culated from the data of Curran, *et al.*[10]) postulated from the work of Martin,[11] does not result in a rapid halogen activity transfer between the two halides, since this would have been observed under the conditions of the present exchange runs.

The absence of exchange in the homogeneous gas phase between the two chlorosilanes tested and BCl_3 also appears to be in consonance with the suggested ionic exchange mechanism. It may be further noted that absence of halogen exchange between $SiCl_4$ and BCl_3 is in agreement with the previously reported[5,12] exchanges of silicon tetrachloride in which absence of halogen transfer between $SiCl_4$ and symmetrical covalent chlorides was predicted.

Acknowledgments.—The author is indebted to Mr. C. T. Bishop and Miss S. C. Chang for assistance in the present work and to his colleague, Prof. L. A. Hiller, Jr., for helpful discussions of the exchange mechanisms proposed.

[10] C. Curran, R. M. Witucki and P. A. McCusker, THIS JOURNAL, **72**, 4471 (1950).

[11] D. R. Martin, *J. Phys. Colloid Chem.*, **51**, 1400 (1947).

[12] R. H. Herber, *J. Chem. Phys.*, **27**, 653 (1957).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Reactions of Triethylsilane and Diethylsilane with Inorganic Halides and Acids

BY HERBERT H. ANDERSON

RECEIVED MAY 22, 1958

Triethylsilane reduces certain halides or sulfates of at least 10 transitional elements and 5 elements in regular groups either to a lower oxidation state or sometimes to the free element. Oxidation of triethylsilane primarily to hexaethyldisiloxane occurs with a deficiency of 100% sulfuric acid or with 15 *M* nitric acid or chlorosulfonic acid. Table I lists 24 reactions of triethylsilane, with a median yield of approximately 81%. In a new modification, diethylsilane and a deficiency of mercuric bromide yield new diethylbromosilane. Other new compounds include diethyliodosilane and *sym*-tetraethyldisiloxane. As before, the two main explanations for the reaction of triethylsilane with a given halide depend on heats of formation per equivalent of available halogen in the compounds and on the appropriate ionization potentials of the elements.

Earlier papers establish the use of halides of certain transitional elements and elements in regular groups in the replacement of hydrogen attached to germanium[1] in $(C_2H_5)_3GeH$ or to tin[2] in $(C_2H_5)_3SnH$. This paper, in turn, studies the similar replacement of hydrogen attached to silicon in the exactly analogous $(C_2H_5)_3SiH$.

An apparently new modification in this paper uses gradual addition of a halide of a transitional element to an excess of $(C_2H_5)_2SiH_2$ in the preparation of $(C_2H_5)_2SiHCl$ and $(C_2H_5)_2SiHBr$. This modification is under study in the continuing investigation of alkylhalosilanes with Si–H bonding.

Other investigators of alkylsilanes with Si–H bonding report a number of preparative methods. Partial reaction of $SiHCl_3$ with the Grignard reagent furnishes intermediates[3] $SiHCl_3 + C_2H_5MgBr \rightarrow C_2H_5SiHCl_2 + (C_2H_5)_2SiHCl$. Aluminum chloride catalyst allows numerous reactions such as: $(C_2H_5)_3SiSH + (C_2H_5)_2SiCl_2 \rightarrow (C_2H_5)_3SiCl + (C_2H_5)_2SiHCl + (C_2H_5)_2SiH_2$,[4] also $(C_2H_5)_3SiH + n\text{-}C_6H_{13}Cl \rightarrow (C_2H_5)_3SiCl + n\text{-}C_6H_{14}$,[4] and also $C_2H_5SiHCl_2 \rightarrow C_2H_5SiH_2Cl + C_2H_5SiCl_3$.[5]

Experimental Results

Table I lists 24 reactions of $(C_2H_5)_3SiH$ with halides or sulfates of 10 transitional elements and 5 elements in regular groups, or with sulfuric, nitric or chlorosulfonic acids. A median yield of 81% in Table I is based on the starting material present in the lesser amount as before.[2] When both $(C_2H_5)_3SiOH$ and $(C_2H_5)_3SiOSi(C_2H_5)_3$ are among the products calculations of yield in Table I exclude the minor organosilicon product. Direct conversion of a trialkylsilane to a hexaalkyldisiloxane occurs in the one-step reaction of triethylsilane and $HgSO_4$; this appears promising as a special method with trialkylsilanes.

Gradual addition of a deficiency of AgCl, $HgCl_2$ or $CuCl_2$ to excess $(C_2H_5)_2SiH_2$ gives favorable yields of $(C_2H_5)_2SiHCl$; similarly $HgBr_2$ and excess $(C_2H_5)_2SiH_2$ furnish new $(C_2H_5)_2SiHBr$. This general procedure seems to offer considerable promise in the preparation of alkylchlorosilanes or alkylbromosilanes with Si–H bonding.

Reaction of $(C_2H_5)_2SiH_2$ with a deficiency of iodine yields new $(C_2H_5)_2SiHI$, hydrolysis of which furnishes new $(C_2H_5)_2Si(H)O(H)Si(C_2H_5)_2$.

Discussion

Three different explanations for the reactions of $(C_2H_5)_3SiH$, $(C_2H_5)_3GeH$[1] and $(C_2H_5)_3SnH$[2] appear possible: heats of formation or free energies per equivalent of available halogen or oxygen in the compounds, also the appropriate ionization potentials of the elements, also, although they are definitely *not exactly comparable* and the value for silicon seems doubtful, oxidation potentials in aqueous solution. In the case of silicon the oxidation potential for Si(O) to Si(IV) is sufficiently questionable to eliminate any emphasis on it as a criterion.

Differences in bonding may have some importance. Triethylsilane reacts with $PtCl_4$ but not with K_2PtCl_6; $(C_2H_5)_3SiH$ reacts with 100% H_2SO_4 or HSO_3Cl but not with $C_6H_5SO_3Cl$. Triethylsilane does not react with powdered $KMnO_4$.

In keeping with available heats of formation or free energies, silicon has a strong preference for fluorine, oxygen or chlorine and a weaker preference for bromine or iodine. Triethylsilane and AgF yield a mixture containing at least $(C_2H_5)_3SiF$ and $(C_2H_5)_2SiF_2$.

Reactivity increases progressively from $(C_2H_5)_3SiH$ to $(C_2H_5)_3GeH$ to $(C_2H_5)_3SnH$ in reactions with halides of transitional elements or elements in regular groups. The *weak* acid CH_3COOH reacts

---

[1] H. H. Anderson, THIS JOURNAL, **79**, 326 (1957).

[2] H. H. Anderson, *ibid.*, **79**, 4913 (1957).

[3] H. J. Emeleus and S. R. Robinson, *J. Chem. Soc.*, 1592 (1947).

[4] F. C. Whitmore and others, THIS JOURNAL, **69**, 2108 (1947).

[5] B. N. Dolgov and others, *J. Gen. Chem. (USSR)*, **27**, 710 (1957).

TABLE I

REACTIONS OF $(C_2H_5)_3SiH$, 0.50 G./RUN. WITH INORGANIC SALTS AND ACIDS

Salt or acid at start			Reaction products				
			Chief product				
Compound	Wt., g.	Reflux, min.	Compound	B.p., °C.	Wt., g.	Yield %	Other products
$CuCl_2$	0.80	15	$(C_2H_5)_3SiCl$	145	0.59	91	$CuCl$, H_2
$CuBr_2$	.89	15	$(C_2H_5)_3SiBr$	164	.69	88	$CuBr$, H_2
$AgNO_3$	.43	20[a]	$(C_2H_5)_3SiOH$	155	.38	67	Ag, NO_2, $(C_2H_5)_3SiOSi(C_2H_5)_3$[b]
Ag_2SO_4	1.53	10	$[(C_2H_5)_3Si]_2O$	235	.44	83	Ag. SO_2. H_2O, $(C_2H_5)_3SiOH$[c]
Ag_2O	0.84	2[a]	$(C_2H_5)_3SiOH$	155	.22	45	Ag. O_2
$KAuCl_4$	0.68	10	$(C_2H_5)_3SiCl$	145	.60	92	KCl, Au, H_2
$HgBr_2$	1.57	75	$(C_2H_5)_3SiBr$	164	.65	78	Hg_2Br_2. H_2
$Hg(OCOCH_3)_2$	1.37	90	$(C_2H_5)_3SiOCOCH_3$	167	.69	91	Hg. CH_3COOH[d]
$HgSO_4$	1.26	3[a]	$[(C_2H_5)_3Si]_2O$	234	.49	91	Hg, SO_2. H_2O
VCl_4	0.43	5	$(C_2H_5)_3SiCl$	144	.57	87	VCl_3, VCl_2. H_2
$VOCl_3$	.57	15	$(C_2H_5)_3SiCl$	145	.56	87	$VOCl_2$. VOCl, H_2
CrO_2Cl_2	.20	3[e]	$(C_2H_5)_3SiCl$	143	.19	49	Cr_2O_3. H_2O
$MoCl_5$	.40	10	$(C_2H_5)_3SiCl$	144	.34	79	$MoCl_3$. $MoCl_2$.[f] $MoCl_4$,[f] H_2
$RuCl_2$	.69	12	$(C_2H_5)_3SiCl$	145	.48	74	Ru, H_2
$PdCl_2$	.38	20	$(C_2H_5)_3SiCl$	145	.58	90	Pd. H_2
$PtCl_4$	.43	25	$(C_2H_5)_3SiCl$	144	.45	68	Pt. H_2
$SnCl_4$	.59	4	$(C_2H_5)_3SiCl$	144	.47	72	$SnCl_2$. H_2
$SbCl_3$	.44	10	$(C_2H_5)_3SiCl$	142	.55	85	Sb. H_2
$BiCl_3$	.71	18	$(C_2H_5)_3SiCl$	144	.51	79	Bi. H_2
$SeCl_4$	.39	5	$(C_2H_5)_3SiCl$	144	.49	86	Se, H_2. HCl[f]
$TeCl_4$	.42	30	$(C_2H_5)_3SiCl$	145	.49	76	Te. H_2. HCl[f]
100% H_2SO_4	.46	10	$[(C_2H_5)_3Si]_2O$	236	.50	95	SO_2. H_2O
HSO_3Cl	.45	2[a]	$[(C_2H_5)_3Si]_2O$	236	.49	77	SO_2, HCl. H_2
15*M* HNO_3	.39	5[g]	$[(C_2H_5)_3Si]_2O$	232	.42	79	NO_2. H_2O. $(C_2H_5)_3SiOH$[h]

[a] After reaction ended. [b] Wt., 0.14 g. [c] Wt., 0.03 g. [d] Wt., 0.17 g. [e] Reaction in 0.15 ml. of CCl_4. [f] Small amount present. [g] Gentle reflux with caution. [h] Wt., 0.08 g.

rapidly with $(C_2H_5)_3SnH$ in reflux,[2] while the *strong* acid CF_3COOH is needed to convert $(C_2H_5)_3GeH$ into an ester in reflux[1]; CF_3COOH reacts with $(C_2H_5)_3SiH$ at a rate of approximately 4%/hr. in reflux. Oxygen in the air reacts most easily with $(C_2H_5)_3SnH$.[2]

Experimental

Equipment, similar to that used before,[1] included distilling units with ground joints, transfer micropipets, a pycnometer for density and some very small distilling units.

Triethylsilane and Diethylsilane.—Trichlorosilane and C_2H_5MgBr in diethyl ether yielded $(C_2H_5)_3SiH$. A solution of $(C_2H_5)_2SiCl_2$ and $LiAlH_4$ in di-*n*-butyl ether stood two days at room temperature; then distillation of $(C_2H_5)_2SiH_2$ from the unhydrolyzed mixture gave a 40% yield. Careful fractional distillation of each alkylsilane followed, with final storage in sealed glass tubes.

Starting materials other than commercial products included special preparations of $KAuCl_4$, VCl_4. $VOCl_3$, CrO_2Cl_2, $MoCl_5$, $RuCl_2$, $SeCl_4$ and $TeCl_4$. With the latter four, the same unit served for the reaction of chlorine with the appropriate element and later, after sweeping out the unused chlorine with dry air, for the reaction with triethylsilane. Heating the commercial hydrate furnished $CuCl_2$; heating H_2PtCl_6 for a short time at 300° yielded $PtCl_4$. All the solids were dry; if they were stable in air, they were powdered.

Reactions of $(C_2H_5)_3SiH$.—These followed the same general method used first with $(C_2H_5)_3GeH$[1] and later with $(C_2H_5)_3SnH$.[2] Table I lists yields based upon the starting materials present in the lesser amounts. Identification of the chief organosilicon product in Table I involved a primary total distillation to separate the chief organosilicon product from any non-volatile material such as CuCl or Pt, and then a fractional distillation to establish the identity and amount of the chief organosilicon compound. Rarely, a second fractional distillation was necessary. Volumes and boiling points of the various liquid fractions established the identities and amounts of the compounds formed in the reactions of $(C_2H_5)_3SiH$. Accepted b.p.s and densities are: $(C_2H_5)_3SiH$, b.p. 107°, d^{20}_4 0.730; $(C_2H_5)_3SiCl$, b.p. 144°. d^{20}_4 0.897; $(C_2H_5)_3SiBr$, b.p. 162.5°. d^{20}_4 1.140; $(C_2H_5)_3SiOCOCH_3$. b.p. 168°, d^{20}_4 0.903; $(C_2H_5)_3SiOH$. b.p. 154°, d^{20}_4 0.865; $(C_2H_5)_3SiOSi(C_2H_5)_3$, b.p. 231°, d^{20}_4 0.832. Identification of other products in Table I depended on physical properties of the metals, the color of NO_2, the odor of SO_2, the insolubility in water or the color of aqueous solutions of any solids such as $VOCl_2$ and VOCl, also the reducing power of $SnCl_2$ toward aqueous $HgCl_2$.

Reactions of $(C_2H_5)_2SiH_2$; **New Compounds.**—Five minutes reflux of 0.38 g. of $(C_2H_5)_2SiH_2$ and 0.48 g. of $PdCl_2$ gave 0.38 g. of $(C_2H_5)_2SiCl_2$, a yield of 91% based on $PdCl_2$. However, the same reaction with 1.1 moles of $(C_2H_5)_2SiH_2$ per mole of gradually added $PdCl_2$ gave only about a 10% yield of $(C_2H_5)_2SiHCl$; the reaction is too fast to allow good isolation of $(C_2H_5)_2SiHCl$. Addition of 1.58 g. of powdered AgCl to 1.72 g. of $(C_2H_5)_2SiH_2$ over 4 hr. produced 1.50 g. of $(C_2H_5)_2SiHCl$, b.p. 99°, for a yield of essentially 100% based on AgCl. The same amount of $(C_2H_5)_2SiH_2$ similarly gave 1.46 g. of $(C_2H_5)_2SiHCl$ after adding 3.00 g. of $HgCl_2$, letting stand 2 hr. and then giving 20 minutes of gentle warming and next five minutes of reflux; Hg_2Cl_2 formed, along with 0.02 g. of $(C_2H_5)_2SiCl_2$. Similarly 1.49 g. of $CuCl_2$ gave 1.59 g. of $(C_2H_5)_2SiHCl$ and 0.13 g. of $(C_2H_5)_2SiCl_2$; the main reduced product was CuCl, but some copper metal was present.

Nine g. of $HgBr_2$ and 4.14 g. of $(C_2H_5)_2SiH_2$ after standing for 55 hr. at 24° with soda-lime tube attached, then upon distillation furnished 5.97 g. of new $(C_2H_5)_2SiHBr$, b.p. 121.3° under 760 mm. pressure. Redistillation gave a center fraction of b.p. 121.3° under 760 mm., of n^{20} 1.449$_1$ and d^{20}_4 1.193. *Anal.* Calcd. for $(C_2H_5)_2SiHBr$: Br, 47.8; Si, 16.8; mol. wt., 167.14; *R* (Vogel), 37.64. Found: Br, 47.8, 47.7; Si, 16.4; mol. wt. (naphthalene), 179; *R*, 37.59.

Addition of 9.5 g. of I_2 to 4.14 g. of $(C_2H_5)_2SiH_2$ over a period of 1 hr. at 0° was followed by slow warming to room temperature. Then distillation in the presence of copper wire gave 8.75 g. of crude $(C_2H_5)_2SiHI$, the center 5.5 g. of which had the following properties: distillation range 84.3–84.7° under 91 mm.; b.p. 149.6° under 760 mm.; n^{20} 1.500$_2$; d^{20}_4 1.458; *R* (mol. refr.) 43.21. *Anal.* Calcd. for $(C_2H_5)_2SiHI$: I. 59.3; Si. 13.1; mol. wt., 214.14. Found: I. 59.1. 59.2; Si. 12.9; mol. wt. (naphthalene),

230. Qualitative tests showed the presence of Si–H bonding in the new bromo and the new iodo compounds.

Careful treatment of 5.40 g. of $(C_2H_5)_2SiHI$ with 7-, then 5- and then 3-ml. portions of water, with removal of the acid layer each time, finally yielded 2.58 g. of a liquid of density less than 1.00. Fractional distillation under 49 mm. pressure resulted in the rejection of 0.65 g. of b.p. 90–91.5°, followed by collection of 1.75 g. of b.p. 91.5–92.0°, while 0.20 g. of residue remained undistilled. This largest fraction of $(C_2H_5)_2Si(H)O(H)Si(C_2H_5)_2$ had these observed properties: b.p. 170.6° under 760 mm.; n^{20} 1.416_2; $d^{20}{}_4$ 0.820; *R* 58.95 (calcd., 58.72).[6] *Anal.* Calcd. for $(C_2H_5)_2Si(H)O(H)Si(C_2H_5)_2$: Si, 30.2; mol. wt., 192.54. Found: Si, 29.9; mol. wt. (camphor), 201. Also, Si–H bonding was present according to a test with alcoholic $AgNO_3$, or to the great care needed in the addition of concd. HNO_3 in analysis. This oxide had very little odor.

These last two preparative methods differ from those used with $(CH_3)_2SiHI$, b.p. 92°, and $(CH_3)_2Si(H)OSi(H)(CH_3)_2$, b.p. 73°, both b.p.s being extrapolated values.[7]

Other Reactions of $(C_2H_5)_3SiH$ Tried.—In the same procedure as in Table I $(C_2H_5)_3SiH$ failed to react appreciably in 15 minutes reflux with any of the compounds: HgO, $KMnO_4$, HgI_2, $SnCl_2$, $TiCl_4$, K_2PtCl_6, *n*-C_3H_7COCl (without $AlCl_3$), $GeBr_4$ or $C_6H_5SO_3Cl$. However, CF_3COOH in reflux appeared to give an ester at about 4%/hour; SbF_3 gave a small amount of $(C_2H_5)_3SiF$ evidently. In contrast to all these, AgF reacted vigorously with $(C_2H_5)_3SiH$ to give $(C_2H_5)_3SiF$ and at least $(C_2H_5)_2SiF_2$. Similarly, $(C_2H_5)_2SiH_2$ failed to react with K_2PtCl_6.

---

[6] A. I. Vogel, *J. Chem. Soc.*, 607 (1948); A. I. Vogel and others, *J. Phys. Chem.*, **58**, 174 (1954).

[7] H. J. Emeleus and L. E. Smythe, *J. Chem. Soc.*, 609 (1958).

PHILADELPHIA 4, PA.

[CONTRIBUTION NO. 2206 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

A Further Study of the Flash Photolysis of Iodine[1]

BY DON L. BUNKER AND NORMAN DAVIDSON[2]

RECEIVED MARCH 15, 1958

The rate of the third-order homogeneous gas-phase recombination of iodine atoms in the presence of argon has been remeasured by a flash photolysis technique. The data at 298°K., obtained in this Laboratory and two others, are now in substantial agreement. Measurements have been extended to 548°K. for comparison with shock tube results. The rate constant for the reappearance of I_2, over the full temperature range 298–1600°K., can be represented by $k = 2.98 \times 10^9 (298/T)^{1.33}$ $l.^2$ $mole^{-2}$ $sec.^{-1}$. If the third body is *n*-butane rather than argon, the measured rate constant from 298 to 493°K. is $3.5 \times 10^{10} (298/T)^{2.16}$. The third-body efficiencies of H_2 and D_2 were compared at 326°K. and found to be nearly equal. In the course of the above measurements the rate of the recombination reaction in which the third body is I_2 itself was determined. The ratio k_{I_2}/k_{Argon} is 600 near 300°K. and decreases markedly with increasing temperature. The rate constant k_{I_2} is given by $10^{4.65}T^{3/2}e^{5320/RT}$. A calculation of the effect of temperature inhomogeneity in a recombining system has been made; errors from this source were found to be negligible under our conditions.

The third-order homogeneous combination of iodine atoms has been extensively investigated in the gas phase by the method of flash photolysis. The over-all reaction may be written

$$I + I + M \longrightarrow I_2 + M \qquad (1)$$

$$d[I_2]/dt = k(M,T)[I]^2[M]$$

in which M represents any third body. The notation adopted for the rate constant indicates that it is a function of both the temperature and the nature of the third body M.

Early attempts to measure $k(A,T)$ by the flash photolysis of iodine in the presence of excess argon[3-5] produced somewhat misleading and contradictory results. The source of error was traced to the unexpectedly high efficiency of I_2 as a third body and to insufficient attention to thermal effects arising from the irradiation of the sample by the high energy flash.[6] This Laboratory and two others[7,8] have undertaken independent remeasurements of the room temperature rate of recombination in the presence of argon. The results of these three measurements are compared in this paper. We shall refer to references 7 and 8 as SCGW and CHNP, respectively.

Values of the same recombination rate have been obtained from measurements of the rate of dissociation of I_2 at 1000-1600°K. in a shock tube.[9] The results reported here include measurements in argon from room temperature to 548°K., which, when combined with the shock tube investigation and the high temperature data of SCGW, provide a fairly complete picture of the temperature dependence of this reaction. In the course of the temperature dependence investigation we have also carried out measurements at various temperatures in which *n*-butane, hydrogen or deuterium replaced argon as third body.

Experimental

The experiments were carried out in a horizontally mounted cylindrical furnace constructed by winding resistance wire over asbestos on an 18 inch length of 6 inch aluminum pipe. The temperature inside was spatially uniform and could be controlled to within 1°. The furnace was divided into two compartments by a horizontal layer of Corning

---

[1] (a) This work was supported by the Office of Naval Research. (b) Further experimental details may be found in the Ph.D. thesis submitted by D. B. to the California Institute of Technology, 1957. (c) Presented in part before the Division of Physical and Inorganic Chemistry, National Meeting of the American Chemical Society, New York, September 11, 1957.

[2] To whom inquiries concerning this paper should be addressed.

[3] R. Marshall and N. Davidson, *J. Chem. Phys.*, **21**, 659 (1953).

[4] K. E. Russell and J. Simons, *Proc. Roy. Soc.* (*London*), **A217**, 271 (1953).

[5] M. I. Christie, R. G. W. Norrish and G. Porter, *ibid.*, **A216**, 152 (1953).

[6] M. I. Christie, R. G. W. Norrish and G. Porter, *Disc. Faraday Soc.*, **17**, 107 (1954).

[7] R. L. Strong, J. C. W. Chien, P. E. Graf and J. E. Willard, *J. Chem. Phys.*, **26**, 1287 (1957).

[8] M. I. Christie, A. J. Harrison, R. G. W. Norrish and G. Porter, *Proc. Roy. Soc.* (*London*), **A231**, 446 (1955).

[9] D. Britton, N. Davidson, W. Gehman and G. Schott, *J. Chem. Phys.*, **25**, 804 (1956).