

Supplementary information

¹³C and ¹H NMR of acid/ Si(OMe)₄ mixtures in CD₃OD – the acid and ester signals

Acid	Form	Alpha <i>H</i>	Beta <i>H</i>	Ester CH ₃	Alpha <i>C</i>	Beta <i>C</i>	Carboxyl <i>C</i>	Ester C H ₃
OA+	free	-	-	-	-	-	161.65	-
Si(OMe) ₄	monomethyl ester	-	-	3.854 s	-	-	160.90; 160.33	53.64
	dimethyl ester	-	-	3.863 s	-	-	159.53	53.86
	Free	4.480 dd, J=7.78, 4.33	2.799 dd, J=16.13, 4.33; 2.649, J=16.05, 7.80	-	68.45	40.03	176.50; 174.11	-
Si(OMe) ₄	monomethyl ester	4.491 dd, J=7.50, 4.50	2.770 dd, J=16.00, 4.50; 2.661 dd, J=16.00, 7.50	3.739 s	68.61	39.85	175.13; 173.83	51.59
	dimethyl ester	4.507 dd, J=7.25, 4.75	2.801 dd, J=15.00, 4.50; 2.702 dd, J=16.25, 7.25	3.739 s; 3.679 s	68.56	39.86	174.94; 172.49	51.59; 51.66
	TA+	free	4.531 s	-	-	73.38	-	174.70
Si(OMe) ₄	monomethyl ester	4.510 d, J=2.0; 4.569 d, J=2.0	-	3.780 s	73.48; 73.80	-	174.44; 173.58	51.60
	dimethyl ester	4.553 s	-	3.775 s	73.81	-	173.34	52.86
	transient	4.484 s	-	-	76.93	-	177.10	-
	TA+	monoethyl ester	4.500 d J=2.5; 4.561 d J=2.5	-	1.295 t, J=7.0; 4.239 q, J=7.0	73.40; 73.70	-	174.31; 173.47
Si(OEt) ₄	diethylester	4.545 s	-	1.290 t, J=7.25; 4.234 q, J=7.17	73.74	-	173.22	62.48; 14.48
	transient	4.465 s	-	-	76.82	-	177.09	-
	TA+	free	4.495 s	-	-	73.04	-	174.23
Si(OEt) ₄ / EtOD ^a	monoethyl	4.465 d,	-	4.222 q, J=7.17	73.13;	-	173.88;	61.99

	ester	J=2.0; 4.510 d, J=2.0		(-CH ₃); 1.286 t, J=7.25 (-OCH ₂ -)	73.40		172.58	(-OCH ₂ -); 14.41 (-CH ₃)
	diethylester	4.494 s	-	4.222 q, J=7.17 (-CH ₃); 1.283 t, J=7.00 (-OCH ₂ -)	73.46	-	172.33	62.03 (-OCH ₂ -); 14.41 (-CH ₃)
CA+	free	-	2.791 d, J=15.73; 2.906 d, J=16.05	-	74.16	43.83	176.73; 173.44	-
Si(OMe) ₄	monomethyl ester	-	2.787 d, J=15.25; 2.817 d, J=14.38; 2.918 d, J=15.63; 2.922 d, J=15.63	3.658 s	74.20	43.82; 44.03	176.56; 173.39; 171.91	51.60
	dimethyl ester	-	2.816 d, J=15.33; 2.938 d, J=15.83	3.658 s	74.23	44.01	176.38; 171.87	52.21

Table S1. Assignment of signals in ¹H and ¹³C NMR spectra. Measured in CD₃OD except ^a measured in C₂D₅OD.

When MA was incubated with MeOH or with Si(OMe)₄, the concentrations of the products were calculated from the integrals of the four regions A-D in Figure 4a). The concentration of monomethyl MA was calculated as

$$[\text{monomethyl MA}]_t = \left(1 - \frac{\text{intA}_t}{0.485} - \frac{\text{intD}_t}{0.515} \right) \times [\text{MA}]_0 \quad [\text{S1}]$$

and of diester as

$$[\text{dimethyl MA}]_t = \frac{\text{intA}_t}{0.485} \times [\text{MA}]_0 \quad [\text{S2}]$$

where intA_t etc are the normalised integrals of the four regions A etc. at time t, and 0.485:0.515 is the ratio of the two left-hand peaks of the doublet of doublets to the two right-hand peaks, measured for both the pure acid and pure diester.

When CA was incubated with MeOH or with Si(OMe)₄, the concentrations of the products were calculated from the integrals of the nine regions A-I in Figure 4b). The concentration of monomethyl CA was calculated as

$$[\text{monomethyl CA}]_t = \frac{\text{intB}_t + \text{intD}_t}{\text{intA}_t + \text{intB}_t + \text{intC}_t + \text{intD}_t} \times [\text{CA}]_0 \quad [\text{S3}]$$

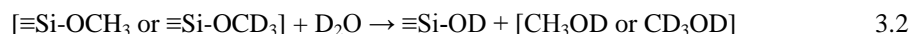
and of diester as

$$[\text{dimethyl CA}]_t = \frac{\text{intA}_t}{0.369 \times (\text{intA}_t + \text{intB}_t + \text{intC}_t + \text{intD}_t)} \times [\text{CA}]_0 \quad [\text{S4}]$$

where $\text{int}A_t$ etc are the normalised integrals of the nine regions A etc. at time t , and 0.369:0.631 is the ratio of the left-hand peak of the left-hand doublet to the right-hand peak of the left-hand doublet, measured for both the pure acid and pure triester so extrapolated to the diester.

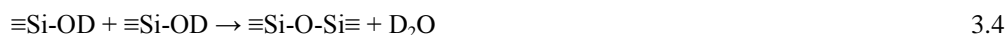
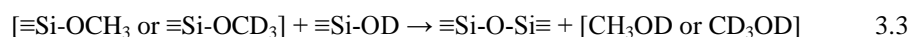
^{13}C and ^1H NMR of acid/ $\text{Si}(\text{OMe})_4$ mixtures in CD_3OD – the siloxane signals

Additional information regarding the mechanism of interaction and esterification in each case might be drawn from studying the changes in the siloxane signals. When $\text{Si}(\text{OMe})_4$ is incubated alone in CD_3OD , slow processes of ligand exchange (3.1) and hydrolysis (3.2) are observed:



(where D_2O is derived from H_2O , which is initially present or which ingresses into the tube and exchanges its protons with the deuteriums of the more abundant CD_3OD). Both processes lead to the loss of the SiOCH_3 (3.56 ppm singlet, figure 2b) and SiOCH_3 (51.6 ppm singlet, figure 2e) signals but the growth of new CH_3OD (3.35 ppm singlet) and CH_3OD (49.9 ppm singlet) signals, almost overlaying the CHD_2OD and CD_3OD signals. The ligand exchange process 3.1, additionally leads to a signal for SiOCD_3 (50.8 ppm septet), which subsequently decays due to process 3.2.

In the presence of added H_2O these processes are accelerated and, because $\equiv\text{Si}-\text{OD}$ is formed in larger quantities, condensation reactions to form $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ also become significant:



Each of these processes leads to further signals due to $\equiv\text{Si}-\text{OCH}_3$ or $\equiv\text{Si}-\text{OCD}_3$ within hydrolysed or oligomeric species which can also be seen in figures 2b) and 2e).

It was shown in the previous paper that the concentrations of SiOCH_3 , SiOCD_3 and $\text{CH}_3\text{O}[\text{D}/\text{H}]$ change ~ 1000 fold faster in mixtures of $\text{Si}(\text{OMe})_4$ with 2HOAs in CD_3OD than in $\text{Si}(\text{OMe})_4 + \text{H}_2\text{O}$ in CD_3OD . All of these processes are accelerated for OA, MA, TA and CA also. Figure 5 shows the rapid growth of the SiOCD_3 signal for each of these acids immediately after addition of $\text{Si}(\text{OMe})_4$, and its slow decay due to hydrolysis and condensation. It can be seen that the processes occur at similar rates for each acid, though the removal of SiOCD_3 is perhaps slower in the case of MA. Thus, changes in the ^1H and ^{13}C spectra due to the siloxane species reveal little about any differences in the mechanism of reactions for the four acids.

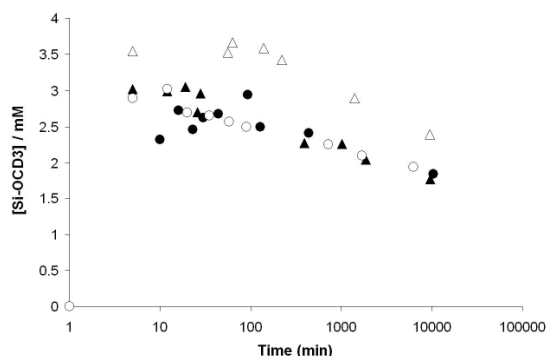
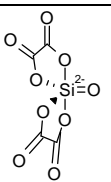
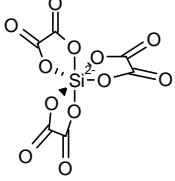
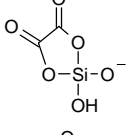
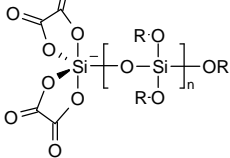
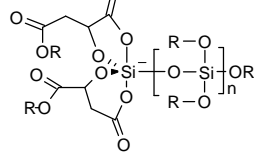
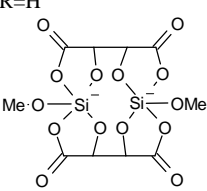


Figure S1: Changes in the concentration of $\equiv\text{SiOCD}_3$ after $\text{Si}(\text{OMe})_4$ (0.75 mmol) is added to CD_3OD containing 0.375 mmol of OA (open circles), MA (open triangles), TA (filled circles) or CA (filled triangles).

ES-MS analysis of acid/Si(OMe)₄ mixtures in CH₃OH

Sample	Observed ions	Assigned	Calculated m/z (difference in ppm)	Possible structure
OA+ Si(OMe) ₄	109.9655	SiC ₄ O ₉ ²⁻	109.9661 (+6.6)	 A
	145.9589	SiC ₆ O ₁₂ ²⁻	145.9585 (-2.6)	 B
	148.9537	SiC ₂ HO ₆ ⁻	148.9548 (+7.1)	 C
	220.9398	SiC ₄ HO ₉ ⁻	220.9395 (-1.2)	 D n=0, 1×R=H
	292.9248	SiC ₆ HO ₁₂ ⁻	292.9243 (-1.6)	B+H ⁺
	314.9054	NaSiC ₆ O ₁₂ ⁻	314.9062 (+2.7)	B+Na ⁺
	432.9571	Si ₃ C ₈ H ₁₃ O ₁₅ ⁻	432.9568 (-0.7)	D, n=1, 2×R=CH ₃ , 3×R=H
	446.9728	Si ₃ C ₉ H ₁₅ O ₁₅ ⁻	446.9724 (-0.9)	D, n=2, 5×R=CH ₃
	552.9806	Si ₄ C ₁₁ H ₂₁ O ₁₈ ⁻	552.9810 (+0.7)	D, n=3, 7×R=CH ₃
	MA+ Si(OMe) ₄	133.0143	C ₄ H ₅ O ₅ ⁻	133.0142 (-0.2)
323.0066		SiC ₉ H ₁₁ O ₁₁ ⁻	323.0076 (+2.9)	 F n=0, 1×R=CH ₃ , 2×R=H
337.0227		SiC ₁₀ H ₁₃ O ₁₁ ⁻	337.0233 (+1.8)	F, n=0, 2×R=CH ₃ , 1×R=H
415.0009		Si ₂ C ₁₀ H ₁₅ O ₁₄ ⁻	415.0006 (-0.7)	F, n=1, 2×R=CH ₃ , 3×R=H
429.0182		Si ₂ C ₁₁ H ₁₇ O ₁₄ ⁻	429.0162 (-4.6)	F, n=1, 3×R=CH ₃ , 2×R=H
443.0308		Si ₂ C ₁₂ H ₁₉ O ₁₄ ⁻	443.0319 (+2.4)	F, n=1, 4×R=CH ₃ , 1×R=H
535.0227		Si ₃ C ₁₃ H ₂₃ O ₁₇ ⁻	535.0249 (+4.0)	F, n=2, 5×R=CH ₃ , 2×R=H
549.0392		Si ₃ C ₁₄ H ₂₅ O ₁₇ ⁻	549.0405 (+2.4)	F, n=2, 6×R=CH ₃ , 1×R=H
641.0300		Si ₄ C ₁₅ H ₂₉ O ₂₀ ⁻	641.0335 (+5.4)	F, n=3, 7×R=CH ₃ , 2×R=H
TA+ Si(OMe) ₄ 10 min ^a		149.0092	C ₄ H ₅ O ₆ ⁻	149.0092 (-0.6)
	204.9810	Si ₂ C ₁₀ H ₁₀ O ₁₄ ⁻	204.9810 (+0.2)	R=H  H

322.9701	$\text{SiC}_8\text{H}_7\text{O}_{12}^-$	322.9712 (+3.4)		I
			R=H	
336.9880	$\text{SiC}_9\text{H}_9\text{O}_{12}^-$	336.9869 (+1.1)	I, R=CH ₃	
354.9973	$\text{SiC}_9\text{H}_{11}\text{O}_{13}$	354.9974 (+0.5)		
				J
			n=0, 1×R=CH ₃ , 2×R=H	
369.0132	$\text{SiC}_{10}\text{H}_{13}\text{O}_{13}^-$	369.0131 (-0.3)	J, n=0, 2×R=CH ₃ , 1×R=H	
378.9435	$\text{Si}_2\text{C}_9\text{H}_7\text{O}_{13}$	378.9431 (-1.0)		
				K
			R=CH ₃	
383.0291	$\text{SiC}_{11}\text{H}_{15}\text{O}_{13}^-$	383.0287 (-0.9)	J, n=0, 3×R=CH ₃	
410.9734	$\text{Si}_2\text{C}_{10}\text{H}_{11}\text{O}_{14}$	410.9693 (-10.0)		
				L
			n=0, 2×R=CH ₃ , 1×R=H	
461.0058	$\text{Si}_2\text{C}_{13}\text{H}_{17}\text{O}_{16}^-$	461.0061 (+0.5)	J, n=1, 3×R=CH ₃ , 2×R=H	
475.0213	$\text{Si}_2\text{C}_{12}\text{H}_{19}\text{O}_{16}^-$	475.0217 (+0.9)	J, n=1, 4×R=CH ₃ , 1×R=H	
484.9518	$\text{Si}_3\text{C}_{11}\text{H}_{13}\text{O}_{16}$	484.9517 (-0.3)		
				M
			3×R=CH ₃	
489.0370	$\text{Si}_2\text{C}_{13}\text{H}_{21}\text{O}_{16}^-$	489.0374 (+0.8)	J, n=1, 5×R=CH ₃	
516.9789	$\text{Si}_3\text{C}_{12}\text{H}_{17}\text{O}_{17}^-$	516.9779 (-1.9)	L, n=1, 4×R=CH ₃ , 1×R=H	
581.0305	$\text{Si}_3\text{C}_{14}\text{H}_{25}\text{O}_{19}^-$	581.0303 (-0.3)	J, n=2, 6×R=CH ₃ , 1×R=H	
622.9864	$\text{Si}_4\text{C}_{14}\text{H}_{23}\text{O}_{20}$	622.9865 (+0.2)	L, n=2, 6×R=CH ₃ , 1×R=H	
728.9950	$\text{Si}_5\text{C}_{16}\text{H}_{29}\text{O}_{23}$	728.9951 (+0.2)	L, n=3, 8×R=CH ₃ , 1×R=H	
TA+	149.0099	$\text{C}_4\text{H}_5\text{O}_6$	149.0092 (-4.8)	G, R=H
Si(OMe) ₄	163.0241	$\text{C}_5\text{H}_7\text{O}_6$	163.0248 (+4.1)	G, R=CH ₃
	354.9963	$\text{SiC}_9\text{H}_{11}\text{O}_{13}^-$	354.9974 (+3.3)	J, n=0, 1×R=CH ₃ , 2×R=H
	369.0113	$\text{SiC}_{10}\text{H}_{13}\text{O}_{13}^-$	369.0131 (+4.8)	J, n=0, 2×R=CH ₃ , 1×R=H
	383.0268	$\text{SiC}_{11}\text{H}_{15}\text{O}_{13}^-$	383.0287 (+5.0)	J, n=0, 3×R=CH ₃
	396.9534	$\text{Si}_2\text{C}_9\text{H}_9\text{O}_{14}$	396.9536 (+0.5)	L, n=0, 1×R=CH ₃ , 2×R=H

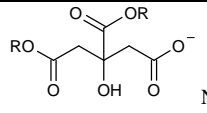
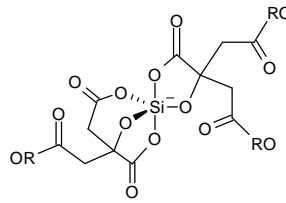
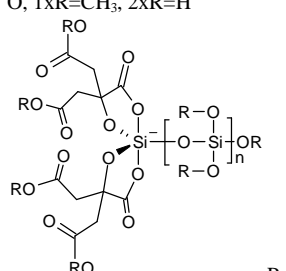
410.9678	Si ₂ C ₁₀ H ₁₁ O ₁₄ ⁻	410.9693 (+3.7) L, n=0, 2×R=CH ₃ , 1×R=H
461.0055	Si ₂ C ₁₁ H ₁₇ O ₁₆ ⁻	461.0061 (+1.2) J, n=1, 3×R=CH ₃ , 2×R=H
475.0203	Si ₂ C ₁₂ H ₁₉ O ₁₆ ⁻	475.0217 (+2.9) J, n=1, 4×R=CH ₃ , 1×R=H
489.0360	Si ₂ C ₁₃ H ₂₁ O ₁₆ ⁻	489.0374 (+2.9) J, n=1, 5×R=CH ₃
502.9628	Si ₃ C ₁₁ H ₁₅ O ₁₇ ⁻	502.9623 (-1.1) L, n=1, 3×R=CH ₃ , 2×R=H
516.9782	Si ₃ C ₁₂ H ₁₇ O ₁₇ ⁻	516.9779 (-0.6) L, n=1, 4×R=CH ₃ , 1×R=H
567.0160	Si ₃ C ₁₃ H ₂₃ O ₁₉ ⁻	567.0147 (-2.3) J, n=2, 5×R=CH ₃ , 2×R=H
581.0300	Si ₃ C ₁₄ H ₂₅ O ₁₉ ⁻	581.0303 (+1.1) J, n=2, 6×R=CH ₃ , 1×R=H
595.0447	Si ₃ C ₁₅ H ₂₇ O ₁₉ ⁻	595.0460 (+2.2) J, n=2, 7×R=CH ₃
608.9714	Si ₄ C ₁₃ H ₂₁ O ₂₀ ⁻	608.9709 (-0.8) L, n=2, 5×R=CH ₃ , 2×R=H
622.9867	Si ₄ C ₁₄ H ₂₃ O ₂₀ ⁻	622.9865 (-0.3) L, n=2, 6×R=CH ₃ , 1×R=H
687.0386	Si ₄ C ₁₆ H ₃₁ O ₂₂ ⁻	687.0390 (+0.6) J, n=3, 8×R=CH ₃ , 1×R=H
701.0550	Si ₄ C ₁₇ H ₃₃ O ₂₂ ⁻	701.0546 (-0.5) J, n=3, 9×R=CH ₃
793.0486	Si ₅ C ₁₈ H ₃₇ O ₂₅ ⁻	793.0476 (-1.3) J, n=4, 10×R=CH ₃ , 1×R=H
807.0638	Si ₅ C ₁₉ H ₃₉ O ₂₅ ⁻	806.9725 (-0.8) J, n=4, 11×R=CH ₃
CA+	191.0202 C ₆ H ₇ O ₇ ⁻	191.0197 (-2.5)
Si(OMe) ₄		
		2×R=H
205.0355	C ₇ H ₉ O ₇ ⁻	205.0354 (-0.7) N, 1×R=CH ₃ , 1×R=H
406.9942	SiC ₁₂ H ₁₁ O ₁₄ ⁻	406.9924 (-4.5)
		
		3×R=H
421.0101	SiC ₁₃ H ₁₃ O ₁₄ ⁻	421.0101 (-5.0) O, 1×R=CH ₃ , 2×R=H
425.0031	SiC ₁₂ H ₁₃ O ₁₅ ⁻	425.0029 (-0.4)
		
		n=0, 5×R=H
439.0189	SiC ₁₃ H ₁₅ O ₁₅ ⁻	439.0186 (-0.7) P, n=0, 1×R=CH ₃ , 4×R=H
453.0343	SiC ₁₄ H ₁₇ O ₁₅ ⁻	453.0342 (-0.2) P, n=0, 2×R=CH ₃ , 3×R=H
467.0500	SiC ₁₅ H ₁₉ O ₁₅ ⁻	467.0499 (-0.4) P, n=0, 3×R=CH ₃ , 2×R=H
516.9958	Si ₂ C ₁₃ H ₁₇ O ₁₈ ⁻	516.9959 (+0.2) P, n=1, 1×R=CH ₃ , 6×R=H
531.0116	Si ₂ C ₁₄ H ₁₉ O ₁₈ ⁻	531.0115 (-0.1) P, n=1, 2×R=CH ₃ , 5×R=H
545.0270	Si ₂ C ₁₅ H ₂₁ O ₁₈ ⁻	545.0272 (+0.3) P, n=1, 3×R=CH ₃ , 4×R=H
559.0424	Si ₂ C ₁₆ H ₂₃ O ₁₈ ⁻	559.0428 (+0.8) P, n=1, 4×R=CH ₃ , 3×R=H
573.0586	Si ₂ C ₁₇ H ₂₅ O ₁₈ ⁻	573.0585 (-0.1) P, n=1, 5×R=CH ₃ , 2×R=H
623.0015	Si ₃ C ₁₅ H ₂₃ O ₂₁ ⁻	623.0045 (+4.8) P, n=2, 3×R=CH ₃ , 6×R=H
637.0183	Si ₃ C ₁₆ H ₂₅ O ₂₁ ⁻	637.0183 (+2.9) P, n=2, 4×R=CH ₃ , 5×R=H
651.0326	Si ₃ C ₁₇ H ₂₇ O ₂₁ ⁻	651.0358 (+4.9) P, n=2, 5×R=CH ₃ , 4×R=H
665.0492	Si ₃ C ₁₈ H ₂₉ O ₂₁ ⁻	665.0515 (+3.4) P, n=2, 6×R=CH ₃ , 3×R=H

Table S2. Assignment of ES-MS spectra shown in Fig. 6

FTIR analysis of 2HOA+ Si(OMe)₄ mixtures in d₄-methanol

The mixtures of acids with Si(OMe)₄ in CD₃OD as studied by NMR above were also studied by FTIR and their spectra compared with those recorded for the pure acid and pure ester (where available) at the same concentration in CD₃OD (Table S3), as had previously been done with monocarboxylic acids³¹.

Spectra were recorded on a Perkin-Elmer Spectrum One instrument using a solid sample holder attachment. Acid (0.375 mmol) was dissolved completely in CD₃OD (0.75 mL). Aliquots were withdrawn, spotted onto the sample holder, and spectra, corrected for the empty sample holder, were recorded. Si(OMe)₄ (0.750 mmol) was then added and the sample incubated at room temperature. Further spectra were recorded after varying intervals. Spectra were also recorded for CD₃OD and Si(OMe)₄ in CD₃OD controls.

The spectra recorded after 1 wk displayed signals previously assigned to CH₃O[D/H] produced by hydrolysis/condensation of Si(OMe)₄³¹. Mixtures of Si(OMe)₄ with OA, MA, TA and CA displayed C-O and C=O stretch absorbances closer to those of the esters than those of the starting acids, as expected.

	C-O stretch			C=O stretch			absorbance ~ 823 cm ⁻¹		
	acid	ester	acid + Si(OMe) ₄ , 1 wk	acid	ester	acid + Si(OMe) ₄ , 1 wk	acid	ester	acid + Si(OMe) ₄ , 1 wk
OA	1238	1219 ^b	1224 ^a		1708		823	823	816
		1334 ^b		1747	1748	1748			
	1398	1367 ^b	1361		1774	1771			
MA	1317	1288 ^c	1306	1727	1746	1742	824	824	804
	1385	1372 ^c	1386						
TA	1310	1282 ^d	1292	1732	1754	1753	823	824	807
	1373	1367 ^d	1371						
CA	1249	1207 ^e	1230 ^a	1726	1746	1742	823	825	810
	1383	1364 ^e	1368						

Table S3: Selected FTIR absorbances for the various acids, their esters, and their mixtures with Si(OMe)₄ after 1 wk, all recorded in CD₃OD. ^a Overlaps with bands due to Si(OMe)₄ and/or MeOH at ~ 1200 cm⁻¹. ^b dimethyloxalate ^c dimethyl L-malate ^d dimethyl L-tartrate ^e trimethyl citrate.

The absorbance in the 750-850 cm⁻¹ region of the spectra of the mixtures is again included in table S3. The only absorbance observed in this region with pure samples of the acids and esters was the band at ~823 cm⁻¹ attributed to CD₃OD. Ignatyev *et al.* suggest two Si-O stretches appear at 843 and 827 cm⁻¹ in Si(OCH₃)₄ but at 801 and 779 cm⁻¹ for Si(OCD₃)₄. For Si(OCH₃)₄+H₂O in CD₃OD this band appears initially at 832 cm⁻¹ and after 1 wk at 821 cm⁻¹ due to the replacement of SiOCH₃ with SiOCD₃. Interestingly with Si(OMe)₄+acetic acid and Si(OMe)₄+3-hydroxybutyric acid in CD₃OD this band moved further, to 798 cm⁻¹, as more SiOCD₃ was present after 1 week³¹. In the current work the band moves further for MA than for OA, TA and CA, corresponding with the ¹³C results which suggest more SiOCD₃ is present after 1 wk in the MA+ Si(OMe)₄ sample.

Samples of acid+ Si(OMe)₄ in CD₃OD that had been incubated for just 30 min were also subjected to FTIR in the hope that this might show evidence of different absorbances that might be attributed Si-acid complexes or other reaction intermediates. However, these spectra were essentially intermediate between the initial spectra for the acids alone and the spectra recorded for acids+ Si(OMe)₄ at 1 week, suggesting any absorbances due to transient siloxane-acid complexes were weak and/or obscured by the other absorbances.

¹³C, ¹H and ²⁹Si NMR and ESI-MS of TA/ Si(OEt)₄ mixtures

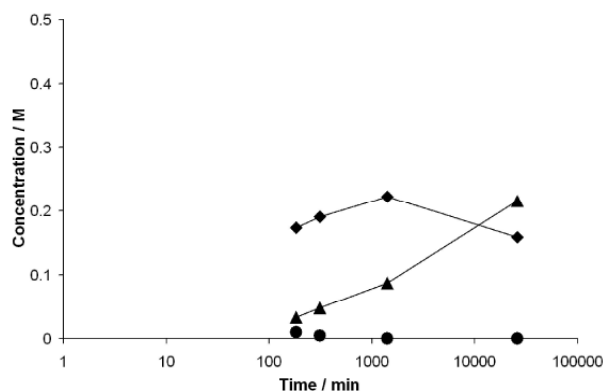


Figure S2: Concentrations of product monoester (diamonds), diester (triangles) and transient intermediate (circles) *versus* time for the mixture of TA (0.40M) with Si(OEt)₄ (0.79 M) in C₂D₅OD.

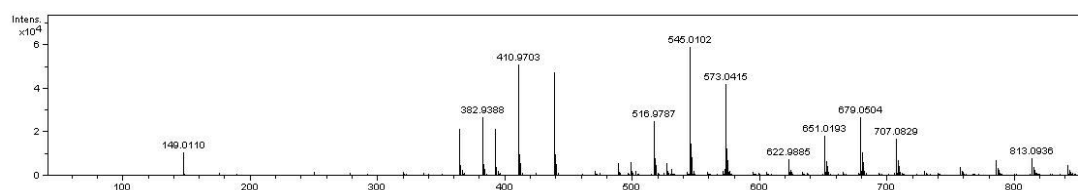


Figure S3 ES-MS spectra obtained in negative ion mode with direct infusion of samples. Si(OEt)₄ (0.79 M)+ TA (0.40 M) in EtOH, collected *c.* 2h after mixing.

TA+ Si(OEt) ₄	149.0110	C ₄ H ₅ O ₆ ⁻	149.0092 (-12.7)	G, R=H
	364.9278	Si ₂ C ₈ H ₅ O ₁₃ ⁻	364.9274 (-1.1)	K, R=H
	382.9389	Si ₂ C ₈ H ₇ O ₁₄ ⁻	382.9380 (-2.5)	L, n=0, 3×R=H
	392.9599	Si ₂ C ₁₀ H ₉ O ₁₃ ⁻	392.9587 (-3.0)	K, R=C ₂ H ₅
	410.9703	Si ₂ C ₁₀ H ₁₁ O ₁₄ ⁻	410.9693 (-2.5)	L, n=0, 1×R=C ₂ H ₅ , 2×R=H
	439.0017	Si ₂ C ₁₂ H ₁₅ O ₁₄ ⁻	439.0006 (-2.5)	L, n=0, 2×R=C ₂ H ₅ , 1×R=H
	488.9473	Si ₃ C ₁₀ H ₁₃ O ₁₇ ⁻	488.9466 (-1.5)	L, n=1, 1×R=C ₂ H ₅ , 4×R=H
	498.9678	Si ₃ C ₁₂ H ₁₅ O ₁₆ ⁻	498.9673 (-0.9)	M, 2×R=C ₂ H ₅ , 1×R=H
	516.9786	Si ₃ C ₁₂ H ₁₇ O ₁₇ ⁻	516.9779 (-1.4)	L, n=1, 2×R=C ₂ H ₅ , 3×R=H
	545.0101	Si ₃ C ₁₄ H ₂₁ O ₁₇ ⁻	545.0092 (-1.6)	L, n=1, 3×R=C ₂ H ₅ , 2×R=H
	573.0413	Si ₃ C ₁₆ H ₂₅ O ₁₇ ⁻	573.0405 (-1.3)	L, n=1, 4×R=C ₂ H ₅ , 1×R=H
	622.9880	Si ₄ C ₁₄ H ₂₃ O ₂₀ ⁻	622.9865 (-2.4)	L, n=2, 3×R=C ₂ H ₅ , 4×R=H
	651.0191	Si ₄ C ₁₆ H ₂₇ O ₂₀ ⁻	651.0178 (-2.0)	L, n=2, 4×R=C ₂ H ₅ , 3×R=H
	679.0507	Si ₄ C ₁₈ H ₃₁ O ₂₀ ⁻	679.0491 (-2.3)	L, n=2, 5×R=C ₂ H ₅ , 2×R=H
	707.0827	Si ₄ C ₂₀ H ₃₅ O ₂₀ ⁻	707.0804 (-3.3)	L, n=2, 6×R=C ₂ H ₅ , 1×R=H

Table S4 Assignment of ES-MS spectrum shown in figure S3.