

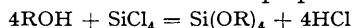
555. *Studies in the Formation Mechanisms of Alkyl Orthosilicates.*

By DUDLEY RIDGE and (MISS) MARGARET TODD.

A mechanistic theory of formation and reaction is presented in view of the results obtained during the preparation of alkyl orthosilicates and the investigation of their properties. Alcohols containing groups of strongly  $+I$  or  $-I$  inductive effect react most readily with silicon tetrachloride, but the highest yields of orthosilicate are obtained when *n*-propyl or *n*- or *iso*-butyl alcohol is used. Alcohols with substituent groups of  $-I$  inductive effect react most easily with ethyl orthosilicate, to yield the appropriate silicon ester. Orthosilicates containing  $-I$  inductive groups are unstable to heat and fairly stable to moisture, whilst the converse is true for silicon esters containing substituents of  $+I$  effect.

MUCH of the early work on the reaction of alcohols with silicon tetrachloride was undertaken by von Ebelmen (*Annalen*, 1846, **57**, 334), Friedel and Crafts (*ibid.*, 1863, **127**, 28; 1865, **136**, 203; *Ann. Chim. Phys.*, 1866, [iv], **9**, 5), and Ladenburg (*Annalen*, 1874, **173**, 151). This was continued by Kipping *et al.* (*J.*, 1901, **79**, 449), and more recently by Helferich and Hausen (*Ber.*, 1924, **57**, 795), Dearing and Reid (*J. Amer. Chem. Soc.*, 1928, **50**, 3058), and others (Kaufmann, D.R.-P. 528,988, 641,075, 625,077; *Chem. Abstr.*, 1931, **25**, 5177; 1937, **31**, 6416; 1938, **32**, 7678; B.P. 343,165; *Chem. Abstr.*, 1931, **25**, 5432; Sugden and Williams, *J.*, 1931, 126; Signer and Gross, *Annalen*, 1931, **488**, 56; Kalinin, *Compt. Rend. Acad. Sci. U.R.S.S.*, 1938, **18**, 433; Post and Hofrichter, *J. Org. Chem.*, 1940, **5**, 572). No correlation of the results, from a mechanistic viewpoint, has however been previously undertaken.

In the present work the orthosilicates were prepared, in the first instance, by treating the appropriate alcohol with silicon tetrachloride in such proportions as to satisfy the equation :



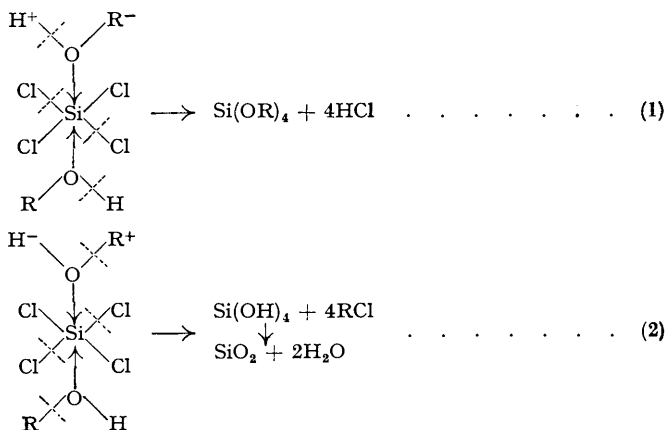
It was noted that the vigour of the reaction was greatest for alcohols containing strongly  $+I$  or  $-I$  inductive groups and decreased for normal alcohols as the carbon chain was lengthened. The yield of orthosilicate increased up to the *n*-propyl and *n*-butyl ester and then decreased again, whereas the amount of silica deposited during the reaction was greatest when methyl alcohol was used and decreased as the carbon chain was lengthened. With the isomeric butyl alcohols, the yield decreased from the *n*- to the *tert.*-ester, whereas the silica content increased until it became the main product when *tert.*-butyl alcohol was used.

Two modes of reaction appear possible, both involving the initial co-ordination of a lone pair of electrons on an alcoholic oxygen atom with silicon tetrachloride, along the lines suggested by Sidgwick (*J.*, 1924, **125**, 532, 2672), followed by a break in either the hydroxyl or alkoxy link. This is governed by the inductive effect of the substituent group in the alkyl radical and yields the orthosilicate and hydrogen chloride, or silica and the alkyl chloride respectively [see (1) and (2) on following page].

In either case, the addition of the lone pair at the silicon atom increases the electron density at this atom and thus weakens the silicon-halogen link.

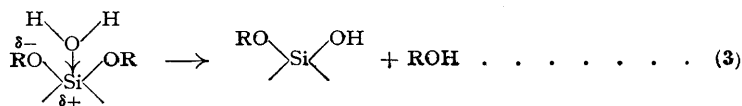
It would therefore be expected that those alcohols, which have groups of strongly  $+I$  or  $-I$  effect, would react most vigorously since, in either case, the electron density at the oxygen atom would be increased and it would therefore co-ordinate more readily. It was found experimentally

that ethylene chlorohydrin ( $-I$ ) and *sec.*-butyl alcohol ( $+I$ ) reacted more vigorously than did the higher alcohols. Also the lower alcohols reacted more vigorously than the higher members of the series, as would be expected in view of the proximity of the methyl ( $+I$ ) group to the oxygen atom.

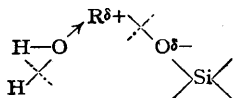


Alcohols containing  $-I$  inductive groups react in accordance with mechanism (1), and no silica deposit is obtained (*e.g.*, ethylene chlorohydrin). A strongly  $+I$  inductive grouping, as in *tert.*-butyl alcohol, causes the reaction to follow mechanism (2). When normal alcohols are used, both mechanisms occur, but (2) is more marked in those alcohols where the methyl group is most operative, so that the amount of silica deposited during the reaction decreases as the carbon chain is lengthened. It would therefore be expected that the yield of ester should increase accordingly. In fact, *n*-propyl and *n*-butyl alcohol gave the best yield. Here the heat stability of the ester must be considered.

Experiment has shown that those orthosilicates which have a  $-I$  inductive or fairly non-reactive substituent groups tend to decompose when distilled at atmospheric pressure without previous drying, yielding the alcohol and a resinous residue (Dearing and Reid, *J. Amer. Chem. Soc.*, 1928, 50, 3058). This was observed whether or not the starting reagents were dried before use and suggests that the electronic effect of the substituent groups reduces the electron density of the silicon atom, thus making it a suitable point of attack for the lone pair of a water molecule. Electronic displacement then causes the loss of alcohol, and the residual hydroxyl group reacts with other ester molecules to form polymers.



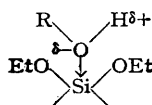
When aliphatic esters were exposed to atmospheric moisture, however, those in which the  $+I$  group was most operative were the least stable, and the most stable were those containing a  $-I$  group. This is the converse of the results obtained for heat stability and suggests that in this case the point of attack by the water molecule is the carbon and not the silicon atom. Electron balance is then restored by the fission of the ester and water molecule thus:



Orthosilicates containing a  $-I$  inductive group react in accordance with mechanism (3) in the presence of moisture. So do the higher alkyl orthosilicates since the  $+I$  inductive effect of the methyl group is too remote to counteract the general  $-I$  effect of the alkoxy-group. Since silicon is capable of a co-valency of six, the higher alkyl-, chloro-, and phenyl-substituted alkyl esters are hygroscopic and absorb water without any immediate rupture of the Si-O bond. There is therefore no precipitation, and the effect of water is discernible only on distillation. The carbon atom of the alkyl group cannot increase its covalency beyond four and so the R-O link will tend to be broken more easily: hence the greater apparent moisture-sensitivity of the lower

alkyl esters. Furthermore, as the Si-O bond is stronger than the C-O bond (Pauling, "The Nature of the Chemical Bond," 2nd edn., 1940, p. 53), it follows that the former requires greater energy to assist its rupture and therefore breaks down only on distillation. The fact that 2-chloroethyl orthosilicate and benzyl orthosilicate can be distilled at atmospheric pressure, after very careful drying of the crude ester, substantiates this theory.

An alternative method of preparation of the orthosilicates, namely the interchange of an alcohol with ethyl orthosilicate, has been successfully adopted by several investigators (Friedel and Crafts, *Annalen*, 1863, **127**, 28; Hertkorn, *Ber.*, 1885, **18**, 1679; Knorr and Weyland, D.R.-P. 285,285; *Chem. Abstr.*, 1916, **10**, 666; F.P. 827,975; *Chem. Abstr.*, 1938, **32**, 7170; Post and Hofrichter, *J. Org. Chem.*, 1939, **4**, 363; Peppard, Brown, and Johnson, *J. Amer. Chem. Soc.*, 1946, **68**, 73; Falkenburg, Teete, and Cowan, *J. Amer. Chem. Soc.*, 1947, **69**, 486), but no comprehensive mechanism has been recorded (Post and Hofrichter, *J. Org. Chem.*, 1940, **5**, 572; Dolgov and Volinov, *J. Gen. Chem., Russia*, 1931, [1], **63**, 330). The present work shows that those alcohols react the most easily which tend to ionise thus:  $\text{ROH} \longrightarrow \text{RO}^- + \text{H}^+$ . If it is assumed that the addition of the alcohol takes place as in the reaction with silicon tetrachloride, it would appear that it is the Si-O link of the ethyl orthosilicate which is broken:



Thus esters containing  $-I$  substituent groups are the most easily prepared by this method.

#### EXPERIMENTAL.

Silicon tetrachloride was prepared by distillation of the commercial product. The first and last runnings were rejected and the fraction of b. p. 56–58° was collected.

Methyl, ethyl, *n*-propyl, *sec.*- and *tert.*-butyl alcohol were dried by heating under reflux with, and distilling over, freshly roasted lime. The higher alcohols were dried by azeotropic distillation through a fractionating column. Benzyl alcohol, cyclohexanol, methylcyclohexanol, and ethylene chlorohydrin were dried over sodium sulphate.

Silica contents were determined by digestion of the redistilled sample with concentrated sulphuric acid.

*Reactions with Silicon Tetrachloride.*—The molecular ratio of one part of silicon tetrachloride to four parts of alcohol was maintained as far as possible throughout the addition of the reactants. The products were freed from hydrogen chloride by dry aeration and then distilled at atmospheric pressure. Quantities used are recorded below. All the purified orthosilicates were clear, colourless liquids, except cyclohexyl orthosilicate.

*Methyl orthosilicate.* Methyl alcohol, 690 ml.; silicon tetrachloride, 450 ml. A vigorous, endothermic action ensued, silica being deposited. A fine silica deposit was obtained on aeration. The product was not investigated further.

*Ethyl orthosilicate.* Ethyl alcohol, 233 ml.; silicon tetrachloride, 117 ml. The reaction was vigorous and endothermic. A slight deposit of silica was obtained. The crude ester (91.5% yield) gave a 74% yield of purer orthosilicate distilling between 164° and 180° [Found:  $\text{SiO}_2$ , 28.9. Calc. for  $(\text{C}_2\text{H}_5\text{O})_2\text{Si}$ :  $\text{SiO}_2$ , 18.8%].

*n-Propyl orthosilicate.* *n*-Propyl alcohol, 94 ml.; silicon tetrachloride, 35 ml. The reaction was less vigorous than in the previous experiment, and there was only a slight silica deposit. The crude ester (99.0% yield) gave an 81.5% yield of purer orthosilicate, b. p. 220–230° [Found:  $\text{SiO}_2$ , 22.6. Calc. for  $(\text{C}_3\text{H}_7\text{O})_2\text{Si}$ :  $\text{SiO}_2$ , 22.7%].

*n-Butyl orthosilicate.* *n*-Butyl alcohol, 50 ml.; silicon tetrachloride, 16 ml. The reaction was fairly vigorous, but less so than in the previous experiment; practically no silica was deposited. The crude ester (100% yield) gave a 67.5% yield of purer orthosilicate, b. p. 276–286° [Found:  $\text{SiO}_2$ , 18.8. Calc. for  $(\text{C}_4\text{H}_9\text{O})_2\text{Si}$ :  $\text{SiO}_2$ , 18.7%].

*n-Amyl orthosilicate.* *n*-Amyl alcohol, 43.1 ml.; silicon tetrachloride, 11.7 ml. The reaction was fairly vigorous, and practically no silica was deposited. The crude ester (85.8% yield) gave a 46.6% yield of purer orthosilicate, b. p. 302–304° [Found:  $\text{SiO}_2$ , 16.4. Calc. for  $(\text{C}_5\text{H}_{11}\text{O})_2\text{Si}$ :  $\text{SiO}_2$ , 16.3%].

*n-Hexyl orthosilicate.* *n*-Hexyl alcohol, 100 ml.; silicon tetrachloride, 42.5 ml. The reaction proceeded smoothly with a less vigorous evolution of hydrogen chloride than in the previous experiments. The crude ester gave varying yields on distillation depending on the rate of heating.

*isoButyl orthosilicate.* *iso*Butyl alcohol, 100 ml.; silicon tetrachloride, 32 ml. The reaction was more vigorous than was the *n*-butyl alcohol-silicon tetrachloride reaction. No appreciable silica deposit was observed. The crude ester (95.1% yield) gave a 47.8% yield of purer orthosilicate, b. p. 252–255° [Found:  $\text{SiO}_2$ , 18.7. Calc. for  $(\text{C}_4\text{H}_9\text{O})_2\text{Si}$ :  $\text{SiO}_2$ , 18.7%].

*sec.-Butyl orthosilicate.* *sec.*-Butyl alcohol, 92.6 ml.; silicon tetrachloride, 30 ml. The reaction was more pronounced than in the previous experiment, the temperature rising to 50–60° in the early stages of the addition. The crude ester (90.0% yield) gave a 42.4% yield of purer orthosilicate, b. p. 248–249° (Found:  $\text{SiO}_2$ , 18.8. Calc. for  $(\text{C}_4\text{H}_9\text{O})_2\text{Si}$ :  $\text{SiO}_2$ , 18.7%).

*Attempted Preparation of tert.-Butyl Orthosilicate.*—*tert.*-Butyl alcohol (27.0 ml.) was treated with silicon tetrachloride (3.4 ml.). After 30 seconds, the reaction became violent, liquid condensing on the sides of the reaction chamber and silicic acid being ejected from the reaction liquid. The hydrogen chloride evolved was less copious than usual and *tert.*-butyl chloride was identified among the reaction

2640 *Studies in the Formation Mechanisms of Alkyl Orthosilicates.*

products. The reaction was repeated using *tert.*-butyl alcohol diluted with *s*-tetrachloroethane; the same phenomenon was observed although the reaction was slightly less violent.

*cycloHexyl Orthosilicate.*—*cyclo*Hexanol (84.4 ml.) was treated with silicon tetrachloride (23.0 ml.), a vigorous action ensuing. The crude ester (86.0% yield) gave no distillable product, but yielded a white solid, m. p. 86°, when recrystallised from acetone (Helferich and Hausen, *Ber.*, 1924, 57, 795, give m. p. 88.6°).

*Attempted Preparation of Methylcyclohexyl Orthosilicate.*—Methylcyclohexanol (78.0 g.) was treated with silicon tetrachloride (20 ml.). The crude ester (82.0%) did not yield the orthosilicate on distillation.

*2-Chloroethyl Orthosilicate.*—Ethylene chlorohydrin (26.0 ml.) and silicon tetrachloride (11.7 ml.) gave a vigorous and slightly exothermic reaction. The crude ester (87.5% yield) gave no product on distillation unless subjected to preliminary drying ( $\text{Na}_2\text{SO}_4$ ); the orthosilicate boiling at 300° was obtained under these conditions. [Found:  $\text{SiO}_2$ , 17.6. Calc. for  $(\text{C}_2\text{H}_4\text{OCl})_4 : \text{SiO}_2$ , 17.2%].

*Reactions with Ethyl Orthosilicate.*—Ethyl orthosilicate was prepared by treating dried absolute ethyl alcohol with silicon tetrachloride as described above. The fraction, b. p. 165–166° ( $\text{SiO}_2$  content 28.9%), was used in all the interchange reactions. The reactants (4 mols. of alcohol and 1 mol. of ester) were heated in a distillation flask (sillimanite-bath) until distillation commenced. It was advisable to raise the temperature of the bath so that the pre-distillation period was *ca.* ¼ hour. The flame was then adjusted so that a steady distillation of alcohol at *ca.* 80° was obtained. When as much alcohol as possible had been obtained, the residue in the flask was distilled at either atmospheric or reduced pressure. Conditions were kept as constant as possible throughout the reactions so that the time of distillation of the alcohol could be taken as indicative of the relative ease of formation of the orthosilicate. Results are shown in the table.

*Time of distillation for 11.1 ml.*

Alcohol.	Time of distillation.
Benzyl alcohol .....	45 minutes.
<i>cyclo</i> Hexanol .....	4 hours with catalyst.
Ethylene chlorohydrin .....	48 minutes.
<i>n</i> -Hexyl alcohol .....	Very long; faster than amyl alcohol, which in turn was slightly faster than butyl alcohol.
Methylcyclohexanol .....	Very long.

*Benzyl orthosilicate.* Benzyl alcohol (20.7 ml.) was subjected to interchange with ethyl orthosilicate (11.1 ml.), a crude yield of 93% being obtained. Distillation at 50 mm. gave a 45% yield of ester, b. p. 330–360° [Found:  $\text{SiO}_2$ , 13.7. Calc. for  $(\text{C}_7\text{H}_7\text{O})_4\text{Si} : \text{SiO}_2$ , 13.2%]. Atmospheric distillation of the crude ester gave benzyl alcohol and a non-distillable viscous liquid. When dried over sodium sulphate, the crude ester yielded a pure fraction, b. p. 355–357° (Found:  $\text{SiO}_2$ , 13.3%).

*cycloHexyl resin.* *cyclo*Hexanol (21 ml.) was treated with ethyl silicate (11.1 ml.). Distillation of the crude product at atmospheric pressure yielded *cyclo*hexanol (11 ml.) and an amber-coloured resin. Distillation at 40 mm. yielded *cyclo*hexanol and a few drops of liquid, b. p. 230–240°, which solidified in the condenser.

*2-Chloroethyl orthosilicate.* Ethylene chlorohydrin (12.6 ml.) was subjected to interchange with ethyl orthosilicate (11.1 ml.). The crude undried product gave ethylene chlorohydrin when heated, but the dried product yielded the ester, boiling at 300° at atmospheric pressure [Found:  $\text{SiO}_2$ , 17.6. Calc. for  $(\text{C}_2\text{H}_4\text{OCl})_4\text{Si} : \text{SiO}_2$ , 17.2%).

*Attempted preparation of the butyl orthosilicates.* The four isomeric butyl alcohols (14.8 ml.) were treated in turn with ethyl orthosilicate (11.1 ml.). Only slight interchange took place with *n*- and *iso*-butyl alcohol, and 2 ml. of the alcohols were collected. No interchange took place with the other alcohols. Comparable results were obtained on the attempted interchange of *n*- and *tert.*-amyl alcohol with ethyl orthosilicate.

*Hexyl orthosilicate.* *n*-Hexyl alcohol (16.2 ml.) were treated with ethyl orthosilicate (11.1 ml.), a crude yield of 68.5% of ester being obtained. Distillation at 60 mm. gave 40% of yellow liquid distilling at 254° with some decomposition [Found:  $\text{SiO}_2$ , 14.8. Calc. for  $(\text{C}_6\text{H}_{13}\text{O})_4\text{Si} : \text{SiO}_2$ , 13.8%].

No reaction took place on treating methylcyclohexanol with ethyl orthosilicate.

*Stability of the Orthosilicates to Atmospheric Moisture.*—Equal volumes of the ortho-esters prepared were allowed to stand unstoppered in similar vessels; the appearance, noted at intervals, is recorded in the following table.

Ester.	Time of standing.			
	66 hours.	90 hours.	234 hours.	2 months.
Ethyl .....	slight ppt.	slightly more ppt.	ppt. adhering to the base of the vessel	ppt. at the base of the vessel
Propyl .....	no ppt.	no ppt.	very slight ppt.	gel
<i>n</i> -Butyl .....	“	“	no ppt.	no ppt.
<i>iso</i> Butyl .....	“	“	very slight ppt.	unchanged
<i>sec.</i> -Butyl .....	ppt.	slightly more ppt.	ppt.	ppt.
<i>n</i> -Hexyl .....	no ppt.	no ppt.	no ppt.	no ppt.
Benzyl .....	“	“	“	“
2-Chloroethyl	very slight deposit on the glass at surface level	unchanged	unchanged	unchanged