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SOME PROPERTIES OF NORMAL- AND ISO-TETRASILANE

Sudarshan D. Gokhale and William L. Jolly

December 1963
Some Properties of Normal and Iso-Tetrasilane

By Sudarshan D. Gokhale and William L. Jolly

The two isomers of tetrasilane were prepared in an ozonizer-type electric discharge and isolated by gas chromatography. The isomers were identified, consistently, by their nmr spectra, their infrared spectra and their relative volatilities.

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Introduction

Stock et al.\(^2\) obtained normal tetrasilane from the products of the reaction of magnesium silicide with hydrochloric acid, but they were unable to isolate the branched-chain isomer. Fehér et al.\(^3\) achieved a partial separation of the two isomers by fractional distillation and reported the boiling and freezing points, densities, and refractive indexes of the isomers. Borer and Phillips\(^4\) and Fehér and Strack\(^5\)

showed that the mixture of silanes obtained from the reaction of magnesium silicide with aqueous acid can be separated into many components, including n- and iso-tetrasilane, by gas chromatography.

We have prepared a mixture of higher silanes by an electric discharge method similar to that used to prepare the higher germanes\(^6\)


and trisilane. The isomers of tetrasilane were separated by gas chromatography and identified by their relative volatilities, by their infrared spectra, and, most unequivocally, by their nmr spectra.

Experimental

The tetrasilanes were prepared from pure silane by the ozonizer-type electric discharge method, subjecting the products higher than trisilane to gas-liquid chromatographic separation. The details of the method will be published elsewhere. Generally the ratio of n-tetrasilane to iso-tetrasilane was 5:1.

The infrared spectra were obtained with Perkin-Elmer Infracord Spectrophotometers (NaCl Model 137B and KBr Model 137) using a 5-cm. NaCl cell and a 6-cm. KBr cell, respectively. The spectra are given in Figure 1. The infrared spectrum of normal tetrasilane shows bands at the following frequencies (cm\(^{-1}\)): 2155 (s), 1020 (s), 935 (m), 917 (w), 879 (s), 748 (w), 741 (w), 701 (sh; m), 694 (s), 662 (s), 535 (w), 470 (w). The spectrum of iso-tetrasilane shows bands at the frequencies (cm\(^{-1}\)): 2210 (w), 2155 (s), 1000 (w), 945 (sh; w), 935 (m), 915, 906, 898 (m), 871 (s), 866 (s), 698 (sh; m), 693 (s).

The vapor pressure of n-tetrasilane was found to be 10.0 ± 1.0 mm at 0\(^{\circ}\) and 29.5 ± 1.0 mm at 25\(^{\circ}\). The vapor pressure of iso-tetrasilane could not be measured accurately because even our best sample...
contained perhaps as much as 5% impurity. However, we can state that, at 0°, the vapor pressure of iso-tetrasilane is more than 5 mm higher than that of n-tetrasilane. In the chromatographic separation, the iso-isomer preceded the normal isomer, in keeping with the vapor pressure measurements.

The mass spectrum of n-tetrasilane showed a fragmentation pattern of the four different types of ions with the following relative order of intensities: \( \text{Si}_3^+ > \text{Si}_2^+ > \text{Si}_4^+ > \text{Si}_1^+ \); this order is the same as that found for n-tetragermane. The mass spectrum of iso-tetrasilane was not obtained.

The isomers were diluted with "conditioned" tetramethylsilane (TMS) for measurement of the nmr spectra. "Conditioned" TMS was prepared by treating the middle fraction of a fractional distillation of TMS with silane, followed by fractional condensation on the vacuum line using traps at -78°, -130°, and -196°. The TMS which collected in the -130° trap was used to dilute the tetrasilanes enough to fill the nmr tubes to the optimum height. It also served as an internal standard. The proton magnetic resonance spectra were obtained using the A-60 and 100 Mc Varian Associates nmr spectrometers.

The cooperation and help given by Varian Associates in permitting us to use their 100 Mc spectrometer is gratefully acknowledged.
The spectra are presented in Figures 3 to 5. For completeness, spectra were obtained for disilane and trisilane also. Figure 2 shows the $^{29}\text{Si}$ satellite spectra for trisilane at 100 Mc and 60 Mc. The ppm values given are to lower field of the TMS.

**Discussion**

The more volatile isomer of tetragermane was assumed to be the branched-chain isomer, in analogy to the relative volatilities of the butane isomers. In our following discussions of the infrared spectra and nmr spectra, it will be seen that this assignment is born out.

**Infrared Spectra**- In the infrared spectrum of iso-tetrasilane [(SiH$_3$)$_3$SiH], one expects the presence of bands due to the SiH group and the absence of bands due to the SiH$_2$ group. The weak absorption at 2210 cm$^{-1}$, on the high frequency side of the main Si-H stretching frequency band, probably corresponds to a stretching frequency of the SiH group. It is apparent from our study of the nmr spectrum that the SiH proton is shielded more than the SiH$_3$ protons. We conclude that the SiH bond has a higher electron density, and that therefore it is stronger and has a higher stretching frequency than a corresponding bond in an SiH$_3$ group.

There is no significant absorption in the KBr region or in the 720 - 830 cm$^{-1}$ region in the case of iso-tetrasilane at 10 mm pressure, whereas there is a strong absorption band at 662 cm$^{-1}$ and a weak absorption band at 748 cm$^{-1}$ in the case of $\pi$-tetrasilane. The infrared spectrum of trisilane shows similar, but much weaker, absorptions in
the 740 - 750 cm\(^{-1}\) and 570 - 590 cm\(^{-1}\) regions. It is therefore suggested that these bands are due to the SiH\(_2\) group.

The strong absorption band near 870 cm\(^{-1}\) in both tetrasilanes, presumably due to the SiH\(_3\) symmetrical deformation, is split in the case of iso-tetrasilane. The analogous type of resonance splitting of the methyl symmetrical deformation band, due to more than one methyl group on a carbon atom, is observed in the infrared spectra of alkanes.\(^{10}\)


We suggest that the band with distinct PQR branches centered at 906 cm\(^{-1}\) in the iso-tetrasilane spectrum corresponds to an SiH bending mode. Infrared spectra of the silanes seem to be less complex than the corresponding spectra of the alkanes because the Si-Si vibration frequencies are much lower than the Si-H vibration and bending frequencies.\(^{11}\)


\[\text{Nmr Spectra: - The nmr spectrum of trisilane at 60 Mc is complicated, just as it is at 40 Mc,}\]\(^{12}\) because the chemical shift and coupling constant between the SiH\(_3\) and SiH\(_2\) protons are of the same order of
magnitude. At 100 Mc, the spectrum is relatively simple, but by far
the best spectra are found in the $^{29}\text{Si}$ satellites. The $^{29}\text{Si}$ satellite
spectra of trisilane at both 100 and 60 Mc are shown in Fig. 2. As
expected, the $^{29}\text{SiH}_3$ resonance is split into a triplet, and the $^{29}\text{SiH}_2$
resonance is split into a septet, of which only five lines are apparent
in Fig. 2.

The nmr spectrum of n-tetrasilane at 60 Mc is shown on the left
side of Figure 3, and that at 100 Mc is shown in Figure 4. It will be
noticed that the main resonance is complicated in each case.\(^{13}\) However,

\(^{13}\) The general shape of the main resonance is similar to that
of n-tetragermane\(^6\) and is a mirror image of that of n-butane.\(^{14}\)

\(^{14}\) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolu-
tion Nuclear Magnetic Resonance", McGraw-Hill Book Co., New York,
1959, p. 235.

the $^{29}\text{Si}$ satellite spectra (shown in Fig. 4 for 100 Mc) are simple.
As expected, the $^{29}\text{SiH}_3$ resonance is split into a triplet. The $^{29}\text{SiH}_2$
resonance is split into a sextet, of which only four components are
apparent in Fig. 4, by the five protons which are nearby. Apparently
the $\text{H}_3\text{Si}-^{29}\text{SiH}_2$- and $^{29}\text{SiH}_2$-$\text{SiH}_2$ coupling constants are of very
similar magnitude. On the low-field side of the main resonance, the
$^{29}\text{SiH}_3$ and $^{29}\text{SiH}_2$ resonances are well separated. On the high-field
side, the resonances overlap but are still recognizable.

The nmr spectrum of iso-tetrasilane at both 60 Mc (Fig. 3) and
100 Mc (Fig. 5) is simple. The strong $\text{SiH}_3$ resonance is a doublet,
and the weak SiH resonance is split into ten components, of which two
or three are lost in the noise and cannot be seen in Fig. 5. The
$^{29}\text{SiH}_3$ satellite bands are shown in Fig. 5.

The chemical shifts are given in Table I. We have included our
data for disilane and trisilane for comparison purposes. It is clear
from the data that, as we increase the number of silicon atoms bonded
to a silicon atom adjacent to a silyl group, the shielding of the pro-
tons in the silyl group decreases. This effect is just the opposite of
that predicted from simple electronegativity considerations, and paral-
lels the variations in chemical shifts of the $\text{CH}_3$ group in ethyl
halides\(^{15}\) and of the $\text{SiH}_3$ group in disilanyl halides\(^{16}\)

\(^{15}\) B. P. Dailey and J. N. Shoolery, \textit{J. Am. Chem. Soc.}, \textbf{77}, 3977
(1955).

\(^{16}\) M. Abedini, C. H. Van Dyke, and A. G. MacDiarmid, unpublished
data.

The increase in shielding on going from the $\text{SiH}_3$ group to the SiH
group is explicable in terms of the reduced electronegativity of sili-
con compared with hydrogen.

The H-H and $^{29}\text{Si-H}$ coupling constants are given in Table II.
They are of the same order of magnitude as those reported by Abedini
\textit{et al.}\(^{16}\) Although the mechanism of the spin-spin interaction is not
clearly understood, it is logical to expect that if this interaction is
through the bonds it should decrease with an increase in the number of
interposed bonds. The value of 3.5 to 4 cps for the coupling constant
of vicinal protons in the higher silanes and the value of 2.75 cps of geminal protons in silane reported by Ebsworth and Turner\(^\text{17}\) indicate

\(\text{(17) E. A. V. Ebsworth and J. J. Turner, } J. \text{ Chem. Phys.}, 36, 2631(1962).}\)

that something other than mere "through-bond" interaction is involved. In the case of saturated hydrocarbons, vicinal proton coupling constants lie in the range of 5-8 cps, and the geminal proton coupling constant in methane is 12.4 cps\(^\text{18}\).

\(\text{(18) Ref. 14, pp. 193, 236.}\)

Acknowledgment.- This research was supported by the U. S. Atomic Energy Commission.
Table I. Chemical shifts in ppm (± 0.02) to low field of TMS

<table>
<thead>
<tr>
<th>Compound</th>
<th>-SiH&lt;sub&gt;3&lt;/sub&gt;</th>
<th>-SiH&lt;sub&gt;2&lt;/sub&gt;</th>
<th>-SiH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>3.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
<td>3.36</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>n-Si&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>3.36</td>
<td>3.26</td>
<td></td>
</tr>
<tr>
<td>iso-Si&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>3.42</td>
<td></td>
<td>2.93</td>
</tr>
</tbody>
</table>
Table II. Coupling constants in cps

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{H}_3\text{Si-SiH}_n )</th>
<th>( \text{Si}-\text{H}_3 )</th>
<th>( \text{Si}-\text{H}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Si}_2\text{H}_6 )</td>
<td>3.5 ± 0.2</td>
<td>199</td>
<td>199</td>
</tr>
<tr>
<td>( \text{Si}_3\text{H}_8 )</td>
<td>4.0 ± 0.2</td>
<td>199</td>
<td>194</td>
</tr>
<tr>
<td>( \text{n-Si}<em>4\text{H}</em>{10} )</td>
<td>3.7 ± 0.2</td>
<td>199</td>
<td>197</td>
</tr>
<tr>
<td>( \text{i-Si}<em>4\text{H}</em>{10} )</td>
<td>4.0 ± 0.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1. Infrared spectra of normal- and iso-tetrasilane.
   a: polystyrene calibration.  b: 5 mm.
   pressure in 5-cm. cell.  c: 10 mm. pressure
   in 5-cm. cell.

Fig. 2. Nmr spectra of trisilane at 100 and 60 Mc.
   Satellite resonances shown are to low field
   of main resonances.

Fig. 3. Nmr spectra of normal- and iso-tetrasilane.
   Main resonances at 60 Mc.

Fig. 4. Nmr spectrum of normal-tetrasilane. Main
   and satellite resonances at 100 Mc.

Fig. 5. Nmr spectrum of iso-tetrasilane. Main and
   satellite resonances at 100 Mc.
Fig. 1
Main resonance and $^{29}$Si satellite

Fig. 2
Fig. 3
Fig. 4
Fig. 5
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