Infrared Spectra of Alkylsilanes I

HENRIK WESTERMARK

Department of Organic Chemistry, University of Lund, Lund, Sweden

The infrared spectra of 26 alkylsilanes and 2 phenylsilanes have been recorded between 2—15 µ. The wavelength shifts of =SiH, =SiH₃ and SiH₄ groups in the range 4.6—4.8 µ are reported as well as key bands of alkylsilanes containing =SiH₃, =SiH₂, =Si(CH₃)₂ and =Si(CH₃)₃ in the range 10—15 µ.

Data on infrared absorption intensities of organic silicon compounds are scarce in the literature. A comparison of spectra of homologues of n-alkylsilanes revealed a qualitative relationship between the length of n-alkyl-groups and the intensity of some absorption bands. In a subsequent paper numerical data on the intensities of five absorption bands between 6.8 and 8.5 µ will be given.

All the silicon hydrides strongly absorbed at 4.6—4.75 µ. It was found that the absorption wavelength was dependent on the number of hydrogen atoms bonded to the silicon atom in alkylsilanes. Thus all monoalkylsilanes (=SiH₃) absorbed at 4.62 µ, the dialkylsilanes (=SiH₂) at 4.68—4.69 µ and the trialkylsilanes (=SiH) at 4.74 µ. Diphenylsilane absorbed at 4.64 µ and triphenylsilane at 4.68 µ.

Of the three alkyilsilane absorption bands between 6.8 and 7.3 µ (see the figures on pp. 948—951) two are also found in the spectra of paraffins. The C—H bending vibrations in methyl (asymmetric) and methylene groups appear at 6.85—6.86 µ and the symmetric C—H bending vibrations of the methyl groups at 7.27 µ. Near 7.1 µ alkyl silanes give absorption which is not found for corresponding alkanes. Alkyilsilanes containing propyl or higher n-alkyl groups absorb at about 7.5 µ. For butyl or longer chains there are some weak absorption bands between 7.5—8.0 µ, in which range CH₂ wagging and twisting modes appear in the alkane spectra.

In the range 7.8—8.6 µ the alkyilsilanes absorbed in the way described by Kay and Tannenbaum ¹ and Harvey et al ².

The range 10—15 µ shows absorption bands which are useful for the correlation of chemical structures of alkyilsilanes. All the monoalkylsilanes investigated showed strong absorption in 10 % solution in carbon disulfide at 10.6—11.0 µ which on dilution to 1 % solution resolved into two bands at 10.6—
10.7 μ (medium) and 10.85 μ (very strong). The —SiH₃ group gave a characteristic triplet of bands of moderate strength at 13.4—13.5, 14.0 and 14.4—14.5 μ. The dialkylsilanes, i. e., compounds containing the =SiH₃ group, all gave a strong band in 10 % solution, medium in 1 % solution, at 10.6—10.7 μ. However, the very strong band at 10.85 μ for the —SiH₃ group was not found here. Weak absorption at 11.2 μ and 14.0 μ was found in the spectra of all dialkylsilanes, but does not seem to be of great value for the correlations.
The tetraalkylsilanes containing the trimethylsilyl group showed strong absorption at 11.6—12.1 μ in 10% solutions in carbon disulfide. In 1% solution the absorption resolved into two bands of about equal strength at 11.6—11.7 μ and 12.0 μ. Wright and Hunter reported the Si—C stretching mode to appear at 11.63 μ in tetramethylsilane and at 11.88 μ in terminal groups O—Si(CH₃)₃ of linear methylpolysiloxanes. Further the trimethylsilyl group gave a less prominent band at 14.4—14.5 μ. The alkylsilanes containing

the group \(-\text{Si}-(\text{CH}_3)_2\) also show strong absorption at 12.0 \(\mu\) in both 10 % and 1 % solutions. This type of compounds can be distinguished from alkyltrimethylsilylamine through the absence of the 11.7 \(\mu\) band.

All the bands in the range 10–15 \(\mu\) described here are, if not otherwise stated, characteristic for the configurations of the investigated substances and should be suitable for identification purposes.

EXPERIMENTAL

The spectra were recorded with a Beckman spectrophotometer model IR-2, equipped with a rock salt prism, and a Brown Electronik pen recorder. Calibration of the wavelength scale was carried out against the values given by Oetjen et al. for CO₂: 4.225, 14.97 μ and H₂O: 6.903 μ. The cell thickness was 0.10 mm. All spectra were measured in about 10% solutions in the wave length range 2-15 μ. In some cases spectra of pure substances or of about 1% solutions were recorded. Carbon tetrachloride was used as the

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solvent between 2 and 8 µ and carbon disulfide in the range 7.6—15 µ. In the figures on
pp. 948—951 the concentrations are given as follows: A ca. 10 %; B ca. 1 %; C = pure
substance.

All molecular refractivities were calculated in the manner previously described 4.
The bond refractivity of the silicon chlorine bond, 7.20, given by Warrick 4 was used.

Preparative part

The substances containing Si-H bonds were prepared by reduction of alkylethoxysilanes 5 or of chlorosilanes with lithium aluminium hydride. The chlorosilanes were prepared either from silicon tetrachloride and alkylmagnesium chloride or from disiloxanes according to the methods of Flood 7 or Voronkov et al. 8

The tetraalkysilanes were prepared from alkylchlorosilanes and alkylmagnesium chloride or bromide or purified from material available in this laboratory. Dimethylid-i-n-propylsilane and methyltri-n-propylsilane were identical to the samples previously reported 9. The methyl-n-butylsilanes were samples from the work of Larsson and van der Gisle van der Pals 10. The refractive indices of the used samples were remeasured.

Trimethylsilane and trimethyl-n-propylsilane were prepared from trimethylchloro-
silane and the appropriate Grignard reagent according to method II of Whitmore et al.11 (These authors used another method for the preparation of the substances described here).

The preparation of trimethyl-n-propylsilane may be described as an example for both synthesis.

-n-Propylmagnesium chloride was prepared from 7.2 g (0.3 g atom) of magnesium, 23.7 g (0.3 mole) of n-propyl chloride, and 40 ml of anhydrous ether in a 500 ml apparatus. To the solution was added 11 g (0.1 mole) of trimethylchlorosilane dissolved in 15 ml anhydrous ether during 20 minutes and the reaction mixture was boiled for one hour. After hydrolysis with 5 N hydrochloric acid, distillation of the product gave 7.5 g (65 %) of trimethyl-n-propylsilane boiling at 88° (1 atm). n_D^20 1.3932.

Ethyl bromide was used in the preparation of trimethylsilane. The yield was 60 %. B. p. 62°. n_D^20 1.3832.

Methyltriethyilsilane was prepared from triethylchlorosilane and Grignard reagent according to Whitmore et al.11 Methylmagnesium chloride was used instead of the bromide. The yield of methyltriethyilsilane was 56 %. B. p. 128—127° (1 atm). n_D^20 1.4165.

Dimethylsilane was prepared by a Flood reaction. 1,1,3,3-tetramethyl-1,3-diethyl-dsioxane (127 g) was shaken with 100 ml of concentrated sulphuric acid. To the solution was added 75 g of sodium chloride and 75 g of ammonium chloride in portions. The upper layer was collected and distilled, giving 105 g of dimethylsilane boiling at 87—92° (1 atm).  

Dimethylsilane. To a slurry of 8.0 g (0.21 mole) of lithium aluminium hydride in 15 ml of anhydrous dibutyl ether was added 92 g (0.75 mole) of dimethylsilane. The reaction mixture was then boiled for two hours. The reaction mixture was then boiled for two hours. When about half of the chlorosilane had been added, slight external heating was applied and the dimethylsilane was removed continuously through a short Vigreux column. The yield of dimethylsilane was 63.6 g (85 %) boiling at 44—46°. (Found: Si 32.0. Calc. for C₂H₆Si: Si 31.8). d^20 0.6679; n_D^20 1.3789; MRD found 30.52, calc. 30.46.

Dimethyl-n-propylchlorosilane was prepared from 56 g of 1,1,3,3-tetramethyl-1,3-di-n-propylsilidinesiloxane (see below), 40 ml of concentrated sulphuric acid and 40 g of ammonium chloride. Distillation yielded 56 g of dimethylid-i-n-propylchlorosilane boiling at 113—115°. (Found: Si 20.6. Calc. for C₄H₈SiCl: Si 20.5). d^20 0.8753; n_D^20 1.4133; MRD found 38.97, calc. 38.97.

1,1,3,3-tetramethyl-1,3-di-n-propylsilidinesiloxane was prepared from dimethyl-n-propyl-
ethoxysilane. Of course it is more convenient to use the ethoxysilane directly for the preparation of the chloride, without isolating the disiloxane.

To 36 g (0.25 mole) of ice-cooled dimethyl-n-propylethoxysilane was added slowly 50 ml of concentrated sulphuric acid. After standing for 14 hours the mixture was poured out on ice. Two layers were formed and separated. The diluted sulphuric acid solution was extracted with ether. The ether solution of all organic material was washed with.

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water, 25 ml of a 5% sodium carbonate solution, water again and dried with calcium chloride. Distillation yielded 25.2 g of tetramethylid-n-propylidisiloxane boiling at 66° (11 mm). (Found: Si 26.6. Calc. for C₉H₆O₂Si₂: Si 26.5). d²₀ 0.8027; nD²₀ 1.4098; MRD found 67.41, calc. 67.46.

*Methylid-n-propylidchlorosilane* was prepared from methylid-n-propylethoxysilane analogous to dimethyl-n-propylchlorosilane, but the disiloxane was not isolated. (See below). Methylid-n-propylidchlorosilane boiled at 161° (1 atm). (Found: Si 17.0. Calc. for C₁₁H₁₆O₂Si: Si 17.0). d²₀ 0.8784; nD²₀ 1.4300; MRD found 48.44, calc. 48.46.

1,3-Dimethyl-1,1,3,3-tetra-n-propylidisiloxane was prepared from methylid-n-propylidethoxysilane in a separate experiment, as described for tetramethylid-n-propylidisiloxane. B. p. 115—116° (12 mm). (Found: Si 20.5. Calc. for C₁₇H₃₄O₄Si₂: Si 20.5). d²₀ 0.8217; nD²₀ 1.4220; MRD found 86.15, calc. 85.99.

The following four alkylsilanes were prepared by reduction of corresponding alkylchlorosilanes with lithium aluminum hydride in diethyl ether:

<table>
<thead>
<tr>
<th>Silane:</th>
<th>B. p. °C</th>
<th>d²₀</th>
<th>nD²₀</th>
<th>found</th>
<th>calc.</th>
<th>MRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl-n-propyl-</td>
<td>73—74</td>
<td>0.6976</td>
<td>1.3927</td>
<td>34.96</td>
<td>35.21</td>
<td></td>
</tr>
<tr>
<td>Methylid-n-propyl-</td>
<td>127</td>
<td>0.7327</td>
<td>1.4140</td>
<td>44.43</td>
<td>44.48</td>
<td></td>
</tr>
<tr>
<td>Triethyl-</td>
<td>107</td>
<td>0.7313</td>
<td>1.4124</td>
<td>39.60</td>
<td>39.40</td>
<td></td>
</tr>
<tr>
<td>n-Butyl-</td>
<td>54</td>
<td>0.6772</td>
<td>1.3926</td>
<td>31.07</td>
<td>31.06</td>
<td></td>
</tr>
</tbody>
</table>

*n-Octylsilane* was also prepared by reduction of the n-octyltrichlorosilane by a modified method, where the chlorosilane was never isolated. n-Octylmagnesium bromide was prepared from 49 g (0.25 mole) of n-octyl bromide and 6.1 g (0.25 g atom) of magnesium in 50 ml of anhydrous ether. The Grignard reagent was filtered and added to a stirred solution of silicon tetrachloride, 43 g (0.25 mole) in 75 ml of ether, during 40 minutes. After rapid filtration through glass wool the solvent and the unreacted silicon tetrachloride were removed by distillation in order to prevent the formation of SiH₄ in the following reduction. Anhydrous ether (ca. 75 ml) was again added and the solution was introduced into a stirred slurry of 9 g (0.25 mole) of lithium aluminum hydride in 50 ml of anhydrous ether.

Direct distillation at 20 mm yielded 19 g (50%) of n-octylsilane boiling at 59—63°. After distillation the following data were found. B. p. 61° (20 mm). (Found: Si 19.4. Calc. for C₈H₁₇Si: Si 19.5). d²₀ 0.7457; nD²₀ 1.4253; MRD found 49.52, calc. 49.61.

The distillation residue was hydrolysed with diluted hydrochloric acid. No di-n-octylsilane could be isolated.

Triphenylsilane. Triphenylchlorosilane was prepared by adding phenyllithium (0.31 mole as a 0.94 N ether solution) to silicon tetrachloride (0.1 mole) dissolved in ether (100 ml). The precipitate was removed and the ether solution was added to 1.2 g (0.032 mole) of lithium aluminum hydride in ether (100 ml). After completion of the reduction the reaction mixture was rapidly filtered and about 400 ml of ether was distilled off. Excess of lithium aluminum hydride was decomposed by adding the solution to 50 ml of 5 N hydrochloric acid. The ether layer was dried with calcium chloride and distilled, yielding 11 g of triphenylsilane, boiling at 148—151° at 1 mm. After one hour the substance solidified. M. p. 35°.

The refractive indices of the following compounds will be given: dimethylidethyldisilane 1.4014, tetraethylsilane 1.4270, tetra-n-propylidisilane 1.4386, tetra-n-butylsilane 1.4468.

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REFERENCES


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