Preparation and Characterization of Silicon(IV) Formate

RAM CHAND PAUL, TRIPITA PURI, and R. KAPOOR
Department of Chemistry, Panjab University, Chandigarh-160014, India

(Z. Naturforsch. 31b, 905-906 [1976]; received March 25, 1976)

Silicon(IV) Formate, Thermogravimetry, IR

Silicon(IV) formate has been prepared by the reaction of silicon(IV) chloride and anhydrous formic acid. The compound has been characterized by elemental analyses, thermogravimetry and infrared spectral data.

The preparation of silicon(IV) formate has been reported in literature. However, very little information exists concerning the properties and structure of this compound. Some of the earlier data regarding the isolation of this compound are partly contradictory and not consistent with the present work. In this communication, we report the preparation, IR spectrum and thermal analysis (T.G.) of silicon(IV) formate.

Experimental

Silicon(IV) chloride reacts with anhydrous formic acid with the evolution of hydrochloric acid gas and the separation of white fluffy precipitate. The reaction is complete in 2-3 h at room temperature. The precipitate was filtered, washed with CC14 and CH2Cl2 and dried in vacuum to give Si(OOCH)4.

Si(OOCH)4
Found  Si 13.50  C 22.60  H 2.08,
Calcd  Si 13.46  C 23.07  H 1.92.

The product is always found to be silicon(IV) formate irrespective of the stoichiometric proportion of the reactants taken.

Requests for reprints should be sent to Dr. R. KAPOOR, Chemistry Department, Panjab University, Chandigarh-160014, India.

Results and Discussion

The compound is highly sensitive to moisture and on exposure to moist air loses formic acid. It is insoluble in common organic solvents which suggests its polymeric nature. It reacts with water to give gelatinous white mass of silicic acid. It does not react even with strong bases such as pyridine and triethylamine indicating that the silicon atom in it is coordinately saturated.

The infrared absorption spectrum of the compound (4000-200 cm⁻¹, as KBr pellets and as nujol mull films on NaCl and CsI plates) has been recorded on a Perkin-Elmer 621 grating spectrophotometer. Important bands and their assignments are given in Table I. The low frequency bands (below 200 cm⁻¹) which are not present in the spectrum of either formic acid or ionic formates have been assigned to the Si-O vibrations. An analysis of the infrared spectrum of Si(OOCH)4 indicates that silicon in this compound acquires six coordination by having both bidentate/bridging and unidentate formato groups. If silicon in this compound had coordination number four, then all the formato groups would be equivalent. However, the infrared spectrum clearly indicates that the formato groups

<table>
<thead>
<tr>
<th>Band (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1715 s</td>
<td>ν(C-O)</td>
</tr>
<tr>
<td>1590 s</td>
<td>ν(COO) asym.</td>
</tr>
<tr>
<td>1355 s</td>
<td>ν(COO) sym.</td>
</tr>
<tr>
<td>1134 s</td>
<td>ν(C-O-Si)</td>
</tr>
<tr>
<td>522 m; 335 w</td>
<td>522 m; 335 w</td>
</tr>
<tr>
<td>425, 400 s</td>
<td>425, 400 s</td>
</tr>
<tr>
<td>3400-3200 bs</td>
<td>3400-3200 bs</td>
</tr>
<tr>
<td>1720 s</td>
<td>1720 s</td>
</tr>
<tr>
<td>1160 s</td>
<td>1160 s</td>
</tr>
<tr>
<td>1070 s</td>
<td>1070 s</td>
</tr>
<tr>
<td>630 m</td>
<td>630 m</td>
</tr>
<tr>
<td>440;</td>
<td>440;</td>
</tr>
<tr>
<td>430 s</td>
<td>430 s</td>
</tr>
</tbody>
</table>

bs = broad and strong, s = strong, m = medium, w = weak.

Table I. Pertinent infrared spectral bands (cm⁻¹) and their assignments.
are non-equivalent. Bands at 1715 and 1134 cm\(^{-1}\) are assigned to \(v_{\text{C=O}}\) and \(v_{\text{C-O(Si)}}\) of unidentate formato groups, by analogy with the spectrum of Si(OOCCH\(_3\))\(_4\). Other bands at 1590 and 1355 cm\(^{-1}\) are assigned to \(v_{\text{COO}^-}\)asym. and \(v_{\text{COO}^-}\)sym. of bridging/bidentate formato groups. The absence of formic acid is confirmed by the absence of a \(v_{\text{O-H}}\) band above 3000 cm\(^{-1}\). The lower value of \(v_{\text{C=O}}\) in Si(OOCH)\(_4\) as compared to the corresponding band in Si(OOCCCH\(_3\))\(_4\) suggests the presence of hydrogen bonding in the former.

The compound loses weight at room temperature when kept in air. Thermogravimetric analysis was carried out on a Stanton Thermobalance Model TR-1 and its T. G. and D. T. G. curves are given in Fig. 1. Decomposition of Si(OOCH)\(_4\) takes place in two stages with the formation of an intermediate product SiO(OH)(OOCH) around 100–110 °C. The observed weight loss is 48.7% (required weight loss for SiO(OH)(OOCH)/Si(OOCH)\(_4\) = 49.0%). Further increase in temperature leads to the formation of SiO\(_2\) which is complete at 310 °C corresponding to a weight loss of 70.9% (required weight loss for SiO\(_2\)/Si(OOCH)\(_4\) = 71.1%). The formation of intermediate SiO(OH)(OOCH) was confirmed by stopping the run at 110 °C and by carrying out its elemental analyses and infrared spectra.

\[
\text{SiO(OH)(OOCH)}
\]

- Found Si 26.2 C 11.2 H 1.8,
- Caled Si 26.5 C 11.3 H 1.9.

Characteristic vibrational bands of the intermediate SiO(OH)(OOCH) are recorded in Table I. The intense absorption bands at 1670 and 630 cm\(^{-1}\) which are not present in the parent compound, Si(OOCH)\(_4\) can apparently be assigned to \(v_{\text{asym.}}\) and \(v_{\text{sym.}}\) vibrations of the Si–O–Si bond. The absence of absorption bands due to \(v_{\text{COO}^-}\)asym. and \(v_{\text{COO}^-}\)sym. indicates the absence of bridging/bidentate formato groups. On the other hand the presence of sharp intense bands at 1720 and 1160 cm\(^{-1}\) indicates the presence of unidentate formato groups. The broad nature of \(v_{\text{O-H}}\) band between 3400–3200 cm\(^{-1}\) suggests some type of hydrogen bonding.

The thermal decomposition of silicon(IV) formate may thus be represented as

\[
\begin{align*}
\text{Si(OOCH)}_4 & \xrightarrow{100–110 \, ^\circ\text{C}} \text{SiO(OH)(OOCH)} \\
\text{SiO(OH)(OOCH)} & \xrightarrow{110–310 \, ^\circ\text{C}} \text{SiO}_2
\end{align*}
\]