397. *Reactions of Titanium Tetrachloride with Ethoxychlorosilanes.*

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In reactions involving ethoxychlorosilanes $SiCl_x(OEt)_{4-x}$ (x = 0—3) and titanium tetrachloride at 0°, exchange of chloride and ethoxide groups became less extensive as x increased, and $TiCl_3{\cdot}OEt$ was the predominant titanium compound formed. Mixtures of ethoxychlorosilanes were analysed by treatment with butan-1-ol, followed by gas chromatography of the resulting butoxyethoxysilanes. The differences in reactivity of titanium and silicon compounds are discussed.

BRADLEY, HANCOCK, and WARDLAW [1] showed that titanium tetra-alkoxides reacted with an excess of titanium tetrachloride to form titanium trichloride monoalkoxides.

$$3TiCl_4 + Ti(OR)_4 \longrightarrow 4TiCl_3{\cdot}OR \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

We have studied exchange reactions involving titanium tetrachloride and the ethoxychlorosilanes $SiCl_x(OEt)_{4-x}$ ($x = 0$—3). A method was developed for the analysis of a mixture of ethoxychlorosilanes in the presence of titanium tetrachloride. The titanium tetrachloride was precipitated quantitatively as the diethyl ether solvate from pentane solution at —78° and the mixture of ethoxychlorosilanes was converted into the corresponding n-butoxyethoxysilanes by butan-1-ol–pyridine at —78°. The mixture of butoxyethoxysilanes was quantitatively analysed by gas chromatography. During this work it was proved that reaction of ethoxychlorosilanes with butan-1-ol alone was accompanied by alkoxyl exchange owing to the presence of hydrogen chloride. Use of the butanol–pyridine reagent led to replacement of chlorine by butoxy-groups without alkoxyl exchange.

When titanium tetrachloride and ethoxytrichlorosilane were mixed in equimolecular proportions a yellow colour, indicative of the presence of titanium trichloride monoethoxide, developed immediately. However, the amount of this product was insufficient to be precipitated and analysis proved that very little silicon tetrachloride was formed. It appears that an equilibrium (2) is rapidly established, favouring the left-hand side.

$$TiCl_4 + SiCl_3{\cdot}OEt \rightleftharpoons TiCl_3{\cdot}OEt + SiCl_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Equimolecular proportions of titanium tetrachloride and diethoxydichlorosilane reacted slowly at 0°, depositing crystalline titanium trichloride monoethoxide. After 24 hours the reaction (3) was about half complete; it was practically complete after 7 days.

$$TiCl_4 + SiCl_2(OEt)_2 \xrightarrow{\text{Slow}} TiCl_3{\cdot}OEt + SiCl_3{\cdot}OEt \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

Titanium tetrachloride and triethoxychlorosilane in equimolecular proportions reacted slowly at 0° with the formation of titanium trichloride monoethoxide. The reaction (4) was more than half complete after 4 hours but several days were required for full completion. A small proportion of ethoxytrichlorosilane was formed in addition to the main product, diethoxydichlorosilane.

$$TiCl_4 + SiCl(OEt)_3 \longrightarrow TiCl_3{\cdot}OEt + SiCl_2(OEt)_2 \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

Addition of titanium tetrachloride to tetraethoxysilane in equimolecular proportion at 0° gave, after a few hours, a crystalline deposit which was predominantly the titanium monoethoxide mixed with some diethoxide. The mother-liquor also contained these compounds but with a higher proportion of the latter; the silicon was predominantly in the form of triethoxide with some diethoxide. The mother-liquor deposited no crystals during the following 3 days, but its viscosity increased considerably and distillation gave

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[1] Bradley, Hancock, and Wardlaw, *J.*, 1952, 2773.

three volatile fractions. The most volatile was a small amount of ethyl chloride saturated with hydrogen chloride. The next most volatile was mainly titanium trichloride ethoxide, containing some diethoxide; and the least volatile was mainly this diethoxide with some triethoxide. All the silicon remained in the non-volatile solid residue and it was clear that a high polymer had been formed. When the original mother-liquor was kept at 0° for a further 7 days it slowly deposited a crystalline mixture which was mainly titanium diethoxide with some monoethoxide. The mother-liquor became increasingly viscous and after a further 3 days had set to a clear gel. During the experiment about 90% of the titanium was recovered as mono- and di-ethoxide, in almost equimolecular proportions. It appears that reaction (5) proceeds reasonably quickly:

$$\mathrm{TiCl_4 + Si(OEt)_4 \longrightarrow TiCl_3{\cdot}OEt + SiCl(OEt)_3} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

However, it is clear that this reaction is accompanied by the slower reactions (4) and, probably, (6):

$$\mathrm{TiCl_3{\cdot}OEt + SiCl(OEt)_3 \longrightarrow TiCl_2(OEt)_2 + SiCl_2(OEt)_2} \quad . \; . \; . \; . \; . \; . \; . \quad (6)$$

In addition it appears that other reactions, involving the formation of ethyl chloride, hydrogen chloride, and ethoxychlorosiloxane polymers, occur in the later stages.

When the molecular ratio of titanium tetrachloride to tetraethoxysilane was increased to 2 : 1 the formation of titanium trichloride ethoxide at 0° was rapid and practically quantitative. Diethoxydichlorosilane was also produced in accordance with reaction (7):

$$\mathrm{2TiCl_4 + Si(OEt)_4 \longrightarrow 2TiCl_3{\cdot}OEt + SiCl_2(OEt)_2} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

Finally, the ratio of titanium tetrachloride to tetraethoxysilane was raised to 4 : 1; a vigorous reaction ensued at 0° with deposition of the titanium monoethoxide. Evidently, the initial reaction follows the course (7). However, the excess of titanium tetrachloride also reacted slowly with the silicon dichloride diethoxide, as in (3), and to a much smaller extent with the monoethoxide, as in (2).

In all these reactions chlorine attached to titanium was replaced by ethoxy-groups, and ethoxy-groups attached to silicon were replaced by chlorine. We have also found that titanium tetraethoxide reacts with silicon tetrachloride. For example, in a reaction between 1 mol. of the former and 2 mol. of the latter at 0° about two-thirds of the titanium was rapidly precipitated as trichloride monoethoxide. If a stepwise reaction had taken place a mixture of diethoxydichloro- and monoethoxytrichloro-silane would have been expected, as in expression (8).

$$\mathrm{Ti(OEt)_4 + 2SiCl_4 \longrightarrow TiCl_3{\cdot}OEt + SiCl_3{\cdot}OEt + SiCl_2(OEt)_2} \quad . \; . \; . \; . \; . \; . \quad (8)$$

However, it was shown by gas chromatography that the silicon compounds present were silicon tetrachloride and triethoxymonochlorosilane in practically equimolecular proportion:

$$\mathrm{Ti(OEt)_4 + 2SiCl_4 \longrightarrow TiCl_3{\cdot}OEt + SiCl(OEt)_3 + SiCl_4} \quad . \; . \; . \; . \; . \; . \; . \quad (9)$$

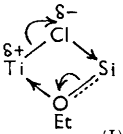
This suggests that ethoxytrichloro- and diethoxydichloro-silane react much more readily with the various titanium alkoxides than does silicon tetrachloride.

Comparison of reactions (5) and (9) suggests that in the competition between silicon and titanium for ethoxy-groups and chlorine the most stable species of titanium is the trichloride ethoxide but for silicon it is the chloride triethoxide. This is roughly in line with the reactivities of titanium and silicon tetrachloride with ethanol, which give titanium-dichloride diethoxide and tetraethoxysilane, respectively.

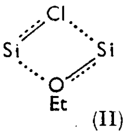
It is noteworthy that other experiments showed that tetraethoxysilane did not react with silicon tetrachloride alone or in the presence of a small amount of titanium tetrachloride. Nor did a mixture, $\mathrm{SiCl(OEt)_3}$ (1 mol.), $\mathrm{SiCl_2(OEt)_2}$ (1 mol.), and $\mathrm{SiCl_3{\cdot}OEt}$ (1 mol.), exchange groups in the presence of titanium trichloride ethoxide. Evidently the reactive species in the reactions depicted in (3—5, 7, and 9) are the titanium compounds.

The identity of the silicon species produced is a reliable guide to the course of the reaction since we have shown that no rearrangement of the ethoxychlorosilanes occurs.

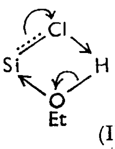
The following facts thus require interpretation: (*a*) Titanium tetrachloride reacts readily with ethanol, titanium tetraethoxide, and tetraethoxysilane, less readily with triethoxychlorosilane, and only slowly with diethoxydichlorosilane. (*b*) Titanium tetraethoxide reacts readily with alcohols and with silicon tetrachloride. (*c*) Silicon tetrachloride reacts readily with ethanol and with titanium tetraethoxide but not with tetraethoxysilane. (*d*) Tetraethoxysilane reacts readily with titanium tetrachloride but not with silicon tetrachloride or alcohols (unless catalysed). Although there is no evidence available concerning the mechanism of these reactions it seems reasonable that titanium tetrachloride should be highly reactive to nucleophilic atoms because titanium has vacant 3*d*-orbitals for covalency expansion and has an appreciable induced positive charge due to polarity in the $\overset{\delta+}{\text{Ti}}$–$\overset{\delta-}{\text{Cl}}$ bonds. Hence, the titanium will co-ordinate with oxygen of the ethoxy-group in ethanol or EtO–Ti or EtO–Si groups and thus raise the electron density on chlorine (of the Ti–Cl bond), which in turn will become more reactive as a nucleophilic atom. If the polarity in the Si–Cl bonds in silicon tetrachloride is less than the polarity in Ti–Cl bonds owing to the difference in electronegativity of silicon and titanium, and perhaps to more *dπ–pπ* bonding in $^{-}\text{Si}{\cdot}\text{Cl}^{+}$ than in $^{-}\text{Ti}{\cdot}\text{Cl}^{+}$, then some of the above reactions are intelligible. Assuming for simplicity (but it is not essential for the argument) that



(I)



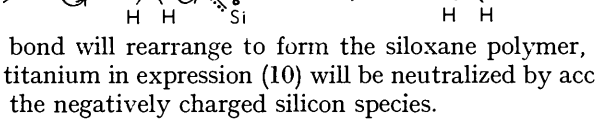
(II)



(III)

four-centred systems are involved, as in (I)—(III), we suggest that the oxygen attached to silicon in (I) is sufficiently nucleophilic to react with the titanium. This makes the chlorine more nucleophilic and withdraws the *pπ–dπ* electron drift from oxygen of the ethoxy-group. The chlorine may then react with the more electrophilic silicon atom, and the ensuing electronic rearrangements causes radical-interchange. In the cases of tetrachloro- and tetraethoxy-silane (II), the oxygen does not react with the silicon of silicon tetrachloride, and reaction cannot occur readily. However, the oxygen in ethanol is sufficiently reactive to cause the electronic rearrangement (III). Similarly the oxygen in Ti–OEt is more reactive than in Si–OEt and that is why titanium but not silicon tetraethoxide reacts readily with silicon tetrachloride. The low reactivity of the oxygen in tetraethoxysilane may well be due to *pπ–dπ* electron drift from oxygen to silicon ($^{-}\text{Si}{\cdot}\text{OEt}^{+}$).

Another interesting feature of the results was the formation of polymeric silicon compounds in the later stages of the reaction involving titanium tetrachloride (1 mol.) and tetraethoxysilane (1 mol.). The first stage (5) of the reaction is fairly rapid, but the second stage (6) must be very slow because here the reactants are the most stable species of these systems. Moreover, the alternative second stage (4) is also slow and it seems that yet another reaction must occur, probably involving titanium trichloride ethoxide and ethoxychloro- or diethoxydichloro-silane. In this case it is suggested that the chlorine in the titanium compound attacks, not the silicon, but the α-carbon of a $\text{Si–OC}_2\text{H}_5$ group. This is feasible if *pπ–dπ* bonding in $^{-}\text{Si}{\cdot}\text{OEt}^{+}$ makes the silicon less prone to nucleophilic attack but increases the electrophilic nature of the α-carbon.



$$\overset{\delta+}{\text{Ti}}-\overset{\delta-}{\text{Cl}}\rightarrow\underset{\text{H H}}{\overset{\text{CH}_3}{\text{C}}}-\overset{\delta+}{\text{O}}\cdots\overset{\delta-}{\text{Si}}\longrightarrow\overset{+}{\text{Ti}}\cdots\text{Cl}-\underset{\text{H H}}{\overset{\text{CH}_3}{\text{C}}}\cdots\text{O}=\overset{-}{\text{Si}}\qquad\cdots\cdots(10)$$

The Si=O double bond will rearrange to form the siloxane polymer, and the positive charge shown on the titanium in expression (10) will be neutralized by accepting a chloride or ethoxide ion from the negatively charged silicon species.

EXPERIMENTAL

Reactions were carried out in dried, all-glass apparatus under dry nitrogen.

Silicon Tetrachloride.—Commercially available material was distilled at atmospheric pressure immediately before use.

Titanium Tetrachloride.—Commercially available material was refluxed over copper turnings for several hours and then fractionally distilled, the first fraction, which contained silicon tetrachloride, being rejected.

Alcohols.—Ethanol, propan-2-ol, and butan-1-ol were dried azeotropically with benzene and then stored in contact with a " molecular sieve " drying agent.

Other Reagents.—Pentane, light petroleum, and pyridine were dried over sodium wire and distilled as required.

Analytical Methods.—*Silicon.* The sample (~0·1 g.) was weighed into a platinum crucible at *ca.* −78° and containing concentrated sulphuric acid (1·5 g.), absolute alcohol (0·7 g.), and water (0·1 g.). The mixture was allowed to attain room temperature, then cautiously evaporated under an infrared lamp, and the residue was ignited at 1000° in a furnace for 1 hr. and weighed as silica. If titanium was also present the ignited mixed oxides were treated with hydrogen fluoride to eliminate the silica, and the residual titanium dioxide was weighed.

Titanium and chlorine. Samples were treated with dilute nitric acid and the titanium precipitated with aqueous ammonia and determined as dioxide. The chloride was determined gravimetrically in the filtrate after removal of the titanium.

Alkoxyl groups. Ethoxyl and isopropoxyl groups separately were determined by the method of Bradley, *et al.*[2] When ethoxide and isopropoxide were present together, a modification of Adams and Nicholls's method [3] was used. The sample was oxidized with chromic acid, and the acetic acid and acetone removed by steam-distillation. The acetic acid was determined by titration with standard alkali (phenolphthalein), and the acetone determined gravimetrically as the 2,4-dinitrophenylhydrazone.[4]

Ethoxychlorosilanes. A sample (*ca.* 0·5 g.) of mixed ethoxychlorosilanes in pentane (1·0 g.) was added to an excess of an equimolar mixture of butan-1-ol and pyridine at 0°. The pyridinium chloride was centrifuged off, and the solution of butoxyethoxysilanes was concentrated by evaporation *in vacuo* and then analysed by gas chromatography. Griffin and George's mark II apparatus was used with silicone elastomer E301 on Celite 545. With hydrogen as carrier gas at a flow rate of 2 l./hr. complete separation of all five species $Si(OEt)_x(OBu^n)_{4-x}$ was achieved at 170—180°. After calibration of the apparatus with known weights of the different species, analysis of mixtures was shown to be quantitative. The reaction was shown to be quantitative by preparing and analysing an equimolecular mixture of the three silicon chloride ethoxides [Found: $Si(OEt)_3{\cdot}OBu$, 33·0; $Si(OEt)_2(OBu)_2$, 32·5; $Si(OBu)_3{\cdot}OEt$, 33·5 mol.%]. It is essential to add the silicon compounds to the butanol–pyridine mixture because, although butanol alone will react, the hydrogen chloride formed causes exchange of ethoxide and butoxide groups. For example, practically pure ethoxytrichlorosilane was treated with the butanol–pyridine reagent and gave: $Si(OBu)_3{\cdot}OEt$, 99·2; $Si(OEt)_2(OBu)_2$, 0·8 mol. %. Addition of the same ethoxychlorosilane, and then pyridine, to butanol, at 0°, and centrifugation gave: $Si(OBu)_4$, 53·0; $Si(OBu)_3{\cdot}OEt$, 40·7; $Si(OEt)_2(OBu)_2$, 6·3 mol. %. Another mixture of ethoxychlorosilanes gave, with the butanol–pyridine reagent: $Si(OBu)_3{\cdot}OEt$, 66·3; $Si(OEt)_2(OBu)_2$, 33·7 mol. %; with butanol followed by pyridine the following were obtained: $Si(OBu)_4$, 13·6; $Si(OBu)_3{\cdot}OEt$, 44·1; $Si(OEt)_2(OBu)_2$, 33·2; $Si(OEt)_3{\cdot}OBu$, 9·1 mole %; $Si(OEt)_4$, trace.

To analyse a mixture of ethoxychlorosilanes in the presence of titanium tetrachloride it was necessary to add the mixture to diethyl ether in pentane at −78° to precipitate the titanium tetrachloride–ether complex. Demetrios and Ladikos [5] reported that a diether solvate, $TiCl_4,2Et_2O$, is formed. The ethoxychlorosilanes were then treated with the butanol–pyridine reagent in pentane at −78°, and the mixture of butoxyethoxysilanes was analysed by gas chromatography. Although Kipping and Murray [6] reported that diethyl ether reacted with

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[2] Bradley, Halim, and Wardlaw, *J.*, 1950, 3450.

[3] Adams and Nicholls, *Analyst*, 1929, **54**, 2.

[4] Addles and Jackson, *Ind. Eng. Chem.*, *Analyt.*, 1934, **6**, 456.

[5] Demetrios and Ladikos, *Praktika Akad. Athen.*, 1930, **5**, 449.

[6] Kipping and Murray, *J.*, 1927, 2734.

silicon tetrachloride at room temperature, forming ethoxytrichlorosilane and ethyl chloride, we were unable to confirm this: after silicon tetrachloride has been refluxed in ether for 4 hr. a sample was treated with the butanol–pyridine reagent in pentane at −78°; gas chromatography revealed that only tetrabutoxysilane was present, showing that no ethoxytrichlorosilane had been formed.

Preparation of Tetraethoxysilane.—Ethanol (103·6 g., 2·25 moles) was added slowly, with stirring, to silicon tetrachloride (84·9 g., 0·5 mole) and light petroleum (40·0 g.; b. p. 60—80°) at 0°. Nitrogen was passed through the apparatus to remove hydrogen chloride, and the solvent was evaporated *in vacuo*. Tetraethoxysilane (82·0 g., b. p. 35°/0·5 mm., was distilled under reduced pressure [Found: Si, 13·4; EtO, 86·4. Calc. for $Si(OEt)_4$; Si, 13·4; EtO, 86·6%].

Preparation of Ethoxychlorosilanes.—The three compounds were prepared by the reaction involving ethanol (1·1 moles) and silicon tetrachloride (1·0 mole) essentially by the method of Peppard, Brown, and Johnson.[7] The products were separated and purified by fractional distillation at 32·0 mm., affording $SiCl_3$·OEt (76·0 g.), b. p. 28·0—28·5°/32 mm. (Found: Si, 15·6; Cl, 58·9%), $SiCl_2(OEt)_2$ (32·5 g.), b. p. 50·5—51°/32 mm. (Found: Si, 14·9; Cl, 37·6%), and $SiCl(OEt)_3$ (7·0 g.), b. p. 67·5/32 mm. (Found: Si, 14·2; Cl, 17·8%).

Preparation of Ethoxyisopropoxysilanes.—The appropriate ethoxychlorosilane was added dropwise to propan-2-ol in light petroleum (b. p. 60—80°); then followed aspiration with nitrogen, evaporation of solvent, and distillation of the ethoxyisopropoxysilane under reduced pressure. Details are reported in Table 1.

TABLE 1.

Reactant		Sol-vent	Pr^iOH	Product		B. p./	Found (%)			Calc. (%)		
Nature	g.	(g.)	(g.)	Nature	(g.)	mm.	Si	EtO	Pr^iO	Si	EtO	Pr^iO
$SiCl_3$·OEt	11·0	13·0	12·2	$Si(OPr^i)_3$·OEt	12·7	42°/1·5	11·1	17·1	71·5	11·2	18·0	70·8
$SiCl_2(OEt)_2$	24·2	20·0	17·0	$Si(OPr^i)_2(OEt)_2$	24·2	41°/2·0	11·9	37·0	52·1	11·9	38·1	50·0
$SiCl(OEt)_3$	5·9	5·0	2·0	$Si(OEt)_3$·OPr^i	5·2	39°/1·5	12·6	57·3	27·3	12·6	60·8	26·6

Addition of Tetraethoxysilane (1 *mol.*) *to Silicon Tetrachloride* (1 *mol.*).—Tetraethoxysilane (26·4 g.) was added to silicon tetrachloride (22·5 g.) at 0° but there was no evidence of reaction. The mixture was allowed to attain room temperature, kept for 7 days, and then separated into two fractions by evaporation at ∼0·5 mm. at room temperature. The more volatile fraction (21·0 g.) condensed at −78° and proved to be silicon tetrachloride (Found: Si, 16·3; Cl, 83·3. Calc. for $SiCl_4$: Si, 16·5; Cl, 83·5%). The less volatile fraction (27·5 g.) (Found: Si, 13·6; Cl, 3·9; EtO, 82·7%; EtO : Si, 3·81 : 1) was separated by distillation at 0·5 mm. into silicon. tetrachloride (1·2 g.) (Found: Si, 16·4; Cl, 83·4%), tetraethoxysilane (25·1 g.), b. p. 37°/0·5 mm [Found: Si, 13·4, Cl, 0·3; EtO, 86·5. Calc. for $Si(OEt)_4$; Si, 13·5; EtO, 86·5%], and a small residue (0·9 g.).

Addition of Tetraethoxysilane (1 *mol.*) *to Silicon Tetrachloride* (1 *mol.*) *in the Presence of Titanium Tetrachloride* (*Trace*).—Tetraethoxysilane (14·06 g.) was added to a mixture of silicon tetrachloride (11·9 g.) and titanium tetrachloride (0·2 g.) at 0°, but no reaction occurred. After the mixture had been kept at room temperature for 4 days it was fractionated as in the foregoing experiment into the two volatile components and a yellow solid residue (1·3 g.). The more volatile fraction (10·4 g.) was silicon tetrachloride (Found: Si, 16·4; Cl, 83·3%), and the less volatile fraction (12·8 g.) was tetraethoxysilane (Found: Si, 13·5; Cl, 0·3; EtO, 86·2%).

Addition of Titanium Trichloride Ethoxides (*Trace*) *to Mixtures of Ethoxychlorosilanes.*—Resublimed titanium trichloride ethoxide (0·1 g.) was added to an equimolecular mixture (10 g.) of triethoxychloro-, diethoxydichloro-, and ethoxydichloro-silane at room temperature. After some hours a sample (0·4 g.) was added to butanol (0·3 g.) and pyridine (0·3 g.) in pentane (1·0 g.) at −78°. After removal of the pyridinium chloride the pentane solution of butoxyethoxysilanes was concentrated and analysed by gas chromatography [Found: $Si(OBu^n)_3$·OEt, 32·0 (33·0); $Si(OEt)_2(OBu^n)_2$, 33·9 (32·5); $Si(OEt)_3$·OBu^n, 34·0 (33·5); $Si(OBu^n)_4$, 0·12 mole %]. The figures in parentheses are the analyses of the products obtained from the original mixture of ethoxychlorosilanes.

Reaction of Tetraethoxysilane (1 *mol.*) *with Titanium Tetrachloride* (1 *mol.*).—Titanium tetrachloride (33·3 g.) at 0° was decanted on to tetraethoxysilane (36·4 g.) at 0°. Yellow

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[7] Peppard, Brown, and Johnson, *J. Amer. Chem. Soc.*, 1946, **68**, 70.

crystals (A) (7·1 g.) were soon deposited leaving mother-liquor (B). After crystallization from carbon tetrachloride, material (A) was analysed (Found: Ti, 24·0, Cl, 51·6; EtO, 24·3%; EtO : Ti, 1·07 : 1; Cl : Ti, 2·91 : 1). The solid (A) was evidently titanium trichloride ethoxide containing a small proportion of diethoxide. A portion of the mother-liquor (B) (12·0 g.) was evaporated at room temperature and 0·5 mm., leaving a yellow solid (C) (6·1 g.) and giving a yellow liquid (D) (5·4 g.) condensate at *ca.* −78°. Solid (C) (Found: Ti, 23·6; Cl, 46·9; EtO, 29·6%; EtO : Ti, 1·33 : 1; Cl : Ti, 2·67 : 1), was a mixture similar to (A) but containing more of the diethoxide. Liquid (D) was treated with propan-2-ol, and the mixed ethoxyisopropoxysilanes were completely recovered by distillation (b. p. 36°/0·5 mm.) (Found: Si, 12·4; EtO, 55·1; $\mathrm{Pr^iO}$, 33·0%; EtO : Si, 2·75 : 1; $\mathrm{Pr^iO}$: Si, 1·26 : 1). Thus material (D) was probably a mixture of mainly triethoxyisoproxy- with some diethoxydi-isopropoxy-silane. The remainder of the liquid (B) was kept at 0° for 3 days. No solid was deposited but the viscosity increased. A portion (25·44 g.) was then fractionally distilled under reduced pressure, leaving a solid residue (E) (8·0 g.), a viscous yellow fraction (F) (6·0 g.), b. p. 97°/1·0 mm. (Found: Ti, 22·3; Cl, 45·5; EtO, 30·7%; EtO : Ti, 1·38 : 1; Cl : Ti, 2·62 : 1), which rapidly solidified, another viscous yellow fraction (G) (7·1 g.), b. p. 117°/0·4 mm. (Found: Ti, 22·8; Cl, 31·2; EtO, 46·5%; EtO : Ti, 2·15 : 1; Cl : Ti, 1·84 : 1), which slowly solidified, and some liquid (2·0 g.) condensing at −78° which appeared to be mainly ethyl chloride and hydrogen chloride. The residue (E) contained silicon and titanium and appeared to be highly polymeric. Material (F) was a mixture of titanium trichloride ethoxide and diethoxide containing more of the latter than was in (C). Material G appeared to be predominantly the diethoxide with some triethoxide. The original mixture (B), when kept at 0° for a further 7 days, increased in viscosity and slowly deposited crystals (10·1 g.) which were separated, washed with carbon tetrachloride, dried, and analysed (Found: Ti, 23·1; Cl, 39·6; EtO, 36·9%; EtO : Ti, 1·70 : 1; Cl : Ti, 2·31 : 1), and were evidently intermediate between materials (F) and (G); the mother-liquor therefrom, kept at 0° for 3 days, set to a clear gel.

Reaction of Tetraethoxysilane with Titanium Tetrachloride.—(*a*) Tetraethoxysilane (36·0 g., 1 mol.) was added at 0° to titanium tetrachloride (65·2 g., 2 mol.) also at 0°; yellow crystals were immediately deposited. The solid (63·0 g.) was separated by decantation and dried by pumping off volatile compounds, which were condensed at −78° and recombined with the mother-liquor. A portion of the solid was crystallized from carbon tetrachloride and proved to be titanium trichloride ethoxide (Found: Ti, 23·9; Cl, 53·3; EtO, 22·6%. Calc. for $\mathrm{TiCl_3{\cdot}OEt}$: Ti, 24·0; Cl, 53·4; EtO, 22·5%). A second crop of this compound (4·0 g.; Found: Ti, 24·1; Cl, 53·2%) was deposited from the mother-liquor after a few hours. A portion of the second mother-liquor was evaporated at room temperature at 1·0 mm. and the condensate (−78°) was shown by analysis to be mainly diethoxydichlorosilane contaminated with some titanium trichloride ethoxide (Found: Si, 14·3; Ti, 0·5; Cl, 37·4; EtO, 46·4%; EtO : Si, 2·02 : 1; Cl : Si, 2·06 : 1; Ti : Si, 0·02 : 1).

(*b*) Tetraethoxysilane (7·95 g., 1 mol.) was added at 0° to titanium tetrachloride (28·06 g., 4 mol.) at 0°. A vigorous reaction occurred with immediate precipitation of titanium trichloride ethoxide (15·9 g.) (Found: Ti, 24·1; Cl, 53·4; EtO, 22·5%). After 24 hr. a second crop (3·4 g.) (Found: Ti, 24·3; Cl, 53·5; EtO, 22·6%) was deposited, leaving a pale yellow mother-liquor (16·6 g.). Attempts to isolate the silicon constituent of the mother-liquor by evaporation were unsuccessful because of the volatile titanium compounds ($\mathrm{TiCl_4}$, $\mathrm{TiCl_3{\cdot}OEt}$) present. Analysis of the mother-liquor (Found: Ti, 15·2; Si, 6·1; Cl, 64·0; EtO, 14·3%; EtO : Ti, 1·00 : 1; Cl : Ti, 5·68 : 1; Si : Ti, 1·46 : 1) suggested that it had a composition near ($\mathrm{2TiCl_4 + TiCl_3{\cdot}OEt + 2SiCl_3{\cdot}OEt}$) or [$\mathrm{3TiCl_4 + SiCl_3{\cdot}OEt + SiCl_2(OEt)_2}$].

In another experiment tetraethoxysilane (15·48 g.) and titanium tetrachloride (55·88 g.) were allowed to react at 0° and immediately deposited titanium trichloride ethoxide (29·4 g.) (Found: Ti, 24·5; Cl, 53·3; EtO, 22·3%), leaving a pale yellow mother-liquor (40·5 g.). A sample (1·0 g.) of the mother-liquor was added in pentane (0·5 g.) to diethyl ether (0·4 g.) in pentane (1·0 g.) at −78°. The titanium tetrachloride ether solvate thus precipitated was centrifuged off and the resulting solution of ethoxychlorosilanes was added to butanol (0·50 g.) and pyridine (0·59 g.) in pentane (0·50 g.) at −78°. After centrifugation of the pyridinium chloride the solution of butoxyethoxysilanes was concentrated and analysed by gas chromatography. The composition of the ethoxychlorosilanes was thus deduced. The results are shown in Table 2. More titanium trichloride ethoxide (9·8 g.) was deposited from the mother-liquor and was collected after 7 and again after 14 days; the products were also analysed (see Table 2).

TABLE 2.

Composition (moles %) of mother-liquor.

	Initially	After 7 days	After 14 days
$SiCl(OEt)_3$	3·6	0·6	—
$SiCl_2(OEt)_2$	80·0	22·7	7·8
$SiCl_3\cdot OEt$	16·4	75·0	89·9
$SiCl_4$	Trace	1·7	2·3

Reaction of Titanium Tetrachloride with Ethoxychlorosilanes.—(*a*) Addition of triethoxychlorosilane (28·07 g.) to titanium tetrachloride (24·12 g.) at 0° gave a deep amber liquid which slowly deposited titanium trichloride ethoxide (20·1 g.) (Found: Ti, 24·0; Cl, 53·1; EtO, 22·5%) during 3 days. After removal of a second crop (3·5 g.) of this a portion of the mother-liquor was treated with propan-2-ol. Analysis of the product, b. p. 55°/4·0 mm. [Found: Si, 11·9; EtO, 38·9; $Pr^{i}O$, 48·1. Calc. for $Si(OEt)_2(OPr^{i})_2$: Si, 11·9; EtO, 38·1; $Pr^{i}O$, 50·0%], suggested that the mother-liquor was diethoxydichlorosilane.

In another experiment involving the addition of the silicon compound (15·3 g.) to titanium tetrachloride (14·5 g.) at 0°, titanium trichloride ethoxide was slowly deposited. After 4 hr. this (8·3 g.) was filtered off and a sample (1·0 g.) of the mother-liquor (20·7 g.) was treated with ether in pentane at −78° to precipitate the residual titanium tetrachloride. After removal of the titanium tetrachloride solvate by centrifugation, the mother-liquor was treated with butanol–pyridine in pentane at −78°. The product was shown by gas chromatography to contain: $Si(OEt)_3\cdot OBu^{n}$, 31·9; $Si(OEt)_2(OBu^{n})_2$, 66·0; and $Si(OBu^{n})_3\cdot OEt$, 2·1 mole %.

(*b*) Ethoxydichlorosilane (38·0 g.) and titanium tetrachloride (39·5 g.) were mixed at 0° to form a deep amber solution which slowly deposited titanium trichloride ethoxide. After 4 days this (33·3 g.) (Found: Ti, 23·4; Cl, 52·8%) was filtered off. The mother-liquor (43·5 g.) deposited more of it (5·4 g.) during a further 3 days, but cooling to −78° then gave only a small deposit of yellow solid (2·0 g.). A portion (9·0 g.) of the mother-liquor was distilled at atmospheric pressure and gave a colourless distillate (7·5 g.) which appeared to be trichloroethoxysilane containing a small amount of titanium tetrachloride or the trichloride ethoxide [Found: Si, 15·5; Ti, 0·4; Cl, 58·5; EtO, 25·2. Calc. for $SiCl_2(OEt)_2$: Si, 15·6; Cl, 58·9; EtO, 25·5%].

In another experiment diethoxydichlorosilane (13·7 g.) and titanium tetrachloride (13·0 g.) were mixed and kept at 0°. After 24 hr. titanium trichloride ethoxide (5·5 g.) (Found: Ti, 24·1; Cl, 53·5%) was filtered off and a small sample of the mother-liquor was treated first with ether at −78° and then with butanol–pyridine reagent at −78°; the resulting butoxyethoxysilanes were analysed by gas chromatography [Found: $Si(OEt)_2(OBu^{n})_2$, 40·2; $Si(OBu^{n})_3\cdot OEt$, 59·8 mole %].

(*c*) When equimolecular proportions of ethoxytrichlorosilane and titanium tetrachloride were mixed at −78° a yellow colour developed immediately but nothing crystallized even in 7 days. A portion (1·0 g.) of the solution was then treated with ether (0·4 g.) in pentane (0·5 g.) at −78° and centrifuged. The mother-liquor was treated with butanol (0·65 g.) and pyridine (0·65 g.) in pentane (0·5 g.) at −78°. After removal of the pyridinium chloride the solution was analysed by gas chromatography [Found: $Si(OBu^{n})_3\cdot OEt$, 98·6; $Si(OBu^{n})_4$, 1·4%].

Reaction of Titanium Tetraethoxide (1 *mol.*) *and Silicon Tetrachloride* (2 *mol.*).—Titanium tetraethoxide (10·1 g.) and silicon tetrachloride (15·2 g.), when mixed at 0°, deposited titanium trichloride ethoxide (5·9 g.) (Found: Ti, 24·1; Cl, 53·3; EtO, 22·6%). A portion of the mother-liquor was treated successively with ether and butanol–pyridine at −78° and the butoxyethoxysilanes formed were analysed by gas chromatography [Found: $Si(OBu^{n})_4$, 60·5; $Si(OEt)_3\cdot OBu^{n}$, 39·5%].

Addition of Titanium Trichloride Ethoxide (1 *mol.*) *to Silicon Tetrachloride* (3 *mol.*).—Titanium trichloride ethoxide (9·1 g.) was dissolved in silicon tetrachloride (25·2 g.) and refluxed for 3 hr. On cooling, the former ingredient (7·0 g.) crystallized and the mother-liquor was shown as usual to contain only silicon tetrachloride.

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