[Contribution from the Mallinckrodt Laboratory of Harvard University]

THE PREPARATION AND HYDROLYSIS OF SOME ORGANOSILANOLATES

WILLIAM S. TATLOCK[1] AND EUGENE G. ROCHOW

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The metallic salts of the organosilanols have been described only briefly since the time of the first preparation by Ladenburg (1) of sodium triethylsilanolate, but recent interest is indicated by the publications of Sommer, Pietrusza, and Whitmore (2) and Sommer, Green, and Whitmore (3), who have investigated some of the physical properties and chemical reactions of sodium trimethylsilanolate. The utility of this and related compounds in silicone polymerization methods has been disclosed in the patent literature (4, 5). In the present investigation, a series of metallic organosilanolates has been prepared in order to study the general properties of this type of compound, and particularly to investigate the rate of hydrolysis.

It has previously been shown that although the action of a strong base on hexamethyldisiloxane resulted in the formation of an alkali metal silanolate, the competing demethylation reaction made it impossible to separate the products in a sufficiently pure form for the purposes of the present work (6). Consequently, the alkali metal salts of trimethylsilanol have now been prepared by direct reaction with the pure metals.

It was found that lithium metal reacts vigorously with a solution of trimethylsilanol in diethyl ether or in ligroin to yield lithium trimethylsilanolate. The solubility of lithium trimethylsilanolate in ligroin is rather high, but the product may be obtained as a white powder from a sufficiently concentrated solution. The solubility in ether is considerably less, but crystallization yields transparent anisotropic rhombohedra which rapidly become white and opaque on exposure to air. This behavior is not due to extensive hydration and appears to be due to loss of ether. The lithium salt does not display a sharp melting point, but decomposes on slow heating at a temperature as low as 120°. It hydrolyzes rapidly and completely to trimethylsilanol and an alkaline solution. This reaction apparently is not reversible at attainable concentrations of lithium hydroxide, since the addition of the silanol to a saturated solution of the hydroxide yielded no precipitate on prolonged stirring. The reaction of solid lithium hydroxide with trimethylsilanol results only in the dehydration of the silanol to the siloxane.

Sodium trimethylsilanolate has been characterized by Sommer, Pietrusza, and Whitmore (2), who obtained it as a white solid from the reaction of trimethylsilanol with 12 *N* sodium hydroxide. The solid was reported to be insoluble in anhydrous ethyl ether and to be recrystallized by dissolving a small portion in acetone and adding ether. However, we have found that when a clear solution of the sodium salt in ethyl ether is prepared by the action of

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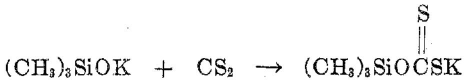
[1] Harvard University Procter and Gamble Fellow, 1948–1950.

metallic sodium on pure trimethylsilanol, it is impossible to obtain a filterable, crystalline product even when the solution is concentrated until distinctly viscous. It is necessary to remove the last trace of ether to obtain the sodium salt as a white, somewhat waxy solid. This material, in direct contrast to the properties previously reported, is exceedingly soluble in ether. These conflicting results would seem to indicate that when sodium trimethylsilanolate is formed in the presence of small amounts of water, a different solid phase is formed which may be hydrated. The product formed by action of sodium is believed to contain ether of solvation. It is possible to sublime the latter product *in vacuo* at a temperature of about 150° to obtain a white, hard-packed mass of extremely small, anisotropic, and presumably unsolvated crystals. As would be expected, the salt is extremely hygroscopic and hydrolyzes to sodium hydroxide and trimethylsilanol.

The potassium salt of trimethylsilanol also is formed by the action of the metal on trimethylsilanol. However, we found that two distinct forms of the product are obtained, depending, apparently, on the purity of the starting materials and solvent used. If a solution of pure trimethylsilanol in anhydrous ether is used for the reaction, a clear solution of the salt is obtained. If the solution then is concentrated until a precipitate appears and is allowed to crystallize slowly, it is found that the crystals formed are cubic, isotropic, and readily soluble in ether. When the reaction is carried out in moist ether and with pure trimethylsilanol, or with dry ether and a mixture of hexamethyldisiloxane and trimethylsilanol which contains some of the water of condensation of the silanol, copious amounts of a crystalline form precipitate during the course of the reaction from a rather dilute solution. This material is not soluble to any great extent in ether, and on microscopic examination is found to be anisotropic. Moreover, these crystals belong to the orthorhombic system. The potassium content of these anisotropic crystals is lower than the theoretical value, indicating the presence of an inert impurity. Moreover, when the crystals are heated at 100° they rapidly lose water. The loss in weight at 100° roughly corresponds to the inclusion of one mole of water for each mole of silanolate but the increase in potassium content (to a value greater than theoretical after heating) also indicates the presence of hydroxide contaminant in the original preparation.

Further evidence for the influence of water on the crystalline habit is obtained when small amounts of water are added to a clear ether solution of potassium trimethylsilanolate. In addition to the white powder of potassium hydroxide which forms immediately, crystals develop which correspond to the orthorhombic form just described.

Pure potassium trimethylsilanolate is practically insoluble in benzene and petroleum ether, but dissolves to a small extent in hexamethyldisiloxane. The salt sublimes slowly and with difficulty. A solution of the potassium salt in ether reacts with carbon disulfide in benzene with the precipitation of an orange-colored solid which has a strong mercaptan-like odor. This reaction may be analogous to the reaction of sodium alkoxides with carbon disulfide, and so may proceed according to the following equation:



$$(CH_3)_3SiOK + CS_2 \rightarrow (CH_3)_3SiO\overset{\overset{S}{\|}}{C}SK$$

In addition to the compounds mentioned thus far, samples of sodium triethylsilanolate, sodium triphenylsilanolate, and disodium diphenylsilanolate were found to result from the action of sodium on the proper organosilanol. These compounds were not investigated thoroughly, but were characterized by infrared spectroscopy.

The reaction of trimethylsilanolate with various alkylchlorosilanes (3) would indicate that some of the silanolates of the heavier and multivalent metals might be available through metathesis reactions with the metallic chlorides. The general equation for this reaction would be:

$$MX_n + n(CH_3)_3SiOK \rightarrow [(CH_3)_3SiO]_nM + nKX$$

An interesting series of compounds was found to result from this reaction. Using tin(II) chloride and sodium trimethylsilanolate, a crystalline salt of divalent tin was obtained, tin(II) trimethylsilanolate. This salt was readily soluble in common organic solvents, and in the solid form reacted slowly with water and more quickly with acid, with the formation of a water-insoluble liquid layer (hexamethyldisiloxane). A more vigorous reaction was obtained with tin tetrachloride and potassium trimethylsilanolate, yielding large transparent crystals of tin(IV) trimethylsilanolate. The crystals were soluble in organic solvents and even to some extent in mineral oil.

A similar salt, *bis*(trimethylsiloxy)dimethyltin was obtained by the reaction of dimethyltin dichloride with potassium trimethylsilanolate. The product was soluble in organic solvents and could be crystallized from benzene to yield glittering needles. The solid material did not seem to be wet by water, but the addition of small amounts of acid caused rapid hydrolysis with the formation of trimethylsilanol. When a methanol solution of the salt was added to water, it hydrolyzed rapidly to yield dimethyltin oxide, indicating that even the silanolates which are somewhat water-repellent hydrolyze rapidly in a homogenous medium.

Mercury(II) chloride reacted with sodium trimethylsilanolate in 1,4-dioxane to form a salt which was soluble in ether and in dioxane, and was so sensitive to traces of moisture that the final product always was contaminated with yellow mercuric oxide resulting from its hydrolysis.

With the availability of pure potassium trimethylsilanolate established, quantitative data concerning the rate of its hydrolysis were sought. Since the hydrolysis of each mole is accompanied by the appearance of one mole of strong base, one should be able to determine the rate of reaction as a function of the *p*H of the solution. However, when pure cold water was used for the hydrolysis, a solid sample of potassium trimethylsilanolate reacted so quickly that in less than five seconds the limiting value of the pH meter was reached. With water-dioxane mixtures, the apparent time of a hydrolysis could be increased, but it was found that the actual reaction was faster than the rate of solution of the salt or of the electrode response, so that the observed time merely reflected the particle size of the sample used and the high resistance of the hydrolysis medium.

It should be possible to establish at least the comparative rates of hydrolysis of the alkali metal silanolates by using an acid-base indicator in solvent which might be cooled well below 0° to slow down the reaction. Here again, however, the reaction time was found to be a function of the particle size of the sample, and it was shown that in solution potassium trimethylsilanolate was hydrolyzed immediately even at $-15°$. Since the hydrolysis reaction involves the production of a neutral molecule and two ions, the progress of the reaction should also be indicated by an increase in the dielectric constant of the hydrolysis mixture. However, measurements of dielectric constant during hydrolysis merely confirmed the rapidity of the reaction; no rates could be determined.

EXPERIMENTAL

Trimethylsilanol was prepared by the procedure outlined by Sommer, Pietrusza, and Whitmore (2).

Lithium trimethylsilanolate was prepared in petroleum ether (30–60°) by the reaction of metallic lithium with trimethylsilanol. When the trimethylsilanol apparently had completely reacted, the solution was vacuum-filtered through a sintered glass funnel under dry nitrogen. The white powder was transferred to a vacuum desiccator and the solvent was removed from the filtrate until solid material began to appear. Analysis of the solid for lithium was carried out by dissolving a sample in standard acid and back-titrating with standard base.

Anal. Cal'cd for C_3H_9LiOSi: Li, 7.22. Found: Li, 7.05.

Other preparations were carried out in ethyl ether instead of petroleum ether and transparent rhombohedra were obtained, but during the filtration and subsequent transfer they became a chalky white. The lithium content was determined as before, and found to be 7.1%. The crystals were anisotropic, with 90° extinction in three directions. They could be sublimed at a pressure of about 1 mm. and a temperature of about 180° to yield fine, transparent needles.

In an attempt to prepare the lithium salt by the reaction of trimethylsilanol with lithium hydroxide, trimethylsilanol was added with stirring to a saturated solution of lithium hydroxide. Two layers were formed, with no signs of solution or precipitation. Stirring was continued for 12 hours with no change in this condition. In a second trial, solid lithium hydroxide was shaken for three days in a stoppered flask containing trimethylsilanol. At the end of this time, a white solid persisted under the liquid layer. A sample of this solid was analyzed and was found to be hydrated lithium hydroxide, apparently produced by the dehydration of trimethylsilanol to hexamethyldisiloxane.

Sodium trimethylsilanolate was prepared by the action of sodium on trimethylsilanol. The reaction was very vigorous and at times the flask was cooled with cold water to slow the evolution of hydrogen. When the sodium no longer reacted, the excess was removed. Ether was evaporated slowly from the clear solution but no precipitation appeared even at a concentration where the liquid had become quite viscous. Cooling to $-78°$ yielded a solid mass of crystals, but on slight warming a clear solution was again obtained. A portion of the ether solution was evaporated to the viscous point and frozen at $-78°$. The flask was then evacuated and left under reduced pressure in an attempt to remove the ether, but after 12 hours no change could be observed and on warming to room temperature a solution was once more obtained containing no crystalline product. Another sample was evaporated to complete dryness on a steam-bath, leaving an amorphous-looking white mass of sodium trimethylsilanolate. On addition of a small amount of ether the white solid began to dissolve with the evolution of heat as soon as the first vapors touched it. It was found that the dry solid could be purified only by sublimation at 150°. Analysis of the sublimed and unsublimed materials was carried out by titration as before.

Anal. Calc'd for C_3H_9NaOSi: Na, 20.5. Found: Na, 20.6 (sublimed salt), 22.8 (unsublimed salt).

Potassium trimethylsilanolate was made in a similar manner and was purified by recrystallization from ether. The large cubic crystals were filtered and washed with a little cold petroleum ether, and the potassium content was determined by titration.

Anal. Calc'd for C_3H_9KOSi: K, 30.5. Found: K, 29.2.

Because preliminary experiments had yielded hexagonal plates instead of cubic crystals, the preparation was repeated using pure trimethylsilanol and damp ether. The product precipitated from a dilute solution, and microscopic examination showed the crystals to consist of rhomb-shaped tablets with obtuse angles of 120°, or various irregular, six-sided forms, all six angles of which were 120°. All of the crystals were anisotropic, and in the case of the diamond-shaped crystals, the planes of vibration were at angles of 90° parallel and perpendicular to the long axis. This behavior is consistent with the orthorhombic system.

A sample of the orthorhombic crystals was heated to 100° *in vacuo* and a small amount of volatile product distilled over into a cold receiver. This material was a liquid at room temperature and was odorless; when a small amount of anhydrous copper sulfate was added, a blue color formed indicating the presence of water. The orthorhombic form must therefore be considered to be a hydrate.

The cubic form of potassium trimethylsilanolate decomposed on a hot stage at 131–135°. Decomposition of the orthorhombic form began as low as 125°, and a new solid phase appeared which seemed to melt with ebullition at 140–150°. Measurements of the density of the crystals were carried out in a bottle pycnometer, using mercury as the displaced liquid: cubic form, 1.11 g./cc., orthorhombic form, 1.21 g./cc., both at 25°.

The *sodium salts* of triethylsilanol, triphenylsilanol, and diphenylsilanediol were prepared from the silanols by the methods previously described. The infrared absorption spectra of these compounds will be found in Figure 2.

Tin(II) trimethylsilanolate was prepared by the metathetical reaction of anhydrous stannous chloride with sodium trimethylsilanolate in 1,4-dioxane. The solution was filtered by suction in a dry-box and dioxane was completely removed from the filtrate under reduced pressure, leaving a hard, white solid. This residue was found to dissolve readily in petroleum ether and ethyl ether, and when a solution in ethyl ether was concentrated to near dryness and cooled with trituration, a crystalline product separated. When the ether was completely removed, a clear glass was obtained. An analysis for divalent tin was carried out by hydrolyzing a sample of the salt in excess acid and titrating the solution with a standard solution of iodine to an end-point with starch as indicator.

Anal. Calc'd for $C_6H_{18}O_2Si_2Sn$: Sn, 39.8. Found: Sn, 35.0.

An infrared absorption spectrum was taken and the presence of methyl groups and silicon-methyl bonding was established.

Tin(IV) trimethylsilanolate was prepared in a similar manner from potassium trimethylsilanolate and tin tetrachloride in ether. The mixture was refluxed for three days and then centrifuged, and the clear ether layer was evaporated to a small volume. After four days, large well-formed crystals had grown in the solution. These crystals apparently belonged to the monoclinic system, in which flattening had occurred perpendicular to the plane of symmetry. Extinction occurred at 90° intervals, parallel and perpendicular to the long axis of the principal view. The density was determined in a bottle pycnometer, using mercury, and was found to be 1.41 g./cc. at 25°. The infrared absorption spectrum appears in Fig. 1.

bis(Trimethylsiloxy)dimethyltin was prepared from potassium trimethylsilanolate and dimethyltin dichloride.[2] After refluxing for three hours, the resulting mixture was cen-

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[2] This sample was kindly furnished by A. C. Smith, Jr., Metal and Thermit Fellow, Harvard University.

trifuged to yield a clear ether solution and a white, gummy solid. The ether was evaporated and the flask was cooled to yield crystals which were recrystallized once from benzene with the formation of small glittering needles. The density of the crystals was found to be 1.56 g./cc. at 25°.

Mercury (II) trimethylsilanolate was prepared by the reaction of sodium trimethylsilanolate with powdered mercuric chloride. The solution was filtered in a dry-box, and the dioxane solution was evaporated under reduced pressure to yield a light-colored residue. The infrared absorption spectrum of this material indicated the presence of methyl groups bonded to silicon (Fig. 1).

Infrared absorption spectra of the silanols and their salts described herein were obtained using a Baird Recording Spectrophotometer, and are shown in Figures 1 and 2. The spectra for trimethylsilanol, triethylsilanol, and tin(II) trimethylsilanolate were obtained by using 4% solutions in carbon tetrachloride in the range from two to seven microns, and a 2% solution in carbon disulfide in the range from seven to sixteen microns. The entire spectrum for triphenylsilanol was covered using a 4% solution in carbon disulfide. All of the other substances, including diphenylsilanediol, were used by grinding in mineral oil and coating the suspension on plates of sodium chloride. No assignments have been made, but the spectra have proved useful in the identification of important groups. It has been shown in a qualitative way that the strong absorption band which appears near 8 μ in methyl siloxane systems is some function of the Si—CH_3 grouping (7). The presence of this band in the spectra of trimethylsilanol and the salts prepared from it show that this absorption is not peculiar to the siloxane systems (8). It is interesting to note that in the silanol series association of the hydroxyl function may readily be demonstrated. The sharp peak at 2.7 μ thus corresponds to the stretching vibration of the free hydroxyl group, while the rounded peak near 3 μ represents the associated or bonded silanol. The effect of dilution in increasing the ratio of unbonded to bonded hydroxyl functions also is demonstrated. In the case of the solid diphenylsilanediol, the large proportion of association in the solid state is shown by the large peak at 3.1 μ. Similar results have been reported by Richards and Thompson (9) for the phenylsilanols.

The *hydrolysis* of potassium trimethylsilanolate first was studied by following the *p*H of the reaction mixture with a Beckman *p*H meter equipped with a high-*p*H electrode. The reactions were carried out in an open beaker and the hydrolysis solution was stirred with either a magnetic or an air-operated stirrer. It was necessary to use as high as 30 mole-% of water and to saturate the solution with an electrolyte to obtain stable readings, but even then it was not possible to reproduce the values from one trial to the next. The samples of potassium trimethylsilanolate were weighed in a thin glass bulb which was broken beneath the surface of the solution at zero time, and the rising values of the *p*H were followed by manual operation of the dial at five-second intervals. While the results of several runs were consistent, on the basis of the experiments with indicators which follow it is evident that the rate of solution (rather than the rate of hydrolysis) was being observed.

In an attempt to establish relative rates of hydrolysis by using solutions of indicator, 20 ml. of acetone, 5 ml. of water, and ten drops of a stock solution of Alizarine Yellow were stirred in a beaker at $-15°$. Samples of solid potassium trimethylsilanolate were introduced as before, and the time of hydrolysis was measured to the development of the basic color, using a blank as a standard. In the first four runs the time of hydrolysis was about proportional to the amount of material used. Inconsistent results were obtained with more finely divided material, however, indicating that the state of subdivision of the added sample must have been of importance in determining the apparent rate of hydrolysis. A *solution* of the potassium salt in ether was added to the standard hydrolysis mixture, and in this homogeneous medium, the color change was nearly instantaneous .

The instrument described by Fischer (10) for the measurement of dielectric constant over wide ranges was used in the final investigation. It was intended to utilize a solution of potassium trimethylsilanolate, and, by adding small amounts of water, to obtain the change in dielectric constant with respect to time. Using an ether solution of the potassium

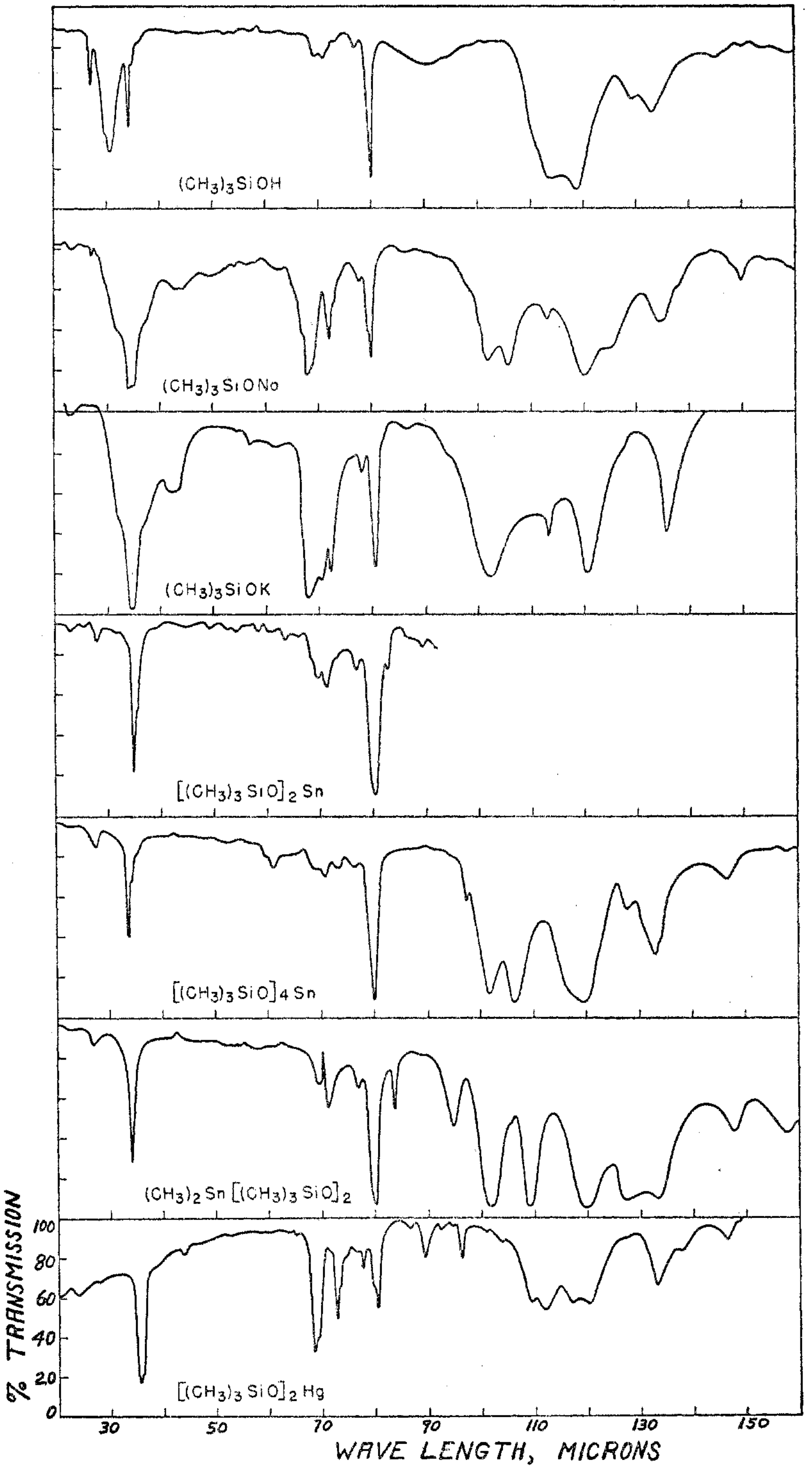

Fig. 1. Infrared Adsorption Spectra of Trimethylsilanol and Related Salts

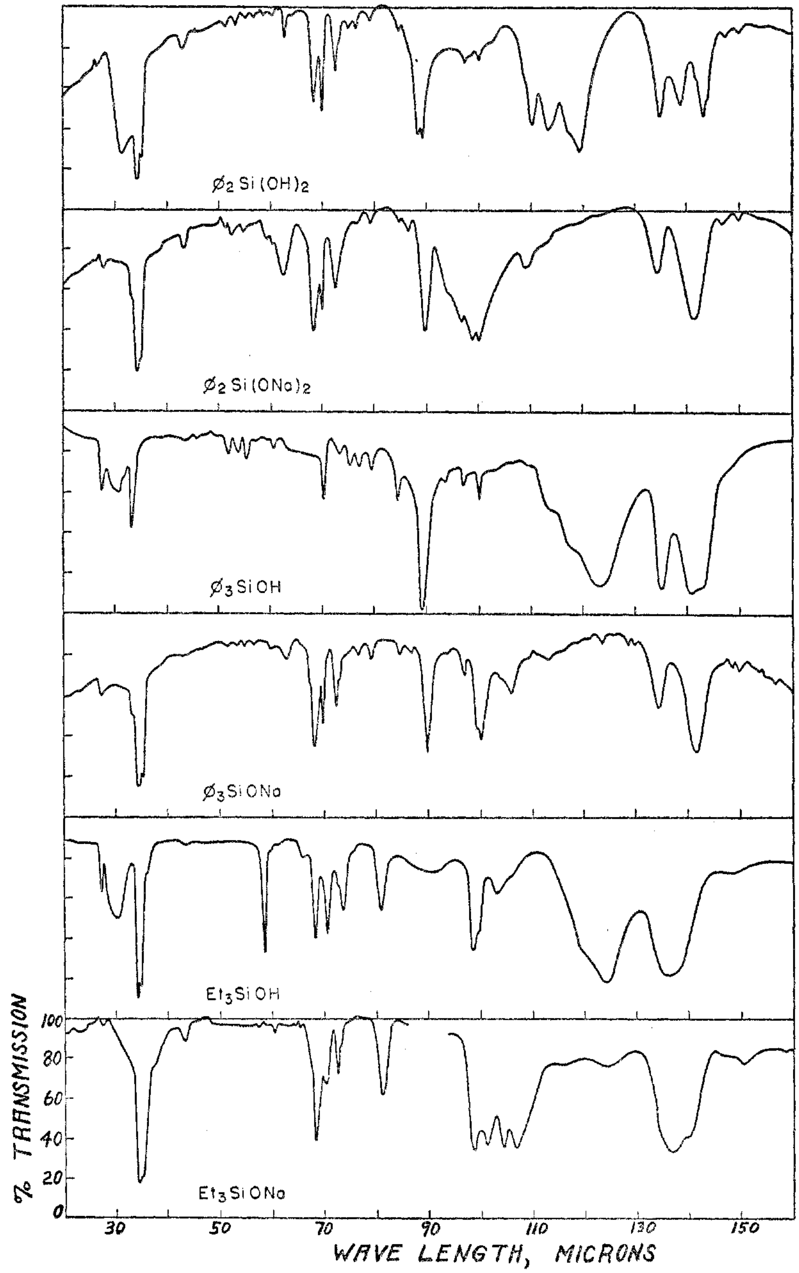

FIG. 2. INFRARED ADSORPTION SPECTRA OF TRIETHYLSILANOL, TRIPHENYLSILANOL, AND DIPHENYLSILANEDIOL AND THEIR NA SALTS.

salt, no significant change in the dial reading could be obtained upon addition of water, probably due to the lack of solubility of potassium hydroxide in this solvent. Other variations were equally unsuccessful in obtaining useful data, except to substantiate the very rapid hydrolysis already shown.

SUMMARY

The sodium, lithium, and potassium salts of trimethylsilanol have been prepared, and their chemical and crystallographic properties studied. The hydrolysis of potassium trimethylsilanolate has been found to be so rapid even at −15° and low concentrations of water as to make measurements impossible. Metathetical reactions of sodium and potassium trimethylsilanolates have yielded the new compounds tin(II) trimethylsilanolate, tin(IV) trimethylsilanolate, and *bis*(trimethylsiloxy)dimethyltin.

CAMBRIDGE, MASSACHUSETTS.

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