311. *Stability of Isomeric Butoxysilanes with Respect to Silicon Tetrachloride and Hydrogen Chloride.*

By W. Gerrard and J. V. Jones.

It is shown that disproportionation between the isomeric tetrabutoxysilanes (excluding the *tert.*-butoxy-compound) and silicon tetrachloride is very slow at the reflux temperature of the latter. In a sealed tube at 150° the *n*-butyl ester undergoes primary disproportionation into the tri- and the mono-chlorosilane; but in the same time the *iso*butyl and the *sec.*-butyl ester are scarcely affected. These esters show resistance to dealkylation by hydrogen chloride. Such observations are necessary for a detailed description of alcohol–silicon tetrachloride systems.

Precise description of the reaction sequences in alcohol–inorganic non-metallic halide systems requires detailed knowledge of the behaviour of the primarily liberated hydrogen halide and of the disproportionation tendencies of the relevant esters with respect to the original halide reagent. Disproportionation between tetra-alkoxysilanes and silicon tetrachloride has been listed as a method of preparation of chlorosilanes, because of the original observation by Friedel and Crafts (*Annalen*, 1863, **127**, 28; 1865, **136**, 203) who worked with methyl and ethyl homologues which were heated in a sealed tube at 160°.

Conditions for disproportionation in examples of the isomeric butyloxysilanes have now been determined. At the reflux temperature of silicon tetrachloride these tetra-esters (except that of *tert.*-butyl) showed no definite sign of disproportionation even after many hours. Whereas a trace of pyridine hydrochloride encouraged reaction of the *n*-butyl ester, it had no such obvious effect with the other two. The tetra-*n*-butyl ester suffered no definite disproportionation when heated with silicon tetrachloride in a sealed tube at 100° for 3 hours, but at 150° in the same time it underwent primary change into the tri- and the mono-chlorosilane. At 200° a secondary reaction would account for the dichlorosilane found. With the other two butyl tetra-esters, disproportionation at 150° was slow.

We believe that these effects are due to a screening of the silicon atom by alkyl groups which hinder the broadside four-centre approach of silicon tetrachloride, requiring a disposition in which the silicon of the tetrachloride approaches the oxygen atom of an alkyl-oxygen group, and at the same time a chlorine atom of the tetrachloride approaches the silicon atom of the tetra-ester. It is conceivable that hydrocarbon branching can cause more effective screening.

Dealkylation of the three tetra-esters by means of hydrogen chloride is evidently a slow process. Consideration of these data and those presented by Gerrard and Woodhead (*J.*, 1951, 519; *Research*, 1949, **2**, 48) for octan-2-ol shows that the silicon tetrachloride–alcohol system, in which the alcoholic carbon atom has what may be termed an " ordinary " degree of reactivity, entails simply a rapid stepwise dechlorination of the tetrachloride. If the addition of alcohol is stopped when one mol. of it has been added to one mol. of the tetrachloride, the trichlorosilane, $SiCl_3{\cdot}OR$, together with some dichlorosilane, $SiCl_2(OR)_2$, can be isolated; but further addition of alcohol will continue the formation of the dichlorosilane and develop the monochlorosilane as well, and ultimately the tetra-ester will tend to be formed. If, however, the tetrachloride is added dropwise to the alcohol, dechlorination is extensive by the time 0·25 mol. has been added, and further addition will merely delay the last stage of the dechlorination. We examined this point in some detail with *n*-butyl alcohol and found that the reaction mixture, resulting from the addition of 0·25 mol. of the tetrachloride to 1 mol. of alcohol, appeared to comprise the monochlorosilane (equivalent to about 0·75 mol. of alcohol) and alcohol (0·25 mol.) held in a state of comparative inactivity, presumably as ROH,HCl, for even after this mixture had been at 15° for an hour, it gave an approximately equivalent amount of the trichlorosilane on the continued addition of the tetrachloride, the main product being the monochlorosilane. When, however, the volatile matter was removed at 15°/15 mm. at the 0·25-mol. stage, tetra-*n*-butoxysilane was isolated whether or not more tetrachloride was added.

It is now clear why the tetra-ester is formed rapidly and completely when the tetrachloride is added to the alcohol in the presence of pyridine. Furthermore, it may be concluded that, apart from interaction between hydrogen chloride and alcohol, silicon tetrachloride–alcohol systems entail no reaction sequence which proceeds sufficiently quickly to lead to ordinarily perceptible amounts of alkyl chloride.

The situation is very different when the alcoholic carbon atom is much more reactive, *e.g.*, in 1-phenylethanol, which very rapidly gave 1-chloro-1-phenylethane in high yield when mixed with the tetrachloride (Gerrard and Woodhead, *loc. cit.*). Furthermore, tetra-(1-phenylethoxy)silane was readily and completely dealkylated by hydrogen chloride, the alkyl chloride being isolated in high yield.

These observations are now available for comparison with those on the alcohol–phosphorus halide systems (Gerrard, *J.*, 1940, 1464; 1944, 85; 1945, 106; 1946, 741) and with those on the alcohol–boron trichloride systems (Gerrard and Lappert, *J.*, 1951, 1020, 2545; cf. also the zirconium alkoxides, Bradley and Wardlaw, *J.*, 1951, 820).

EXPERIMENTAL

The tetra-alkyloxysilanes were prepared by addition of silicon tetrachloride (1 mol.) to a mixture of the alcohol (4 mols.) and pyridine (4 mols.) in pentane as described by Gerrard and Woodhead (*loc. cit.*).

Disproportionation Experiments.—(a) *At reflux temperature.* Tetra-*n*-butoxysilane, b. p. 106°/0·4 mm., d_{20}^{20} 0·897, n_D^{20} 1·4138 (Found : C, 60·6; H, 11·25. Calc. for $C_{16}H_{36}O_4Si$: C, 60·0;

H, 11·25%) (8 g., 1 mol.) was mixed with silicon tetrachloride (freshly distilled; 17 g., 4 mols.) and heated at the reflux temperature of the latter for 12 hours. The tetrachloride (14·7 g.), b. p. 57—60°, and the tetra-ester (7·8 g.), b. p. 127°/1·5 mm. [redistilled (7·3 g.), b. p. 107°/0·5 mm., n_D^{20} 1·4140], were recovered. There was a primary residue (0·5 g.). The same quantities of materials after being heated at reflux temperature for 10 hours a day for 8 days afforded the tetrachloride (14·5 g.), b. p. 57—60°, the tetra-ester (7·1 g.), b. p. 104°/0·3 mm., n_D^{20} 1·4139, and a residue (0·8 g.).

Tetra*iso*butoxysilane, b. p. 90°/0·4 mm., d_{20}^{20} 0·886, n_D^{20} 1·4090 (Found: C, 60·4; H, 11·28%) (8·0 g., 1 mol.), and the tetrachloride (17 g., 4 mols.) were similarly heated for 12 hours. The tetra-ester (7·3 g.), b. p. 90°/0·2 mm., n_D^{20}1·4090, was recovered.

Tetra-*sec*.-butoxysilane, b. p. 87°/2 mm., d_{20}^{20} 0·883, n_D^{20} 1·4070 (Found: C, 60·2; H, 11·26%) (8·0 g., 1 mol.), and the tetrachloride (17 g., 4 mols.) were similarly heated for 12 hours. The tetra-ester (7·6 g.), b. p. 84—87°/1·5 mm., was recovered.

When undistilled silicon tetrachloride (containing traces of chlorides of iron, titanium, and aluminium) was used instead of the purified material, the *n*-butoxysilane was again recovered as described. Pyridine hydrochloride (0·2 g., 0·05 mol.; for 1 mol. of tetra-ester and 4 mols. of tetrachloride) facilitated disproportionation. After 12 hours at reflux temperature tetra-*n*-butoxysilane (8·0 g.) afforded a liquid (5·5 g.), b. p. 100—120°/15 mm., and another (4·0 g.), b. p. 120—130°/15 mm., there being a small residue (0·4 g.). From the first liquid a fairly pure specimen of di-*n*-butoxydichlorosilane (3·0 g.), b. p. 95—105°/15 mm. (Found: Cl, 28·1. Calc. for $C_8H_{18}O_2Cl_2Si$: Cl, 28·9%), was obtained together with a liquid (2·4 g.), b. p. 105—120°/15 mm. (Found: Cl, 19·7%), which was probably a mixture of the di- and mono-chlorosilane. The liquid of b. p. 120—130°/15 mm. afforded tri-*n*-butoxychlorosilane (2·1 g.), b. p. 120—125°/15 mm. (Found: Cl, 13·0. Calc. for $C_{12}H_{27}O_3ClSi$: Cl, 12·5%), and a further fraction (1·7 g.), b. p. 125—130°/12 mm. (Found: Cl, 6·2%). The base hydrochloride has no such decided influence with the tetra-*iso*- or -*sec*.-butyl esters: the former afforded impure tetra-ester (4·5 g.), b. p. 79—81°/0·4 mm. (Found: Cl, 1%), and a better specimen (2·8 g.), b. p. 82—85°/0·3 mm., n_D^{20} 1·4088, and the *sec*.-butyl ester was largely recovered (7·5 g.), b. p. 77—79°/0·3 mm., n_D^{20} 1·4065.

(b) *In a sealed tube.* Tetra-*n*-butoxysilane (4·0 g.) and the tetrachloride (8·5 g.) were heated in a sealed tube for 3 hours at 200°. The tetrachloride (4·2 g.), b. p. 57—80° (Found: Cl, 82·9. Calc.: Cl, 83·4%), and the following fractions were obtained: *A* (0·8 g.), b. p. 80—100°; *B* (2·5 g.), b. p. 75—105°/57—60 mm.; *C* (2·4 g.), b. p. 110—135°/16 mm.; *D* (0·8 g.), b. p. 75—85°/0·2 mm., and a residue (0·3 g.). Fraction *B* afforded *n*-butoxytrichlorosilane (2·15 g.), b. p. 67—74°/50 mm. (Found: Cl, 50·5; Si, 13·25. Calc. for $C_4H_9OCl_3Si$: Cl, 51·25; Si, 13·5%), and *C* gave impure di-*n*-butoxydichlorosilane (0·7 g.), b. p. 103—110°/13 mm. (Found: Cl, 25·7. Calc. for $C_8H_{18}O_2Cl_2Si$: Cl, 28·9%), a middle fraction (0·3 g.), b. p. 110—128°/13 mm., and tri-*n*-butoxychlorosilane (0·8 g.), b. p. 128—131°/13 mm. (Found: Cl, 13·0. Calc. for $C_{12}H_{27}O_3ClSi$: Cl, 12·55%). Purification of these distillates was not carried further. Repetition at 150° afforded a fraction *A* (1·9 g.), b. p. 60—90°/60 mm., from which *n*-butoxytrichlorosilane (1·6 g.), b. p. 67—69°/48 mm. (Found: Cl, 51·5%), was obtained, and a fraction *B* (3·5 g.), b. p. 100—145°/15 mm., from which tri-*n*-butoxychlorosilane (2·9 g.), b. p. 128—133°/15 mm. (Found: Cl, 12·2%), was obtained.

Repetition at 100°, however, gave mainly tetra-*n*-butoxysilane (3·5 g.), b. p. 106—108°/0·5 mm., n_D^{20} 1·4140.

By the same process and with the same quantities of materials kept at 150° for 3 hours, tetra*iso*butoxysilane afforded two fractions; *A* (1·8 g.), b. p. 69—75°/0·1 mm. (Found: Cl, 2·4%), and *B* (2·0 g.), b. p. 75—82°/0·1 mm. (Found: Cl, 1·9%), and a residue (0·3 g.). Similarly, tetra-*sec*.-butoxysilane afforded silicon tetrachloride (7·0 g.) and contaminated tetra-ester (3·8 g.), b. p. 78—80°/0·3 mm. (Found: Cl, 1%), there being a residue (0·2 g.).

*Interaction of Hydrogen Chloride and Tetra-*n*-butoxysilane.*—Dry hydrogen chloride was passed into the tetra-ester (8·0 g.) for 3 hours at 20°, and the final increase in weight was 0·7 g., corresponding to 0·77 mol. of the gas for 1 mol. of ester. After dry air had been passed through the liquid, the weight (8·05 g.) was almost that of the ester used. On distillation the tetra-ester (7·3 g.), b. p. 95—105°/0·4 mm., and a brown gelatinous residue (0·6 g.) were obtained, and on redistillation, the tetra-ester (7·0 g.), b. p. 101°/0·4 mm., and a residue (0·3 g.). During the approach to distillation temperature and during the passage of gas, a U-tube, cooled at −80°, was attached to the exit tube from the apparatus. No more than a trace of liquid was so collected.

When the gas was passed into the ester at 55° for 3 hours, the increase in weight was 0·1 g.

(0·12 mol.), but the weight returned to 8·0 g. on passage of dry air. From the residue, *n*-butyl alcohol (0·3 g.), b. p. 60—65°/20 mm., d_{20}^{20} 0·810, the tetra-ester (7·1 g.), b. p. 108—113°/1·0 mm., and a brown gelatinous residue (0·5 g.) were obtained. On redistillation, the tetra-ester (6·8 g.), b. p. 95—96°/0·15 mm., and a residue (0·3 g.) were obtained.

Similarly at 20° tetra-*sec.*-butoxysilane (8·0 g.) absorbed 0·5 g. (0·55 mol.) of gas, but most of this was removed in a stream of air. From the residue, the tetra-ester (7·0 g.), b. p. 65—83°/0·3 mm., and a brown gelatinous residue (0·6 g.) were obtained, and on redistillation of the ester fraction, the ester (6·6 g.), b. p. 66—70°/0·05 mm., and a residue (0·4 g.).

Dechlorination of Silicon Tetrachloride by n-*Butyl Alcohol.*—Silicon tetrachloride (9·4 g., 1·1 mols.) in *n*-pentane (15 c.c.) was added dropwise (30 minutes) with shaking to the alcohol (14·8 g., 4 mols.) in pentane (20 c.c.) at —10°. Evolution of hydrogen chloride soon began and, when mixing was complete, dry air was passed (10 minutes) to sweep away most of the gas. Easily volatile matter was removed at 20°/15 mm. (20 minutes), and distillation then afforded tetra-*n*-butoxysilane (15·2 g., 95%), b. p. 92—97°/0·4 mm., and a residue (0·3 g.). On redistillation, the tetra-ester (14·8 g.), b. p. 99—101°/0·5 mm., n_D^{20} 1·4140, and a residue (0·4 g.) were obtained.

Similar addition of the tetrachloride (34 g., 4 mols.) (45 minutes) followed by removal of volatile matter at 15°/15 mm. (1 hour) and distillation afforded crude *n*-butoxytrichlorosilane (3·3 g.), b. p. 82—95°/45 mm. [redistilled (2·5 g.), b. p. 70—75°/45 mm. (Found : Cl, 50·0. Calc. for $C_4H_9OCl_3Si$: Cl, 51·25%)], and crude tri-*n*-butoxychlorosilane (17·4 g.), b. p. 65—70°/0·1 mm. [redistilled (16·8 g.), b. p. 65—67°/0·1 mm. (Found : Cl, 12·5. Calc. for $C_{12}H_{27}O_3ClSi$: Cl, 12·5%)]. There was a residue (0·6 g.) from the primary distillation. It will be noticed that in this experiment the tetrachloride was added about three times as fast as in the first experiment, and furthermore, addition was continued without interruption to the stage of 1 mol. of reagent for 1 mol. of alcohol. Now when the process was interrupted at the 0·25-mol. stage (tetrachloride, 4·25 g.; alcohol, 7·4 g.) (time of addition, 20 minutes) in order to remove volatile matter at 15°/15 mm., and then the tetrachloride (12·75 g., 0·75 mol.) (in pentane, 15 c.c.) was added to the residue (30 minutes), distillation, after the usual removal of volatile matter at 15°/15 mm., afforded tetra-*n*-butoxysilane (7·5 g.), b. p. 95—105°/0·3 mm. [redistilled (7·2 g.), b. p. 102—104°/0·3 mm., n_D^{20} 1·4138]. There was a residue (0·5 g.) from the first distillation. In a final experiment, the addition was again interrupted at the 0·25-mol. stage, but this time the mixture was merely kept for 1 hour at 15° and then cooled at —10° whilst the remainder (12·75 g., 0·75 mol.) of the tetrachloride was added (30 minutes). After volatile matter had been removed at 15°/15 mm., crude trichlorosilane (1·2 g.) (from alcohol, 7·4 g.), b. p. 60—75°/30 mm., an intermediate fraction (0·3 g.), b. p. 75—130°/30 mm., and monochlorosilane (8·6 g.), b. p. 70—90°/0·2 mm. [redistilled (8·2 g.), b. p. 73—77°/0·2 mm. (Found : Cl, 12·8%)], were obtained. There was a residue (0·4 g.), and redistillation of the first fraction (1·2 g.) afforded a good specimen of the trichlorosilane (1·0 g.), b. p. 58—64°/33 mm. (Found : Cl, 50·3%).

THE NORTHERN POLYTECHNIC, LONDON, N.7.

[*Received, January 5th,* 1952.]