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INFRARED ABSORPTION SPECTRA OF ALKYLSILANES

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In connection with a program at this laboratory involving the preparation and physical properties of alkylsilanes, twelve compounds of this type have been prepared in high purity and their infrared spectra have been determined on a Baird double-beam recording spectrophotometer employing sodium chloride optics. The compounds synthesized consisted of all the methyl- and ethyl-silanes as well as *n*-butyl-, isobutyl-, vinyl-, and dimethyldi-*n*-propyl-silane. The preparation of compounds with Si—H bonds was accomplished by the reduction of the appropriate alkylchlorosilane with lithium aluminum hydride in dioxane, except for triethylsilane in which preparation ether was the solvent. The tetrasubstituted homologs were prepared by condensing the appropriate alkylchlorosilane with excess Grignard reagent (1).

Comparison of the infrared spectra of our dialkylsilanes with those of West and Rochow (2) disclosed the conspicuous absence of an intense absorption band at 7.8–8.5 μ in their spectrograms. This apparent discrepancy became readily understandable, however, when it was noted that their spectra were obtained by dissolving the compounds in chloroform which has such a strong absorption in the region 7.8–8.3 μ that the effect of the alkylsilane absorption was completely masked. For those spectra in Figure 1 (parts 1–3) where solvents were used, carbon tetrachloride was used below 7.6 μ and carbon disulfide was used above 7.6 μ. The masking effect by solvents was thereby avoided.

Inspection and comparison of these data with other available spectra permit the following confirmations and observations to be made. The absorption in the 7.8–8.3 μ region may be attributed to an Si—CH_2R frequency as has been pointed out by Tatlock and Rochow (3). When $R = H$ the absorption band appears at 7.8 μ; when $R = CH_3$ it appears at 8.1–8.2 μ. The same absorption band seems to appear at 8.3 μ in dimethyldi-*n*-propylsilane and at 8.4–8.6 μ in the butylsilanes. Further evidence that the band can be assigned to the silicon-methylene frequency is the absence of the band in vinylsilane.

It has been suggested (4) that the small absorption band at 8.8 μ might be due to ether. However, our reaction solvent was dioxane except for the tetraethyl-, triethyl-, and dimethyldi-*n*-propyl-silane preparations for which ether was used. It is pertinent nevertheless that dioxane also has an intense absorption band at 8.88 μ and a weaker one at 7.98 μ. It is therefore of interest to examine the possibility that those compounds which could not have been contaminated with ether might have retained dioxane as an impurity.

On the basis of the following evidence the authors feel that the weak absorption band at 8.8 μ is not due to either dioxane or ether solvent although the possibility is not entirely ruled out. First, it is not present in vinyl- and ethylsilane and is extremely weak in methylsilane. Second, the weak band is more discernible in the spectra of diethyl-, dimethyl-, and trimethyl-silane, but the boiling points of dimethyl- and trimethyl-silane are −19.6° and 6.7°, respectively, so separation from dioxane (b.p. 101°) is believed to be excellent. Freezing point curves for the purity of the products bear this out. Third, the

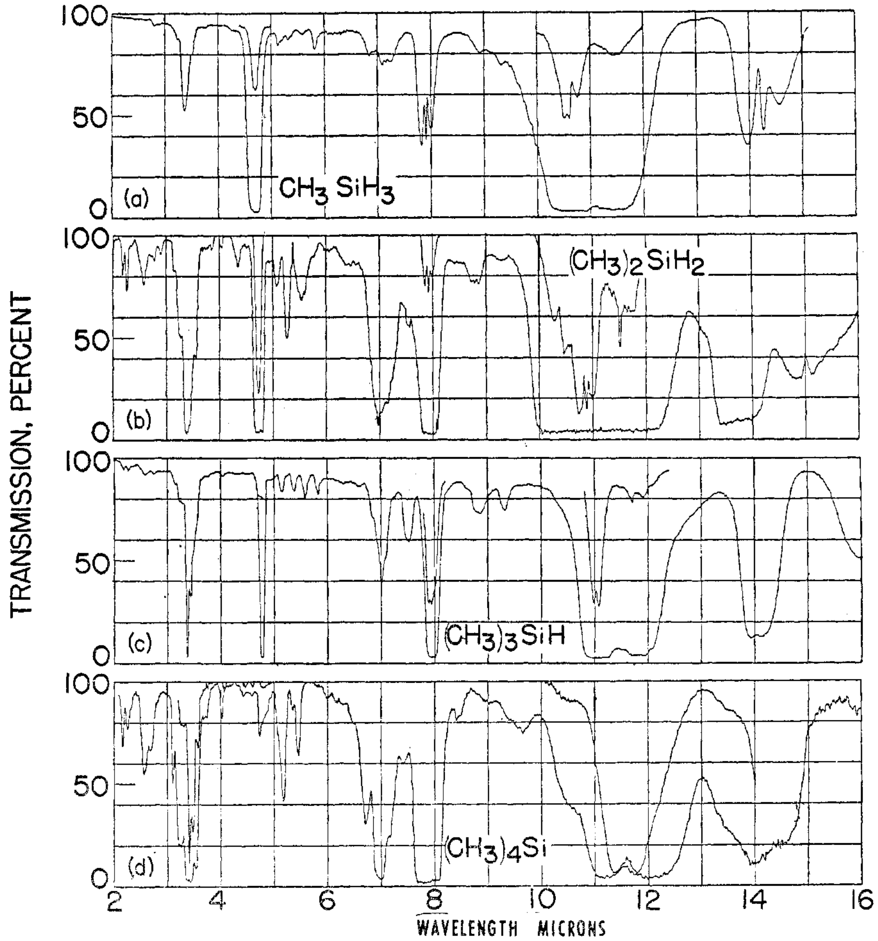

FIG. 1. (PART ONE). (a) Upper, 4 mm.; lower, 120 mm. (b) Upper, 13 mm.; lower, 740 mm. (c) Upper, 11 mm.; lower, 130 mm. (d) Upper, 99 mm.; lower, 600 mm.

absence of the intense band at 8.8 μ when the less intense band at 8.0 μ is present (ethyl-, butyl-, and vinyl-silane) is convincing evidence that the 8.0 band is not due to dioxane. This observation is doubly important because the Si—CH_2 absorption occurs at that wave length.

The band in the region 4.7–4.8 μ is definitely to be attributed to an Si—H frequency. It disappears suddenly for tetramethyl- and tetraethyl-silane in the methyl and ethyl series, in which compounds the silicon is completely substituted and no Si—H bonds remain. It is also absent in dimethyldi-*n*-propylsilane, but is present in vinylsilane.

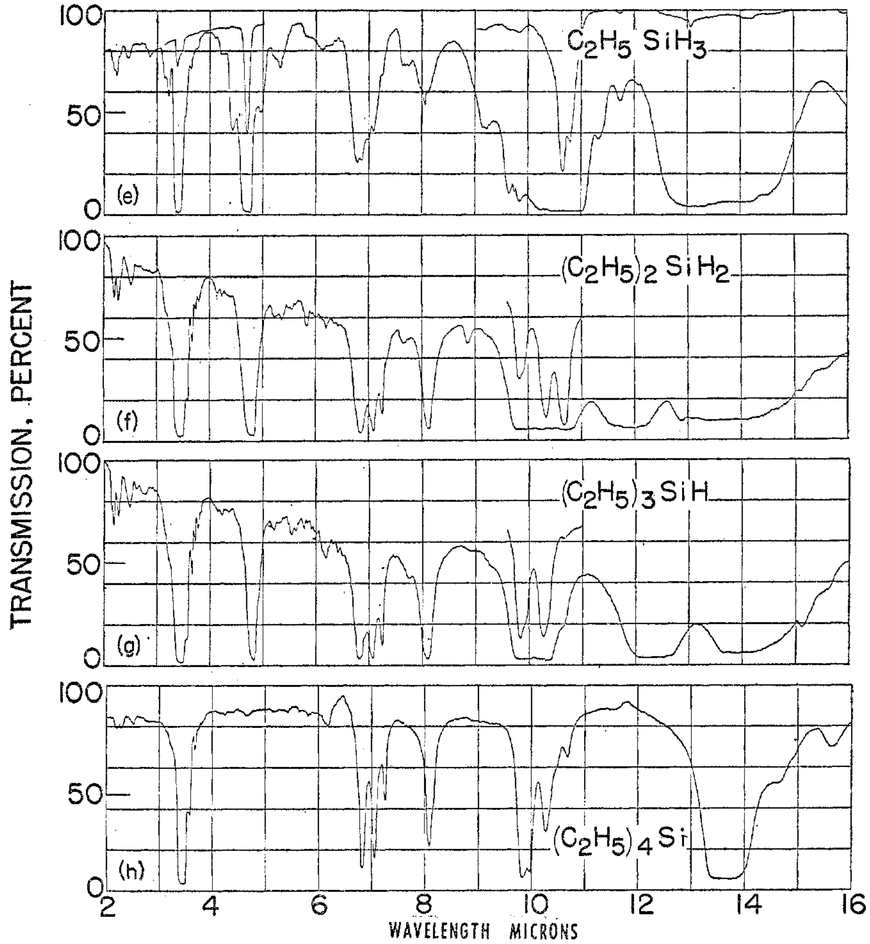

FIG. 1. (PART TWO). (e) Upper, 6 mm.; lower, 350 mm. (f) and (g) Upper, liquid phase diluted 1:10 with CS_2; lower, liquid phase undiluted. (h) Liquid phase diluted 1:5 with CCl_4 from 2.0 to 7.6 μ and diluted 1:5 with CS_2 from 7.6 to 16 μ.

EXPERIMENTAL

The alkylchlorosilanes were obtained from the Dow Corning Corporation in the purest grade available. Tetramethyl- and vinyltrichloro-silane were obtained from Anderson Laboratories, Inc. Lithium aluminum hydride was purchased from Metal Hydrides, Inc. Dioxane was a Carbide and Carbon Chemicals Co., commercial grade and was purified by percolation through a 10-foot column of alumina. The effluent liquid showed no reaction with lithium aluminum hydride indicating the absence of peroxides, aldehydes, and water.

Preparation of methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, triethyl-, butyl-, and vinylsilane. The general procedure has been described in a previous publication from this laboratory (5) and differs from the original method of Finholt, *et al.* (6) only in that dioxane was used as a solvent instead of ether, except for the preparation of triethylsilane. This permitted stripping the products as formed through a reflux condenser. Volumetric measurement of the hydrogen evolved when the purified product was treated with alcoholic potassium hydroxide gave 95 to 99% of the volume calculated for complete hydrolysis. The purity of our products is estimated to exceed 97%.

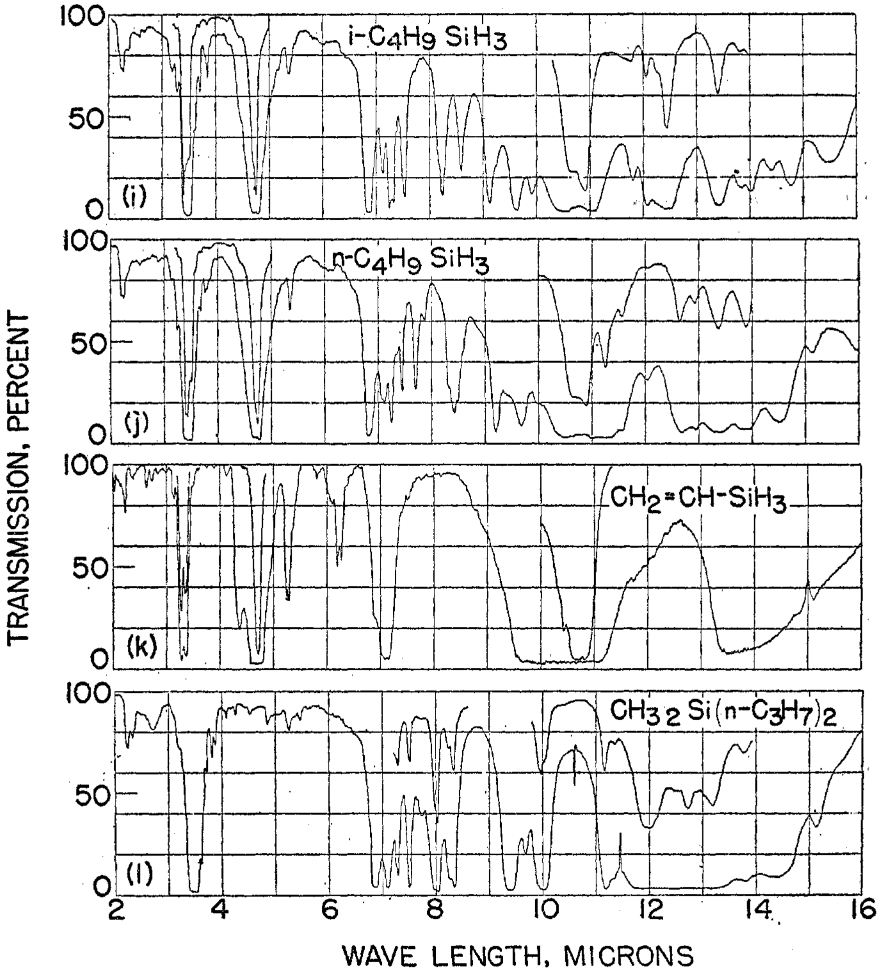

FIG. 1. (PART THREE). (i) and (j) Upper, liquid phase diluted 1:10 with CCl_4 from 3.2 to 5.0 μ and 1:10 with CS_2 from 10 to 14 μ; lower, liquid phase undiluted. (k) Upper, 70 mm.; lower, 740 mm. (l) Upper, liquid phase diluted 1:5 with CS_2; lower, liquid phase undiluted.

Tetramethylsilane. This material was purchased and purified by distillation over lithium hydride through a five-foot vacuum jacketed column packed with glass helices followed by percolation of the distillate through silica gel to remove traces of halide.

Tetraethylsilane and dimethyldi-n-propylsilane. These compounds were prepared by condensing silicon tetrachloride with excess ethylmagnesium chloride for the first compound and by condensing *n*-propylmagnesium bromide with dimethylsilicondichloride for the second compound. The ether layers containing the product were washed, distilled, and finally fractionally distilled in a Podbielniak column rated at an efficiency equivalent to approximately 140 theoretical plates. These compounds could be handled in a conventional combustion train for analytical purposes.

Anal. Calc'd for tetraethylsilane ($C_8H_{20}Si$): C, 66.57; H, 13.98; Si, 19.45.
Found: C, 66.58, 66.73; H, 14.08, 14.09; Si, 19.36, 19.45.
Calc'd for dimethyldi-*n*-propylsilane ($C_8H_{20}Si$): C, 66.57; H, 13.98; Si, 19.45.
Found: C, 66.60, 66.54; H, 14.11, 14.01; Si, 19.38, 19.38.

Infrared absorption spectra were determined with a Baird recording spectrophotometer. The experimental details are noted on the figures of the spectra. In general, undiluted samples were determined in a 0.1-mm. liquid cell or a 5.0-cm. gas cell. Where dilution was required carbon tetrachloride was used as solvent below 7.6 μ and carbon disulfide above 7.6 μ. The pressure of the compounds in the gas cell was adjusted to give the optimum results.

Acknowledgments. Analyses were by Huffman Microanalytical Laboratories, Wheatridge, Colorado. We wish to express our gratitude to Mr. R. R. Hibbard for help in the analysis of the spectra.

SUMMARY

Twelve alkylsilanes including all the methyl and ethyl homologs have been prepared and purified. The infrared absorption spectra of these compounds have heen presented.

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