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## 5-Coordinate Si Compounds as Intermediates in the Synthesis of Silicates in Nonaqueous Media

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Sodium silicoglycolate, an organosilicon compound in which silicon is in 5-coordination with respect to oxygen, is shown to be a reaction intermediate in the synthesis of a purely siliceous sodalite with ethylene glycol as solvent. The presence of silicon-29 nuclear magnetic resonances at  $-105.5 \pm 0.3$  parts per million in solution and -102.7 parts per million in the solid state as well as x-ray powder diffraction patterns demonstrate that 5-coordinate silicon is intimately involved in the synthesis. Silicon compounds of the 5-coordinate type are highly reactive and are promising starting materials for the synthesis of novel silicon polymers, molecular sieves, glasses, semiconductors, and ceramics. We have used sodium silicoglycolate to prepare the molecular sieve silicalite as well as sodalites of different compositions.

In silicates and aluminosilicates, silicon is almost always present in 4-coordination with respect to oxygen (1). Minerals with 6-coordinate Si, such as stishovite, are rare and crystallize under extremely high pressures. Organic complexes with Si in 6-coordination can be prepared by the reaction of O-dihydroxyphenols with silica in mildly alkaline solutions (2, 3).

Although there are glasses (4) and organosilicates (5–7) containing 5-coordinate Si, this coordination number is infrequent to say the least, and the materials are difficult and expensive to prepare. However, a reaction in which  $SiO_2$  dissolves in a mixture of ethylene glycol and an alkali base to produce ionic 5-coordinate silicates has recently been described (8, 9). We refer to the sodium silicoglycolate as Na-Si<sup>V</sup>. The reaction is very easy and inexpensive.



These highly reactive compounds are promising starting materials for the synthesis of silicone polymers, molecular sieves, glasses, semiconductors, and ceramics. The composition of the synthesis mixture is similar to that used in the preparation of purely siliceous zeolite sodalite (with Si in 4-coordination). The difference is that Na-Si<sup>V</sup> is prepared under atmospheric (as opposed to autogeneous) pressure and that excess glycol and the evolving water are distilled off. The question arises as to whether 5-coordinate Si compounds are involved in both syntheses. In 1887, Sir William Thomson (later to become Lord Kelvin) discovered (10) that the tetrakaidodecahedron divides space with minimum partitional area. The framework of sodalite is a periodic array of such  $[4^{6}6^{8}]$  polyhedra, which are known as sodalite or  $\beta$  cages and are in turn built from corner-sharing SiO<sub>4</sub><sup>4-</sup> and AlO<sub>5</sub><sup>5-</sup> tetrahedra. The negative charge of the framework is balanced by cations such as Na<sup>+</sup>. Sodalite cages may also accommodate guest species such as NaCl, so that a typical unit-cell formula is Na<sub>6</sub>Al<sub>6</sub>Si<sub>6</sub>O<sub>24</sub>·2 NaCl, and the framework Si:Al ratio is 1.0 (11, 12).

Sodalite is normally synthesized from strongly basic aqueous media. By using ethylene glycol instead of water, Bibby and Dale (13) prepared a purely siliceous sodalite with a unit-cell composition of  $Si_{12}O_{24}$ ·2  $C_2H_4(OH)_2$  and the glycol encapsulated in the sodalite cages (13, 14). This sodalite has a cubic space group Im3m, with  $a_0 = 8.83$  Å (13, 14). We have examined the synthesis of both Na-Si<sup>V</sup> and sodalite to find that 5-coordinate Si is in both the mother liquor and the solid product. The 5-coordinate Si is thus much more common than was previously thought.

The starting materials for the synthesis of Na-Si<sup>V</sup> were Cab-O-Sil M-5 fused silica (BDH, Poole, England), sodium hydroxide, and ethylene glycol in a molar composition of SiO<sub>2</sub>:NaOH:40 (CH<sub>2</sub>OH)<sub>2</sub>. The SiO<sub>2</sub> was dissolved in the glycol under agitation, the mixture was placed in a magnetically stirred distillation apparatus, and NaOH was added. The temperature was increased to 195°C over 2 hours under flowing nitrogen so that the excess ethylene glycol and the water produced were slowly distilled off, while a solid product precipitated. Samples of the solution were taken at several intermediate temperatures. The container was cooled, and the solid was separated, washed repeatedly with CH<sub>3</sub>CN, and dried at 200°C for 1 hour. Powder x-ray diffraction

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(XRD) shows that Na-Si<sup>V</sup> is highly crystalline (Fig. 1A), while  ${}^{1}\text{H} - {}^{29}\text{Si}$  CP/MAS NMR (magic-angle spinning with crosspolarization nuclear magnetic resonance) gives a single sharp line at -102.7 ppm (15).

Solution <sup>29</sup>Si NMR spectra shown in Fig. 2A monitor the progress of the synthesis as a function of temperature. No isotopic enrichment in <sup>29</sup>Si was used. The lines at -104.3 and -105.3 ppm from 5-coordinate Si already appear at a very early stage (50°C). We do not believe that these lines could come from 4-coordinate Si in (SiO)<sub>3</sub>SiOCH<sub>2</sub>CH<sub>2</sub>OH or (SiO)<sub>3</sub>SiOCH<sub>2</sub>- $CH_2OSi(SiO)_3$  species (16). The broad lines centered at -90.1 and -98.2 ppm probably correspond to 4-coordinate Q<sup>2</sup> and  $Q^3$  silicate units, respectively, although some secondary organosilicon species may also be present. At 110°C, the concentration of the -105.3-ppm line increases, and the peak intensity ratio changes from 1:1.5 to 1:2. At 190°C, the 4-coordinate silicates are gone, which means that they are intermediates in the formation of Na-Si<sup>V</sup>. The intensity ratio is now 1:7. We attribute the larger peak to Na-Si<sup>V</sup>; the smaller comes from some other 5-coordinate Si species. possibly with the fifth site occupied by a different donor, such as -OH or alkoxide. Q<sup>4</sup> units of sodium silicate should give much broader <sup>29</sup>Si resonances (16, 18).



Fig. 1. Powder x-ray diffraction patterns at different reaction times of (A) Na-Si<sup>v</sup> and (B) solid phases in the synthesis of purely siliceous sodalite with TPABr as template. Patterns were recorded with a Philips 1710 powder diffractometer with Cu K $\alpha$  radiation (40 kV, 40 mA), a step size of 0.02°, and a step time of 1 s. Sod, peaks of sodalite; 5, peaks from a 5-coordinate species.

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For the synthesis of purely siliceous sodalite, the same starting materials were used in the molar ratio 4 SiO<sub>2</sub>:NaOH:40  $C_2H_4(OH)_2$ . Sodium hydroxide was added to ethylene glycol, and the mixture was stirred for 6 hours until the base dissolved. Fused silica was then added under stirring. The resulting thick gel was transferred into a Teflon-lined stainless steel autoclave and heated under autogeneous pressure at 180°C for 3 days. The crystalline product was filtered, washed with distilled water, and dried at room temperature. The <sup>1</sup>H – <sup>29</sup>Si and <sup>1</sup>H – <sup>13</sup>C CP/MAS spectra each consist of a single very sharp peak at –117.6 ppm and 64.19 ppm from tetrameth-



**Fig. 2.** Silicon-29 NMR spectra of (**A**) solutions from the synthesis of Na-Si<sup>V</sup> at different temperatures and (**B**) solutions from the synthesis of sodalite with TPABr as template at different reaction times. The spectra were recorded at 71.6 MHz with the use of polymer sample tubes, a 10- $\mu$ s <sup>29</sup>Si 90° pulse, and a 1-s recycle delay. Deuterated chloroform was used for locking. Silicon-29 chemical shifts are given in parts per million from tetramethylsilane (TMS).

Fig. 3. Silicon-29 NMR spectra of (A) fumed silica dissolved in ethylene glycol and (B) sodalite reaction mixture after 48 hours at 25°C (no template) at room temperature. The spectra were measured with the same acquisition parameters as in Fig. 2.



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ylsilane, respectively, corresponding to Si in the cubic environment and to the encapsulated ethylene glycol. The <sup>29</sup>Si NMR spectrum of silica dissolved in ethylene glycol (Fig. 3A) is very broad (from -50 to -110 ppm). By contrast, the sodalite reaction mixture after 48 hours at 25°C gives two peaks at -104.8 and -105.8 ppm in a 1:6 intensity ratio, corresponding to Na-Si<sup>V</sup> (Fig. 3B).

Purely siliceous sodalite was also prepared with tetrapropylammonium bromide (TPABr) as template, from a gel with molar composition 2 SiO<sub>2</sub>:1.5 NaOH:0.3 TPABr:40 C<sub>2</sub>H<sub>4</sub>(OH)<sub>2</sub> at 200°C. Other reaction parameters were the same as before. After 12 hours, the <sup>1</sup>H - <sup>29</sup>Si CP/ MAS spectrum gives lines at -102.8 and -117.4 ppm, corresponding respectively to Na-Si<sup>V</sup> and sodalite (Fig. 4). The broad hump between about -80 and -120 ppm comes from unreacted silica. The XRD pattern (Fig. 1B) supports this assignment. After 24 hours, all the silica disappears (Figs. 1B and 4), and the amount of Na-Si<sup>V</sup> (line at -102.8 ppm) decreases compared to that of sodalite. The sodalite line is split into three components (at -115.7, -116.6, and -117.6 ppm) because the framework is distorted from cu-



-95 -100 -105 -110 -115 -120 -125 -130 Chemical shift (ppm from TMS)

**Fig. 4.** Hydrogen-1–silicon-29 CP/MAS NMR spectra of the solid phases in the synthesis, at different reaction times, of siliceous sodalite with TPABr as template. Spectra were recorded at 79.5 MHz with a Chemagnetics CMX-400 spectrometer (Fort Collins, Colorado), with rotors spun in the air at 3 kHz, a single-contact pulse sequence, an 8-ms contact time, a 4.8- $\mu$ s <sup>1</sup>H 90° pulse, and a 10-s recycle delay. The Hartmann-Hahn condition was established with a sample of kaolinite (*17*).

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bic symmetry by the occluded template. After 408 hours, only sodalite (lines at -116.2 and -117.0 ppm) remains.

Figure 2B shows solution <sup>29</sup>Si NMR spectra of the mother liquor at different reaction times. The <sup>29</sup>Si spectrum measured with proton decoupling detects only the unreacted silica. However, when no decoupling is used, lines from 5-coordinate Si  $(-104.3 \pm 0.4 \text{ and } -105.3 \pm 0.3 \text{ ppm})$ become apparent. They are not observed under decoupling because of the negative nuclear Overhauser effect of <sup>29</sup>Si (16). The intensity of the -105.3-ppm line decreases in the course of the reaction while the intensity of the -104.3-ppm line remains constant, so that their intensity ratio changes from 1:3.5 to 1:1. Silicoglycolate, responsible for the dwindling line, is therefore an intermediate in the synthesis, and we observe a gradual disappearance of 5-coordinate Si. The unchanging line at -104.3 ppm is probably due to some 5-coordinate by-product. Because no other <sup>29</sup>Si line is found either in the mother liquor or in the solid product, 5-coordinate Si is clearly a reaction intermediate.

To prove that Na-Si<sup>V</sup> is indeed an intermediate, we successfully prepared several silicates from crystalline Na-Si<sup>V</sup> as a starting material. Purely siliceous sodalite was obtained at 190°C from a gel with a composition of Na-SiV:0.3 TBABr:6 H<sub>2</sub>O:40 (CH<sub>2</sub>OH)<sub>2</sub>. When no water was present, the product was amorphous. Although the role of water is not completely clear, its presence is essential to break up the 5-coordinate silicate.

Conventional aluminosilicate sodalite was synthesized with Catapal B alumina (70% Al<sub>2</sub>O<sub>3</sub>) (Vista Chemical Company, Houston, Texas) as the source of aluminum. The molar composition of the gel was Na-Si<sup>V</sup>: $Al_2O_3$ :40 (CH<sub>2</sub>OH)<sub>2</sub>:0.3 TPABr. The synthetic procedure was the same as above except that H<sub>2</sub>O came from Catapal B alumina, which contains 30% water.

The molecular sieve silicalite can be prepared from Na-Si<sup>V</sup> in the absence of ethylene glycol and only water as solvent, from a gel with a molar composition of Na-Si<sup>V</sup>:40 H<sub>2</sub>O:0.3 TPABr. Silicoglycolate and then TPABr were stirred in water for 10 min, and then the mixture was heated in an autoclave under autogeneous pressure for 3 days. At temperatures between 200° and 240°C, the product was pure  $\alpha$  quartz; at 180°C, it was silicalite with a small amount (3% by weight) of  $\alpha$  quartz; and at 170°C, it was pure and highly crystalline silicalite.

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## Recent Changes in Atmospheric Carbon Monoxide

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Measurements of carbon monoxide (CO) in air samples collected from 27 locations between 71°N and 41°S show that atmospheric levels of this gas have decreased worldwide over the past 2 to 5 years. During this period, CO decreased at nearly a constant rate in the high northern latitudes. In contrast, in the tropics an abrupt decrease occurred beginning at the end of 1991. In the Northern Hemisphere, CO decreased at a spatially and temporally averaged rate of 7.3 ( $\pm$ 0.9) parts per billion per vear (6.1 percent per vear) from June 1990 to June 1993, whereas in the Southern Hemisphere, CO decreased 4.2 (±0.5) parts per billion per year (7.0 percent per year). This recent change is opposite a long-term trend of a 1 to 2 percent per year increase inferred from measurements made in the Northern Hemisphere during the past 30 years.

The oxidative chemistry of the troposphere is strongly influenced by levels of CO (1, 2). Reaction with the hydroxyl radical (OH) is the primary sink for many gases emitted into the atmosphere, including CO, methane, and the replacements for the chlorofluorocarbons. The largest loss of OH is attributable to the reaction between CO and OH, which is controlled, in part, by CO concentration. Mixing ratios for CO in the troposphere have been reported by a number of laboratories over the past 25 years (3), and despite continuing uncertainties regarding absolute accuracies and calibrations, the qualitative distributions of CO are known. The mixing ratios in the background troposphere range from about 45 to 250 parts per billion (ppb). Levels decrease from north to south, are greatest in the late winter and early spring, and decrease during the summer. There is also

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significant interannual variation in its seasonal cycle, and short-term increases and decreases in CO levels have been observed (4-6).

Less well defined are long-term changes in atmospheric CO levels. Comparison of spectroscopic measurements made in 1950-1951 to measurements made in the 1980s suggest that CO levels in the Northern Hemisphere (NH) increased at an average rate of  $\sim 1\%$  per year over that period (5). In the Southern Hemisphere (SH), continuous measurements made from 1979 to 1987 at Cape Point, South Africa, show no significant trend (6). Grab samples of air collected during the 1980s from six locations worldwide indicate a  $\sim 1\%$  per year increase (7); however, more recent data from these stations suggest a possible decrease in CO (8). The CO growth rates, like mixing ratios, surely vary with time and location; thus, global trends may be difficult to determine on the basis of measurements from a few isolated sites. Here we discuss recent changes in tropospheric CO measured at 27 globally distributed sampling sites in the marine boundary layer (MBL) between June 1990 and June 1993.

Air samples were collected weekly at 10

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