

Elemental silicon and solid SiO give the same products as SiO₂ upon reaction with alkali-metal glycolates

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Treatment of Si, SiO and SiO₂ with lithium or sodium ethylene glycolate gave five-co-ordinate silicon ethylene glycolate derivatives in quantitative yield: Li[Si(OCH₂CH₂O)₂(OCH₂CH₂OH)] in the reactions with lithium glycolate and dimeric Na₂[Si₂(OCH₂CH₂O)₅] with sodium glycolate; reaction of the latter compound with hot methanol resulted in an exchange of the monodentate glycolate group and the formation of Na[Si(OCH₂CH₂O)₂OMe].

Amorphous, solid SiO is technically prepared from Si and SiO₂ at high temperatures and is used for making antireflection layers by CVD. Great efforts have been directed towards the structural and physical characterization of solid SiO. The results are sometimes controversial (possibly also due to the use of ill-defined and differently prepared samples), and no clear-cut structural model has emerged from these studies.^{1,2} However it is unambiguous that solid SiO is not just a homogeneous mixture of finely divided silicon and SiO₂ phases.

The reactivity of solid SiO has only been tested in rather straightforward reactions. By 1907 Potter had already reacted SiO with aqueous and anhydrous HF.³ The products were similar to those expected for a mixture of Si and SiO₂. However, solid SiO is stable up to at least 900 °C, and disproportionation into SiO₂ and silicon phases is only observed at higher temperatures. In all the other known reactions, SiO was used as a reductant, with the concomitant formation of Si^{IV} compounds.^{3–6}

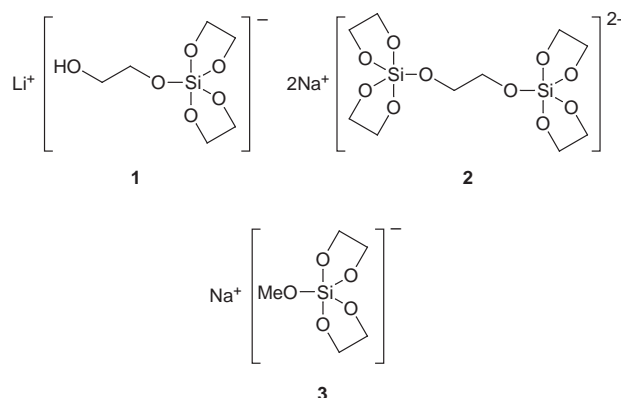
One of the few straightforward reactions of SiO₂ leading to molecular compounds is its reaction with alkali-metal hydroxide and ethylene glycol by which Laine and co-workers obtained monomeric and dimeric five-co-ordinate complexes of composition M[Si(OCH₂CH₂O)₂(OCH₂CH₂OH)] and M₂[Si₂(OCH₂CH₂O)₅] (M = Li, Na, K or Cs) with two chelating and one monodentate glycolate ligand per silicon.^{7,8}

To compare the reactivity of solid SiO with that of SiO₂, we reacted SiO powder † with a solution of lithium or sodium ethylene glycolate in ethylene glycol at *T* > 140 °C. ‡ The glycolate was prepared by reacting one to three molar equivalents of the alkali-metal (relative to SiO) with the glycol. Depending on the temperature, the brown solid SiO dissolved within several hours

† Merck Patinal, particle size <0.044 mm. Elemental analysis of the SiO as delivered gave a stoichiometry of SiO_{1.101}.

‡ All manipulations were carried out under an atmosphere of dry and oxygen-free argon, using standard Schlenk tube techniques and dried solvents; SiO, Si (Merck, particle size <0.15 mm) and SiO₂ (FO Optipur, Merck) were used as received. Lithium (0.57 g) (or 1.86 g of Na) was added to 80 ml of freshly distilled ethylene glycol and stirred at room temperature until all of the metal was dissolved. Silicon (0.652 g) (or 1.0 g of SiO, or 1.388 g of SiO₂) was added and the mixture heated to *T* > 140 °C until all the solid had disappeared. The clear yellow solution was allowed to cool overnight, and a white precipitate was formed. The solution was concentrated to about 30 ml. The white solid was filtered off, washed four times with 50 ml of dry, distilled ethanol, and then dried *in vacuo* at room temperature.

(for example, within 4 h at 160 °C), while a slight gas evolution was observed. When the amount of solvent was less than 70 ml g⁻¹ SiO, a colorless microcrystalline precipitate of **1** (M = Li) or **2** (M = Na) was quantitatively formed during the reaction; in less concentrated solutions the solids were obtained on cooling. The same reactions were observed when lithium or sodium was directly added to a suspension of SiO in ethylene glycol. The MAS ²⁹Si NMR spectra of the precipitates showed only one peak at about δ -101.5. This proves that only one silicon-containing product was formed. The signal was in the typical range for five-co-ordinate silicate species.



Solid SiO did not react with NaOR (R = Me, Et, Bu, Prⁱ or Bu^t) when refluxed in the corresponding alcohol for 1 d.

A suitable crystal of **1** was investigated by an X-ray structure analysis. § The structure contains the monomeric five-co-ordinate glycolato silicate anion with the trigonal-bipyramidally co-ordinated silicon atom bonded to two chelating and one monodentate glycolate ligands. The square-pyramidally co-ordinated lithium cation is bridging two silicate anions, leading to a layered crystal structure (Fig. 1). It has contacts to the OH oxygen of the pendant glycolate ligand (apex of the square pyramid) and to the oxygen atoms of the chelating ligands. The basic features of the structure of the silicate anion are the same as those reported for the corresponding potassium⁸ and sodium derivatives.⁹

We got the same results when elemental silicon was similarly treated. As in the case of SiO, gas evolution was observed. While the reaction of elemental silicon with alkali-metal glycolates has not previously been investigated, reactions of Si with monoalcohols in the presence of metal alkoxides are known to give tetraalkoxysilanes.¹⁰

Thus, the outcome of the reaction of solid SiO or elemental Si with alkali-metal glycolates in ethylene glycol is the same as for SiO₂ under the same conditions (except the hydrogen

§ Crystal data for **1**: orthorhombic, space group *P*2₁2₁2₁, *a* = 798.9(2), *b* = 877.0(2), *c* = 1336.2(2) pm, *U* = 936.2(3) × 10⁶ pm³, *T* = 303 K, *D*_c = 1.534 g cm⁻³ for *Z* = 4, *F*(000) = 456, μ = 0.250 mm⁻¹, *R*1 = 0.0263 for all 1734 reflections, *wR*2 = 0.0532.

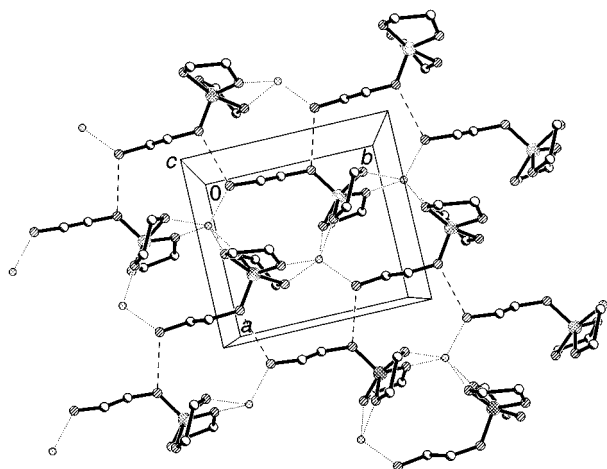


Fig. 1 Crystal structure of compound **1**. The hydrogen atoms have been omitted for clarity. The dashed lines represent hydrogen bridges and the dotted lines Li–O bonds. Selected bond lengths (pm) and angles ($^{\circ}$): Si–O (eq) 167.0(1)–170.5(1), Si–O (ax) 174(1), 174.2(1), Li–O (of OH) 198.1(3), Li–O (of glycolate) 198.8(3)–221.3(3); O (ax)–Si–O (ax) 165.53(5), O (of OH)–Li–O (glycolate) 105.4(1)–122.6(1), O (glycolate)–Li–O (glycolate) 67.19(9)–147.6(1)

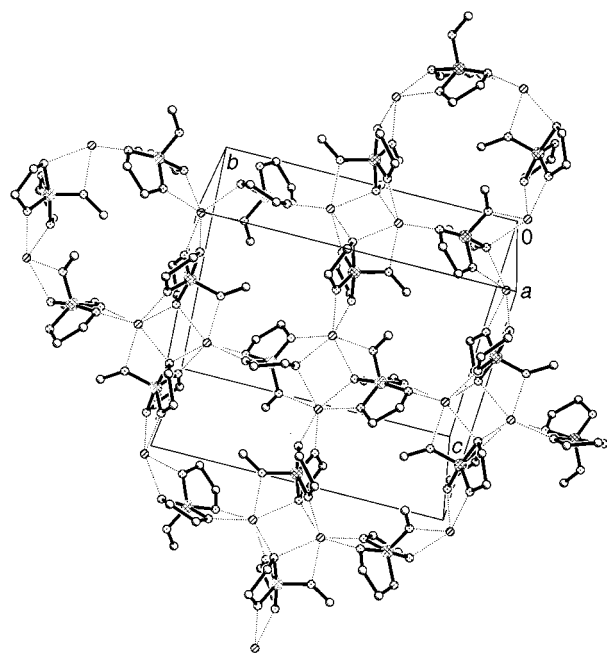


Fig. 2 Crystal structure of compound **3**. The hydrogen atoms have been omitted for clarity. The dashed lines represent hydrogen bridges and the dotted lines Na–O bonds. Selected bond lengths (pm) and angles ($^{\circ}$): Si–O (eq) 166.1(3)–169.4(3), Si–O (ax) 173.4(3)–176.2(3), Na–O 232.1–244.5(3); O (ax)–Si–O (ax) 170.3(2), 172.9(2), O–Na–O (*trans*) 141.6(1)–160.2(1), O–Na–O (*cis*) 59.9(1)–126.2(1)

evolution). The powder X-ray diffraction (XRD) spectra of the solids obtained in the reaction of Si, SiO or SiO₂ with *lithium* glycolate in ethylene glycol were identical, independent of the source of silicon. They were also identical with the XRD profile calculated from the single-crystal structure analysis of **1**, proving that **1** is the only (crystalline) reaction product.

The XRD patterns and TGA profiles of the samples obtained from Si, SiO and SiO₂ with *sodium* glycolate were also identical to each other, but different to the lithium-containing samples. They had the same appearance as that reported for Li₂[Si₂(OCH₂CH₂O)₃].⁸ The products formed with sodium glycolate therefore appear to be the dimeric silicates **2**, in which

one glycolate ligand bridges two Si(OCH₂CH₂O)₂ entities. This agrees with the observation of Laine and co-workers that the dimeric compound is preferentially formed from SiO₂ when *sodium* glycolate is used instead of the lithium glycolate.

It is known that the pendant glycolate group can be exchanged by other alkoxide moieties.⁸ Dissolving **2** in hot methanol resulted in the formation of the methoxy derivative **3** (washing with alcohol at room temperature does not result in an exchange of the alkoxide groups, as shown by XRD powder spectra). The structure of the silicate anion of **3**, as determined by a single-crystal structure analysis[¶] is very similar to that of **1**. The two crystallographically independent silicate anions have a rather similar trigonal-bipyramidal geometry. Both independent sodium cations are six-co-ordinate (strongly distorted octahedral geometry) and bridge the silicate anions. This results in a layered crystal structure (Fig. 2). The main difference between **3** and **1** is that there is an interaction of the cation in **3** with the silicon-bonded oxygen atom of the monodentate ligand.

The results presented here suggest that the reactivity of SiO is a combination of that of silica and silicon. However, this does not imply that SiO is an intimate mixture of Si and SiO₂. If this was the case one would expect reactions typical of elemental silicon. When a suspension of elemental silicon in glycol was heated in the presence of highly dispersed elemental copper, a mixture of alkoxy silanes was obtained as expected for Müller–Rochow type reactions.¹¹ Contrary to this, solid SiO did not react under the same conditions. This result excludes the presence of a distinct silicon phase. However, it does not exclude silicon-rich regions in SiO.

Acknowledgements

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[¶] Crystal data for **3**: monoclinic, space group *P2₁/n*, *a* = 877.8(2), *b* = 1521.2(2), *c* = 1393.2(3) pm, β = 96.80(1) $^{\circ}$, *U* = 1847.3(6) $\times 10^6$ pm³, *T* = 301 K, *D_c* = 1.454 g cm⁻³ for *Z* = 8, *F*(000) = 848, μ = 0.283 mm⁻¹, *R*₁ = 0.0589 for 1882 reflections with *I* > 2 σ (*I*), *wR*₂ = 0.1253. CCDC reference number 186/1057. See <http://www.rsc.org/suppdata/dt/1998/2445/> for crystallographic files in .cif format.

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