NOTES

Trimethylamine Adducts of the Chlorosilanes

By Anton B. Burg

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A recent reiteration of the belief that silicon cannot support a coördination number beyond four when chlorine atoms are employed as ligands[1] prompts me to report some experimental work on this subject, done early in the year 1940, but not pursued further since that time. It is just barely possible to demonstrate the existence of a trimethylamine adduct of silicon tetrachloride, and as chlorine is partially replaced by hydrogen, the electron-acceptor bonding effect is enhanced.

A mixture of 10.9 cc.[2] of $SiCl_4$ and 14.1 cc. of $(CH_3)_3N$, cooled to $-78°$ in the high-vacuum system, quickly produced a white solid from which the excess $(CH_3)_3N$ was recovered by distillation and measured as 3.1 cc. Hence the solid was the adduct $SiCl_4 \cdot (CH_3)_3N$. Its dissociation pressures are given in Table I.

Table I

Dissociation Pressures of $SiCl_4 \cdot (CH_3)_3N$

t, °C.	−68.8	−66.5	−65.2	−63.1	−56.2	−54.1
$p_{mm.}$ (obsd.)	0.70	0.99	1.15	1.54	3.87	6.10
$p_{mm.}$ (calcd.)	0.71	0.98	1.17	1.56	3.86	5.07

These results determine the equation $\log_{10} p_{mm.} = 12.62 - 2610/T$. Assuming complete dissociation into $SiCl_4$ and $(CH_3)_3N$ in the vapor phase, so that $K_{diss.}$ is $(0.5\ p_{atm.})^2$, this would mean that $\Delta F^0 = 23.89 - 0.0864\ T$ kcal./mole. Actually, the deviation of the mixed vapors from ideality is not much greater than expected for van der Waals' forces alone.

The observed pressure at $-54.1°$ deviates sharply from the calculated value because this temperature is just above the point at which the partial pressure of $SiCl_4$ from the adduct becomes equal to that of $SiCl_4$ vapor in equilibrium with liquid $SiCl_4$. Above that point, the solid complex is partially converted to liquid $SiCl_4$ with release of amine vapor, accounting for a sharp rise in the slope of the pressure–temperature curve at higher temperatures.

Trichlorosilane also forms a 1:1 adduct with trimethylamine: 5.7 cc. of the former and 7.4 cc. of the latter reacted well at $-70°$, with recovery of 1.60 cc. of amine, leaving a solid residue which began to develop an observable pressure at $-30°$. At 0° it registered a variety of pressures between 18 and 23 mm. and at room temperature it was even more variable. After treatment of the whole sample (below 20°) with aluminum chloride (freshly sublimed *in vacuo*) to remove the amine, the volatile part was quickly recognized as a mixture of chlorosilanes. The catalytic effect of the amine upon the disproportionation of the trichlorosilane was quite evident, and might be attributed to the formation of the adduct. A similar effect has been noted with chlorosilane.[3]

The 1:1 adduct of dichlorosilane with trimethylamine was somewhat more tractable, as well as less easily dissociated. A mixture of 11.75 cc. of H_2SiCl_2 and 33.50 cc. of $(CH_3)_3N$ reacted quickly at $-78°$ to form a solid, and 21.75 cc. of the amine was regained, partly by fractional condensation, so that the 1:1 ratio of reactants was precisely established in the residue. Two other samples of the adduct (2.10 and 4.80 cc.) were made with similar accuracy. An attempt to recognize an attachment of a second molecule of the amine at $-45.7°$ showed only a solid solution effect: thus as the ratio of $(CH_3)_3N$ to H_2SiCl_2 in the condensed phase was varied from 2.0 to 1.45 the pressure fell from 73 mm. to 28 mm., and then dropped still more sharply, to 1.0 mm. at a ratio of 1.42. It was for this reason that the 1:1 ratio could be established only by a repeated process of fractional condensation under high vacuum; the adduct was trapped at $-78°$, allowing the amine to pass on to a trap at $-196°$.

The dissociation pressures of $H_2SiCl_2 \cdot (CH_3)_3N$ are shown in Table II.

Table II

Dissociation Pressure of $H_2SiCl_2 \cdot (CH_3)_3N$

t, °C.	−9.5	−5.2	0.0	10.3	14.0	25.0	29.9
$p_{mm.}$ (obsd.)	1.36	2.11	3.57	8.63	11.8	28.7	42.2
$p_{mm.}$ (calcd.)	1.38	2.10	3.45	8.67	11.9	29.0	42.2

They determine the equation $\log_{10} p_{mm.} = 11.559 - 3010/T$; this represents very nearly perfect dissociation of the solid into its volatile components, H_2SiCl_2 and $(CH_3)_3N$, since the 4.80-cc. sample of the adduct registered a pressure of 49 mm. in a space of 164.8 ml. at 40°—only 3.5% lower than the sum of the separate vapors even though the mixture was only 8° above the point of final evaporation. Hence one can write with some confidence $\Delta F^0 = 27.55 - 0.0767\ T$ kcal./mole for the dissociation of the solid adduct into its component vapors.

The system SiH_3Cl–$(CH_3)_3N$ was studied briefly, with results very like those observed elsewhere,[3] including the adverse effects of disproportionation. No compound formation could be established between SiH_4 and $(CH_3)_3N$.

From a full comparison of the stabilities of the chlorosilane–trimethylamine adducts, it is clear that the steric effect of chlorine in holding the amine back from access to the Si atom is more important than the electronegativity effect, according to which a greater substitution of chlorine for hydrogen should improve the N–Si dative bond strength. Only as we compare $H_2SiCl_2 \cdot (CH_3)_3N$ with $H_3SiCl \cdot (CH_3)_3N$ do we find comparable stability; but as Emeléus and Miller point out, the latter case may well represent a quaternary ammonium salt.[3] For the amine adducts of the other chlorosilanes

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(1) W. C. Schumb and P. S. Cook, This Journal, **75**, 5133 (1953).

(2) The abbreviation cc. is here used to designate the volume of a gas at standard conditions.

(3) H. J. Emeléus and N. Miller, *J. Chem. Soc.*, 819 (1939).

such a salt-formation seems improbable, for a displacement of chloride as an ion would remove most of the steric hindrance, permitting the electronegativity effect to establish a stability order opposite to that which is observed. This argument would fail only if the differences of lattice energy were sufficiently favorable to the stability of the adducts of the less chlorinated silanes—and the lattice energies in such systems can scarcely be large enough to permit such significant differences.

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Decomposition of Fused Sodium Hydroxide by Fast Electrons

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An experiment was carried out to determine the stability of fused sodium hydroxide under high energy radiation. Approximately six grams of reagent grade NaOH (Baker C.P., 98.9% NaOH) was first melted under vacuum in a cylindrical nickel crucible. After cooling, the crucible was rapidly transferred to a Pyrex irradiation cell of the type shown in Fig. 1, and the system immediately evacuated. By use of a vertical Van de Graaff generator, the sample was irradiated for 40 minutes with 1.3 Mv. electrons at a current of 20 microamperes. This energy was sufficient to maintain the NaOH at about 400° (m.p. 318°). Upon analysis by a micro method, the only gas found in the gas phase was 0.05 ml. (S.T.P.) of hydrogen. This corresponds to an extremely small net yield of 4×10^{-4} molecule per 100 e.v. energy absorbed. Upon dissolving the solid in degassed water, no additional gas was found, and the resulting solution showed negligible oxidizing power. On repeating the experiment by merely heating a degassed sample in the absence of radiation, approximately the same amount of hydrogen was produced. This indicates that the fused NaOH is extremely stable to radiation and that the small amount of hydrogen probably resulted from reaction with the nickel crucible. The corrosion was not visibly observable.

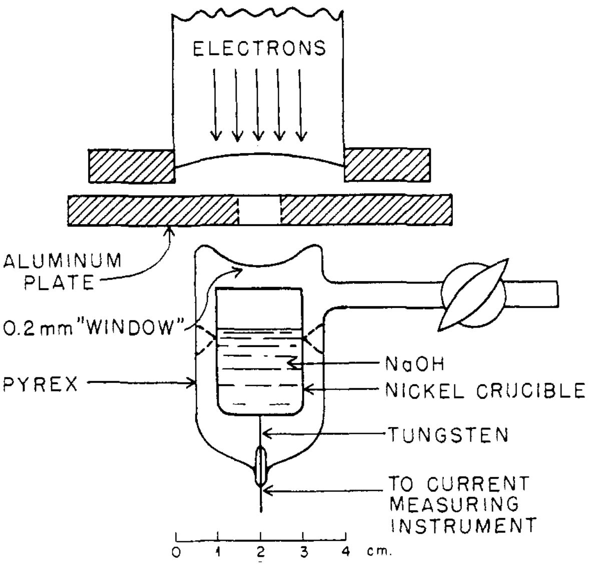

Fig. 1.—Apparatus for irradiating sodium hydroxide with electrons.

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Electrophilic Displacement Reactions. IV. Kinetics of the Brominolysis of *m*-Chlorobenzeneboronic Acid in Aqueous Solution[1-3]

BY HENRY G. KUIVILA AND EDWARD J. SOBOCZENSKI

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The kinetics of the reaction of bromine with *m*-chlorobenzeneboronic acid have been investigated in the *p*H range 2.10–4.74. The dependence of the rate upon bromide ion concentration and *p*H indicates that molecular bromine and the boronate anion are involved in the transition state of the rate-determining step. Sodium fluoride and several chelating agents have been shown to function as specific catalysts for the reaction.

The areneboronic acids comprise a valuable group of compounds for the study of mechanisms of aromatic electrophilic displacement reactions. This is true because the boronic acid group undergoes replacement by several electrophilic reagents at measurable rates. In a previous communication[4] an investigation of the kinetics of the reaction between bromine and benzeneboronic acid, yielding bromobenzene, hydrogen bromide and boric acid, in aqueous acetic acid solution was described. The results indicated that molecular bromine reacts with a quadricovalent boronate anion in the rate-determining step.

Due to the limitations imposed by the use of an acidic solvent it was decided to extend this work using water as the solvent. The rate of reaction between bromine and benzeneboronic acid in water proceeds too rapidly for measurement by the conventional method involving assay of aliquots. Of the several acids which could be conveniently studied in water *m*-chlorobenzeneboronic acid was chosen because it is more soluble than the other

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[1] For preceding publication in this series see H. G. Kuivila, THIS JOURNAL, **76**, 870 (1954).

[2] Taken in major part from the Master's thesis of E. J. Soboczenski, September, 1953.

[3] It is a pleasure to acknowledge substantial support of this work provided by the Office of Naval Research under Contract Nonr 806(01).

[4] H. G. Kuivila and E. K. Easterbrook, THIS JOURNAL, **73**, 4629 (1951).