolved, the silane 2 (0.16 ml, 0.843 mmol) was added and the rate of evolution of H$_2$ from the stirred mixture was monitored. The data in Table 1 were obtained from the procedure described above; that is in volumes the addition of ca. 0.85 mmol alcohol or acid or diacid to ca. 0.85 mol HTES. Vigorous bubbling and completion of the reaction within 30 min was considered a positive result. Table 2 gives details of mixtures prepared, equivalents used, and expected volume of H$_2$ gas (based on 1 mol H$_2$ produced per mole of HTES injected. However, no more than 4 equivalents H$_2$ can be produced per equivalent of tartaric acid. In the case of entry 5, only 4 of the 10 equivalents of HTES were consumed.), volume of H$_2$ produced, and percent conversion.

2.7. NMR data

The ^{29}Si NMR data for the reactions of HTES with tartaric acid are given in Table 3.

Table 3
^{29}Si NMR integrations of solid products from reactions of HTES with tartaric acid [a]

HTES: tartaric acid	TEOS −82	Oligomers			Pentacoordinate/Q^4			
		Q^1 −88	Q^2 −95	Q^3 −102	−109	−110	−113	−114
0.5:1				2.8	8.3	7.79	19.0	8.9
1:1				2.3	1.1	12.1	4.63	17.4	9.9
2:1	0.7	5.5	13.4	8.4	17.4		6.3	17.8
4:1	3.7	33.9	61.9	22.2	25.4		9.4	42.2

[a] All reactions performed in DMSO.

The ^{13}C NMR solution spectra peaks (with relative intensities in parentheses) and IR bands for each mixture are presented below.

2.7.1. HTES:tartaric acid, 0.5:1

HTES (0.14 ml, 0.756 mmol); tartaric acid (0.227 g, 1.512 mmol); DMSO (2.27 ml); ^{13}C NMR (DMSO-d_6, 50.3 MHz): $\delta = 18.1$ (13), 19.7 (14), 37.7 (30), 41.3 (100), 43.2 (29), 54.9 (5), 56.8 (11), 58.6 (4), 61.2 (4), 71.8 (29), 71.9 (11), 73.7 (29), 73.9 (11), 171.8 (4), 172.1 (11), 173.4 (17), 173.7 (48), 174.1 (5), 174.4 (4); IR (DMSO 0.02 M Cr(acac)$_3$): $\nu = 461$, 594, 671, 703, 902, 953, 1024, 1045, 1091, 1137, 1204, 1265, 1212, 1408, 1437, 1742, 1907, 1964, 2231, 2523, 2914, 2997, 3285, 3376 cm^{-1}.

2.7.2. HTES:tartaric acid, 1:1

HTES (0.16 ml, 0.843 mmol); tartaric acid (0.127 g, 0.843 mmol); DMSO (1.67 ml); ^{13}C NMR (DMSO-d_6, 50.3 MHz): $\delta = 14.4$ (26), 15.6 (18), 17.9 (5), 18.8 (100), 34.4 (38), 56.5 (81), 59.3 (2), 61 (22), 72.6 (35), 72.8 (33), 73.2 (18), 75.6 (25), 171.6 (9), 171.9 (10), 173.2 (11), 173.5 (22), 173.9 (13), 174.1 (10); IR (DMSO 0.02 M Cr(acac)$_3$): $\nu = 483$, 706, 819, 906, 952, 1022, 1091, 1137, 1203, 1437, 1742, 2597, 2916, 2998, 3403 cm^{-1}.

2.7.3. HTES:tartaric acid, 2:1

HTES (0.27 ml, 1.44 mmol); tartaric acid (0.108 g, 1.512 mmol); ^{13}C NMR (DMSO-d_6, 50.3 MHz): $\delta = 15.4$ (26), 17.5 (15), 17.9 (9), 18.1 (10), 18.6 (100), 34.3 (52), 56.6 (61), 58.1 (7), 58.4 (11), 58.8 (7), 62.7 (3), 73.2 (27), 75.7 (36), 173.8 (18); IR (DMSO 0.02 M Cr(acac)$_3$): $\nu = 462$, 504, 554, 708, 754, 820, 880, 950, 1053, 1085, 1158, 1276, 1316, 1351, 1436, 1710, 2742, 2919, 2973, 3384 cm^{-1}.

2.7.4. HTES:tartaric acid, 4:1

HTES (0.27 ml, 1.439 mmol); tartaric acid (0.054 g, 0.36 mmol); DMSO (1.80 ml); ^{13}C NMR (DMSO-d_6, 50.3 MHz): $\delta = 15$ (10), 15.3 (34), 17.4 (10), 17.7 (32), 18.3 (100), 21.5 (5), 23.8 (4), 34.2 (73), 56.7 (77), 58.1 (14), 58.3 (35), 62.6 (10), 73.2 (39), 75.6 (34), 94.4 (3), 173.9 (22); IR (DMSO 0.02 M Cr(acac)$_3$): $\nu = 484$, 553, 803, 817, 970, 1074, 1154, 1365, 1439, 1709, 2742, 2896, 2975, 3391 cm^{-1}.

2.8. IR data

IR data for HTES:tartaric acid C=O absorptions are presented in Table 4.

2.9. Other hydrosilanes

The experimental procedure detailed above was repeated with an equimolar amount of the relevant silane.

Table 4
HTES: tartaric acid C=O absorptions

Ratio (HTES: tartaric acid)	C=O absorption [a] ($\nu = $ cm^{-1})
Tartaric acid	1717
0.5 to 1	1743
1 to 1	1742
2 to 1	1710
4 to 1	1709

[a] In DMSO (0.02 M Cr(acac)$_3$).

The relative rates were judged from the rate of H_2 evolution. The alkoxysilanes reacted within minutes, the others over hours and days.

3. Reaction and mechanism

For most of the reactions described below, HTES was added through a syringe to a solution of the alcohol–acid in a sealed vessel connected via Teflon tubing to an inverted, oil-filled burette. In this way the rate of H_2 evolution could be conveniently monitored. Once the reaction was complete, the residual solution was isolated and examined by a variety of spectroscopic techniques, particularly NMR. In attempting to investigate the nature of the reaction, it quickly became clear that the rate of the H_2 effervescence depended on the nature of both reaction partners and the solvent used. An examination of the influence of the structural features of the starting materials on the rate is followed by a description of the characterisation of the products.

3.1. Dependence of the ease of reaction on the nature of the reactants

3.1.1. The hydrosilane

The reactivity of the Si–H bond in a variety of hydrosilanes towards tartaric acid was first examined. The relative reactivity of the hydrosilanes, as determined by the rate of H_2 evolution, follows the order shown below: the reaction is faster with alkoxyhydrosilanes than alkylhydrosilanes.

$HSi(OEt)_3 > MeHSi(OEt)_2 > Ph_3SiH \gg Et_3SiH$

$\gg HSiMe_2Ph, H_2SiPh_2, HSiMePh_2$
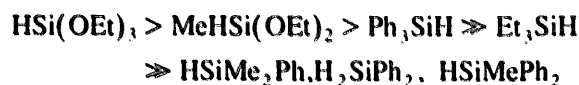
3.1.2. The alcohol and acid

The addition of several different ROH and RCOOH compounds to HTES in a variety of polar solvents was examined. Ethanol and t-butanol were found to be unreactive. To determine whether the occurrence of the reaction with tartaric acid was simply a question of acidity, we examined the behaviour of a series of

different carboxylic acids with HTES under identical conditions. The pK_a of the acid does not seem to be an important factor (Table 1). For instance, neither of the simple organic acids acetic acid or trichloroacetic acid was observed to react with HTES. The reactivity of HTES towards tartaric acid is also not a simple consequence of the presence of both ROH and R'COOH functional groups present: reaction mixtures containing HTES and the same functional groups as tartaric acid, combinations of acetic acid or trichloroacetic acid and ethanol, for example, again gave no H_2 generation.

It was found that a rapid release of H_2 was observed only with molecules bearing certain structural features (Table 1). Unlike simple alcohols or acids, tartaric acid can react with silicon in an intramolecular fashion. In order to determine if such multidentate binding was the source of the tartaric acid reactivity, and whether the binding was of (i) a vicinal diol, (ii) a 1,4-dioic acid or (iii) an α- or β-hydroxyacid, we examined the reactions of a series of various functionalised organic acids and ethylene glycol with HTES (Table 1). On the basis of the results, the diacid and diol structures were ruled out as important components of the reaction because of the

inactivity of the relevant model compounds, succinic acid and ethylene glycol respectively. The reaction of ethylene glycol took several hours and was not studied in detail. Activating structures were thus limited to α- or β-hydroxycarboxylic acids. We are unable to comment on the relative effectiveness of β-hydroxy acids except for salicylic acid, which was not reactive. However, in the reaction of each α-hydroxy acid with HTES evolution of H_2 was vigorous for the first 5 min and then gradually slowed until the reaction was complete after about 30 min.

3.1.3. Effect of solvent: THF vs. DMSO

Otherwise identical reactions carried out in THF or DMSO showed very different rates and rate profiles. Those in DMSO, known to be a good silaphilic nucleophile [12,13], were much faster than those in THF (Fig. 1, Table 2).

3.2. Stoichiometry and kinetics

In order to determine how many mole equivalents of H_2 were formed per mole of hydroxyacid and, in
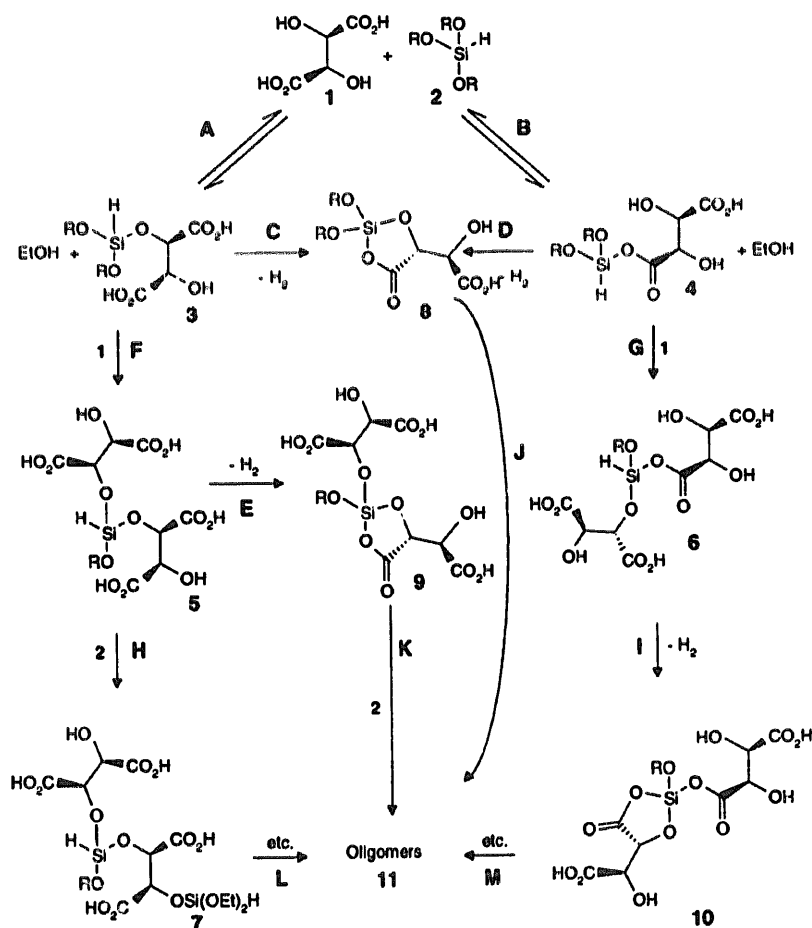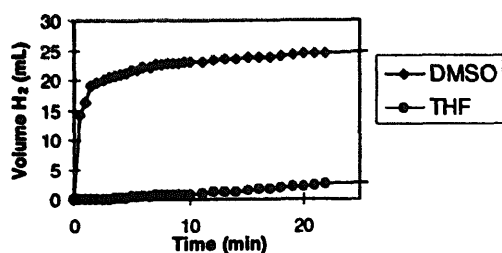

Scheme 2.

Fig. 1. Reaction of HTES with tartaric acid (1:1) in THF and DMSO.

particular, whether alcohols, acids or both were responsible for the formation of H_2, tartaric acid and HTES were used in different ratios (Table 2). In each system, the rate of production and total amount of H_2 produced were determined. These data show that both the COOH and OH hydrogens react with HTES.

In THF, the reaction between HTES and tartaric acid (1:1 ratio) was a simple second order process. By contrast, simple first and second order plots of the H_2 evolution with DMSO as solvent were not linear. Initial rates could, however, be determined from the H_2 evolution over the first 1-2 min. A second order plot over this range, which, depending on the reaction, represented about 1-5 half-lives, was linear. The initial second order rate constants determined by this method are given in Table 2. Except for the reactions performed at high tartaric acid concentration, there is good agreement between the observed rate constants in these reactions. Although it has not yet been established whether ROH or RCOOH reacts more rapidly with Si-H in these reactions, we predict that it is the latter.

3.3. Mechanism of reaction in THF

Alkylhydrosilanes and arylhydrosilanes were found to be less reactive than alkoxyhydrosilanes. One property which may account for the difference in reactivity between these classes of molecule is the facility with which they undergo extracoordination; the greater the number of electronegative groups, the easier this is.

The lack of reactivity of acetic acid and/or ethanol towards HTES suggests that the reactivity of tartaric acid and other α-hydroxyacids is not simply related to the pK_a of the acid or the nucleophilicity of the alcohol. Once, however, one end of the tartaric acid molecule 'interacts' with the silicon atom, other functional groups are held proximal to the silicon centre and, more importantly, the Si-H bond. The most likely type of 'interaction' between tartaric acid and HTES is transesterification to give various structures containing Si-H similar to 3-7 (Scheme 2A, B, F, G, K). The subsequent alcoholysis or acidolysis of the Si-H is then an intramolecular process giving species like 8-11 (Scheme 2C-E, I). In general, the greater ease of intramolecular processes is one factor accounting for the H_2 efferves-

cence. We consider such a process to be the primary operating mechanism in THF.

In THF, the observed kinetics were simple second order. This could arise from the pathway A,C shown in Scheme 2; while B,D is possible, acyloxy groups are much poorer nucleophiles for, and better leaving groups from, silicon than alkoxy groups, so this process should be a minor pathway at best. If the steady-state approximation is applied to path A, the second order rate expression would be Rate = $k_E K_C$[tartaric acid][HTES].

3.4. Mechanism of reaction in DMSO

3.4.1. Role of DMSO

The reaction between tartaric acid and HTES was not simple second order in DMSO. DMSO is known to be one of a group of silaphilic molecules (Nu, Scheme 3) that can activate silicon to nucleophilic attack via pentacoordinate intermediates 12 [13]. Corriu and coworkers, in particular, have demonstrated that in the presence of such catalysts, nucleophilic substitution occurs more rapidly, with a different stereochemical outcome, and with a different rate expression (Scheme 3) [14]. In the HTES reaction, multiple transesterifications (Scheme 2A, B, F, G, K, nucleophilic exchange reactions) should be facilitated by the presence of the DMSO via intermediates such as in 12 → 13 (Scheme 3). Thus, the observed rate of H_2 formation will be a composite of the rates of reaction of many different Si-H-containing species (Scheme 2C-E, I, etc.). The absence of a simple rate expression is therefore not surprising. The initial, second order rates (Initial Rate = k_{obs}[tartaric acid]-[HTES]) are consistent with the path 12 → 13 → 14 (Scheme 3). The catalyst DMSO does not appear in the rate expression because it was present in large excess under pseudo first order conditions.

12   13   14
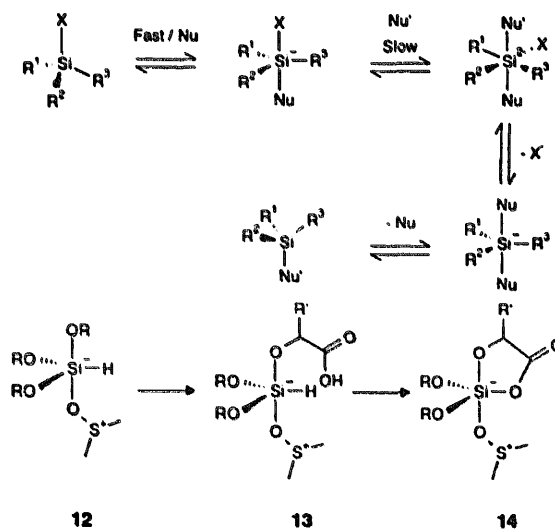
Scheme 3.

3.5. Reaction mechanism: pentacoordinate species

The intermediacy of a pentacoordinate species has an additional effect on the rate of reaction of HTES. Several groups [15–17], notably Corriu and coworkers [18,19], have shown that pentacoordinate hydrosilane complexes possess increased reducing ability compared with analogous tetracoordinate compounds containing Si–H bonds. On the basis of these precedents, an activated, pentacoordinate species 13 would be expected to react rapidly with the COOH to give H_2, as observed (Scheme 3).

4. Product analysis

The products of these reactions generally stayed in DMSO solution and were subjected to ^{29}Si, ^{13}C, and ^{1}H NMR and FT-IR spectroscopic analyses: the samples were characterised after 4 and 29 days. The materials produced were oligomeric species: after evaporation of solvent they showed no clear melting points, could not be separated by distillation or chromatography, and could not be recrystallized from DMSO solutions. They decomposed in water. The samples, furthermore, were insoluble in many solvents, including acetone, hexanes, $CDCl_3$, THF and 1,1,1-trichloroethane, ruling out molecular weight determinations by gel permeation chromatography (GPC).

4.1. Spectroscopic data

The ^{29}Si spectrum consisted of clusters of multiplets in the normal Q^n regions as listed in Table 3 (see also Fig. 2). However, these are also likely chemical shift regions for mixed acyloxy(alkoxy)silanes. Acetoxytriethoxysilane 15 was prepared and found to have a chemical shift of −86.6 ppm. Tartrate orthoesters bonded through the hydroxy and/or carboxy group, similar for example to 8–11 (Scheme 2), might be expected to have even higher upfield shifts. TEOS is included in the table because it was present in some samples. In no samples, however, could unreacted HTES (δ = −58 ppm) be identified by ^{29}Si NMR. The sharpness of the peaks (Fig. 2) is more indicative of well-defined oligomers and of alkoxyl/acyloxysilanes than the normal, broad Q^n (n = 1 to 3) signals from silica [20,21]. It is also unclear where sufficient water could come from to generate significant amounts of SiO_2; during the initial 4 day aging process the samples were kept under a nitrogen blanket [22,23].

The most negative chemical shift peaks are assigned to pentacoordinate species. The ^{29}Si NMR chemical shift change upon coordination expansion from tetra- to pentacoordinate is in the region of −30 to −40 ppm [24]: the typical range for pentacoordinate species is
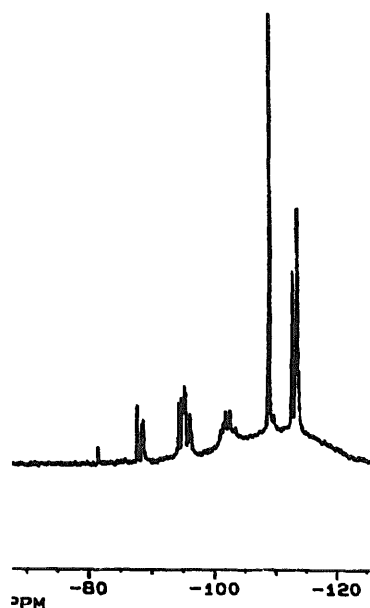

Fig. 2. ^{29}Si NMR spectrum of the HTES:tartaric acid 2:1 ratio.

−150 to −50 [25]. The observed chemical shift region (−109 to −114 ppm) is generally assigned to be the Q^4 region. However, the sharpness of the peaks suggests discrete low molecular weight rather than polymeric species. It is known that the breadth observed in Q^1–Q^4 resonances of sol–gel systems (in TEOS hydrolysis [26]) is due to the overlap of a large number of single resonance lines produced by the many different environments of Si nuclei in a matrix [20].

The peaks were also assigned to pentacoordinate species because of the change in their intensities with time. After 4 days, the peaks at −109 to −114 ppm were very strong and sharp. After 29 days in ambient moisture, however, these peaks collapsed and there was an increase in the proportion of peaks in the Q^2 and Q^3 regions. One would not expect a decrease in the intensities of Q^4 (SiO_2) peaks with time. The nature of the pentacoordinate species is discussed below.

General comments can be made about these spectra as one goes from 0.5:1 to 4:1 HTES:tartaric acid. The relative intensities of the pentacoordinate species decrease and those for TEOS and compounds with peaks in the Q^1, Q^2, and Q^3 ranges increase. It follows that as the molar equivalents of HTES decrease, fewer and fewer of the four possible nucleophilic sites on tartaric acid will react. The resultant, less dense matrix would also allow faster decomposition of any pentacoordinate species.

Characterisation of the products using ^{13}C NMR was difficult owing to the small chemical shift differences for the many tartrate derivatives in the mixture. Peaks for ethanol and small amounts of diethyl tartrate, but not the starting material, HTES, were present. Diethyl tartrate must arise from the transesterification of tartaric
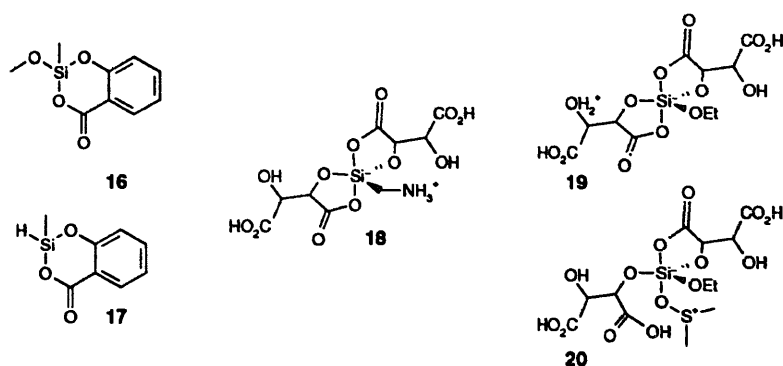
Fig. 3. Products from salicylic acid–alkylalkoxysilane reactions.

acid [27], presumably in an analogous fashion to esterifications promoted by Ti(O^{i}Pr)$_4$ [28].

The shift in the carbonyl band in the IR spectrum was examined after the 4 day aging process. None of the products displayed a signal for the Si–H bond ($\nu = 2196$ cm^{-1}). As the ratio of HTES to acid increased, the carbonyl absorption shifted to lower wavenumbers (Table 4).

4.2. Product structures

There have been reports of the reactions of α- and β-hydroxy acids and alkoxyhydrosilanes. Mehrotra and Narain examined the reactions of HTES with various ratios of mandelic, lactic, and salicylic acids in refluxing benzene [29]. Bubbling was reported only in those reactions involving lactic acid; the proposed product was a monomeric tetra(alkoxy)(acyloxy)silane. Otherwise, the proposed products were monomeric hydro(alkoxy)(acyloxy)silanes.

A related publication dealt with the reactions between alkylalkoxysilanes and α-hydroxy acids [30]. Methyltrimethoxy- and methyldiethoxysilanes were reacted with salicylic, lactic, mandelic and benzilic acids: there was no H$_2$ production noted in the reactions between methyldiethoxysilane and the hydroxyacids. Only the products from reactions involving salicylic acid and methyldiethoxysilane 16, 17, shown in Fig. 3, could be purified by distillation and characterised. The α-hydroxy acids either gave a brown viscous material or white solids which could not be purified; it was suggested that products similar to 16 and 17 were formed in reactions with the α-hydroxyacids. Products in both papers were characterised by elemental analysis, IR-spectroscopy and the molar equivalents of alcohol that could be fractionated out of the system azeotropically.

The lack of spectroscopic data in both the above investigations casts some doubt on the proposed identities of the products. Cragg has expressed concern about these because of the lack of information about the

properties of the products [31]. In his own work, using β-hydroxy acids (salicylic acid), cyclic structures, in agreement with those of 16 and 17 were obtained. Otherwise, Cragg had difficulty in obtaining cyclic products from the reactions of dichlorosilanes and α-hydroxy acids.

Other compounds derived from tartaric acid and alkoxysilanes have been described, but their structures were not determined. For instance, silica nanotubes can be prepared by pyrolysing ormosols [32] (organically modified sol–gels [33]) derived from 1 and Si(OEt)$_4$ [34].

Recently, in an elegant series of papers, Tacke and coworkers described the preparation of monomeric, zwitterionic, crystalline materials derived from alkyltrialkoxysilanes and α-hydroxyacids, including tartaric acid [35]. In many examples, the crystal structures of these compounds showed the presence of pentacoordinate silicon, involving five-membered rings derived from α-hydroxyacids (even those bearing other OH, or COOH groups) with the acyloxy groups in the axial positions 18 (Fig. 3). The structures are zwitterionic by virtue of the intramolecular amino-group which allows monomeric species to exist.

The products of our reactions of HTES with tartaric acid are analogous to those of Tacke and coworkers, except that ours are oligomeric. The network structure is probably a mixture of dimers and higher oligomers of acyloxy/alkoxysilanes (Scheme 2, 8–11). To the degree that extracoordinate species are present, they are likely to resemble those of Tacke and coworkers: the counterion for the extracoordinate system could be intramolecular such as 19 or sulphoxonium 20 (Fig. 3). The loss of extracoordinate peaks and broadening of peaks in the Q^1–Q^3 regions with time suggests that in the presence of moisture the ormosol is converted to an increasingly silaceous material. In order to test this possibility, we are attempting independent synthesis of compounds of the family 3–11 with the goal of studying their hydrolytic behaviour.

5. Conclusion

HTES reacts rapidly with α-hydroxyacids to generate H_2. This is thought in THF to occur through an intramolecular process following transesterification at silicon. In DMSO as solvent, the reaction is much faster. This arises from the activating effect of the DMSO at silicon, through extracoordination, to increase the ease of transesterification, and also raise the nucleophilicity of the silicon hydride. It is concluded from the spectroscopic characterisation of these materials that the products are organically modified sol–gels in which silicon atoms are connected through $SiOW$-$YOSi$ bridges in which W, Y may be hydroxy or carboxy-derived. During aging in the presence of atmospheric moisture, the compounds gradually undergo hydrolysis to liberate tartaric acid, ethanol and silica.

Acknowledgements

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$$RSiH_3 + R'OH \xrightarrow[-H_2]{k_1} RSiH_2(OR') \xrightarrow[+R'OH]{k_2}$$

$$RSiH(OR')_2 \xrightarrow[+R'OH]{k_3} RSi(OR')_3 + H_2$$

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