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Thermodynamics of silica depolymerization with alcohols

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Dedicated to Prof. John E. Bercaw for his superb mentorship on the occasion of his 75th birthday.

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ABSTRACT

Experimental and computational results describe the outlook for silica (polymeric SiO_2) depolymerization with alcohols. The resonance energy of the Si-O-Si segment, calculated as 8.0 kcal/mol, or 16.0 kcal/mol of SiO_2, explains the thermodynamic stability of silica. Acid-catalyzed alkylorthosilicate metathesis reactions between $Si(OMe)_4$ and diols indicate silicon's thermodynamic preference for diols because of favorable entropic chelation. Conversion to $Si(OCH_2CH_2O)_2$ with ethylene glycol is 74.6% and conversion to $Si(OCH_2CH_2CH_2O)_2$ with 1,3-propanediol is 66.2%. The enthalpic stability of $Si(OR)_4$ species correlates to two main factors: (1) the O-Si-O bond angle, with a compression force constant of $k_{\Theta\text{-comp}}$ = 0.0315 (kcal/mol)$(^\circ)^{-2}$ and expansion force constant of $k_{\Theta\text{-exp}}$ = 0.0167 (kcal/mol)$(^\circ)^{-2}$; and (2) the C-O-Si-O dihedral angle, dictated by stabilizing O $n\rightarrow$ Si-O σ^* anomeric interactions of 3.5 kcal/mol in the model compound $Si(OMe)_4$. Computationally, silica depolymerization with methanol is never exergonic, but depolymerization with 1,3-propanediol, forming $Si(OCH_2CH_2CH_2O)_2$ and two equivalents of water, is exergonic above 99 °C in water.

1. Introduction

Oxygen (46%) and silicon (28%) are the most abundant elements in the earth's crust [1]. These atoms combine to form the most abundant crustal material, silica (polymeric SiO_2), and the most abundant bond (Si–O) proximal to humans—about 7 times more prevalent than the O-H bond of water [2]. However, silicon and the Si–O bond garner relatively little attention from chemists. Carbon constitutes about 0.02% of the earth's crust [1], yet dominates the synthetic chemical industry, which is largely fuels, organic feedstocks, pharmaceuticals, and polymers. Of course, carbon manipulation has been vigorously studied for centuries and its chemical versatility and importance to life have been appreciated for a long time. Now, it is recognized that silicon is also important to life [3] with all plants containing measureable amounts (0.1 to 10% by dry weight) [4]. Recent studies have identified an enzymatic silicon transporter in the roots of rice, responsible for uptake of silicon in the form of silicic acid, $Si(OH)_4$ (*a.k.a.* orthosilicic acid) [5].

Our pursuits of sustainable polymers have heretofore focused on carbon-based organics derived from plants. Our pursuits have now evolved to champion silicon oxides as building blocks for new polymers; silicon and oxygen are sustainable because they are inexhaustible elements. One limitation of silicon is its exclusive native oxidation state of +4. Nature supplies ample polymeric SiO_2 and, to a lesser degree, aqueous $Si(OH)_4$. In order to obtain molecular silicon species for facile chemical manipulation, silica is invariably subjected to energy-intensive carbothermal reduction, yielding elemental silicon in the 0 oxidation state [6]. This non-native form of silicon is then oxidized back to the +4 oxidation state to yield convenient molecules such as $SiMe_xCl_{4-x}$. For example, water is polymerized with $SiMe_2Cl_2$ to make polydimethylsiloxane (PDMS), the most common silicon-based polymer [7]. To synthesize 1000 g of PDMS, the energy of 400 g of gasoline is required for just the carbothermal reduction of silica to elemental silicon [8]. Industrial methods to avoid the circuitous redox of silicon have not been developed, but would certainly be advantageous. The non-redox extraction of native silicon from silica has been sporadically reported [9], but the kinetics and thermodynamics of this process remain nebulous. Herein, we report important thermodynamic considerations—experimental and computational—for the depolymerization of silica (SiO_2) with alcohols to yield molecular alkylorthosilicates, $Si(OR)_4$ (Fig. 1).

2. Results and discussion

2.1. Silica hydrolytic depolymerization to silicic acid

The thermodynamic stability of silica mandates that the concentration of its hydrate, $Si(OH)_4$, is generally small in water. At neutral pH, quartz dissociates to about 10^{-5} M silicic acid and

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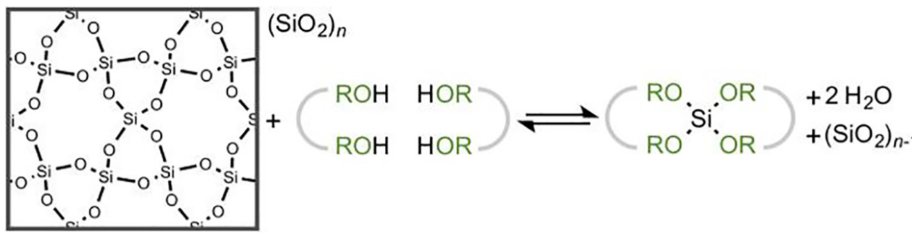

Fig. 1. The depolymerization of silica (polymeric SiO_2) with alcohols (mono-alcohols or diols) yields alkylorthosilicates and water.

amorphous silica dissociates to about 10^{-3} M silicic acid [10]. The typical concentration in the world's oceans is 7×10^{-5} M [11]. This number seems small but amounts to nearly 10^{17} mol of silicic acid dissolved in the oceans, massing to over 8 quadrillion kg—more than 20,000 times the world's annual production of synthetic polymers (4×10^{11} kg) [12]. For another comparison, there is about 1.5 quadrillion kg of proven fossil fuels [13] which, upon full combustion, would make just over 5 quadrillion kg of CO_2.

Fig. 2a models silicic acid dissociation [14] from silica via the computationally manageable Si5 silicate cluster, $Si[OSi(OH)_3]_4$, upon addition of water (DFT/B3LYP/6-31+G*/vacuum). As modeled, the liberation of $Si(OH)_4$ is entropically favorable, with ΔS = +55.9 cal/molK, and enthalpically unfavorable with ΔH = +31.9 kcal/mol. Overall, the ΔG is endergonic by +15.2 kcal/mol, which averages to +3.9 kcal/mol for each of the four Si-O-Si hydrolysis events. A similar analysis (Fig. 2b) of the Si2 cluster $(HO)_3SiOSi(OH)_3$ shows that ΔG is endergonic by +2.1 kcal/mol, representing the hydrolysis of its sole Si-O-Si linkage. These ΔG hydrolysis values are dissimilar for the Si5 and Si2 clusters. One explanation is the differential organization and stabilization imposed by the intramolecular hydrogen bonding present in the clusters and silicic acid. Another is that these calculations are performed in vacuum, which can magnify the effects of O-H polarity. In order to eliminate the influence of hydrogen bonding, the permethylated Si5 cluster analogue $Si[OSi(OMe)_3]_4$ (Fig. 2c) was deconstructed to $Si(OMe)_4$ by etherolysis with dimethyl ether, MeOMe. None of the species involved are capable of hydrogen bonding and this effect is erased. In this case, the ΔG is endergonic by +22.3 kcal/mol, which corresponds to +5.6 kcal/mol for each Si-O-Si etherolysis. The analogous permethylated Si2 cluster (Fig. 2d) registers a similar ΔG of +6.2 kcal/mol for its Si-O-Si etherolysis [15]. The similarity of these numbers suggests their immunity to hydrogen bonding/polarity effects, unlike the reactions of Fig. 2a and 2b.

The isodesmic reactions of Fig. 2 estimate the stability of the Si-O-Si silicate linkage versus the Si-O-H silanol or Si-O-Me silicon alkoxide linkage. Enthalpically, the Si-O-Si stabilization energy for the four reactions of Fig. 2 reactions is worth: (31.9 kcal/mol)/4 = 8.0 kcal/mol; 5.5 kcal/mol; (35.6 kcal/mol)/4 = 8.9 kcal/mol; and 8.6 kcal/mol, respectively [16]. It is precisely this Si-O-Si stabilization that explains the thermodynamic stability of silica, relative to monomeric silicon species. The origin

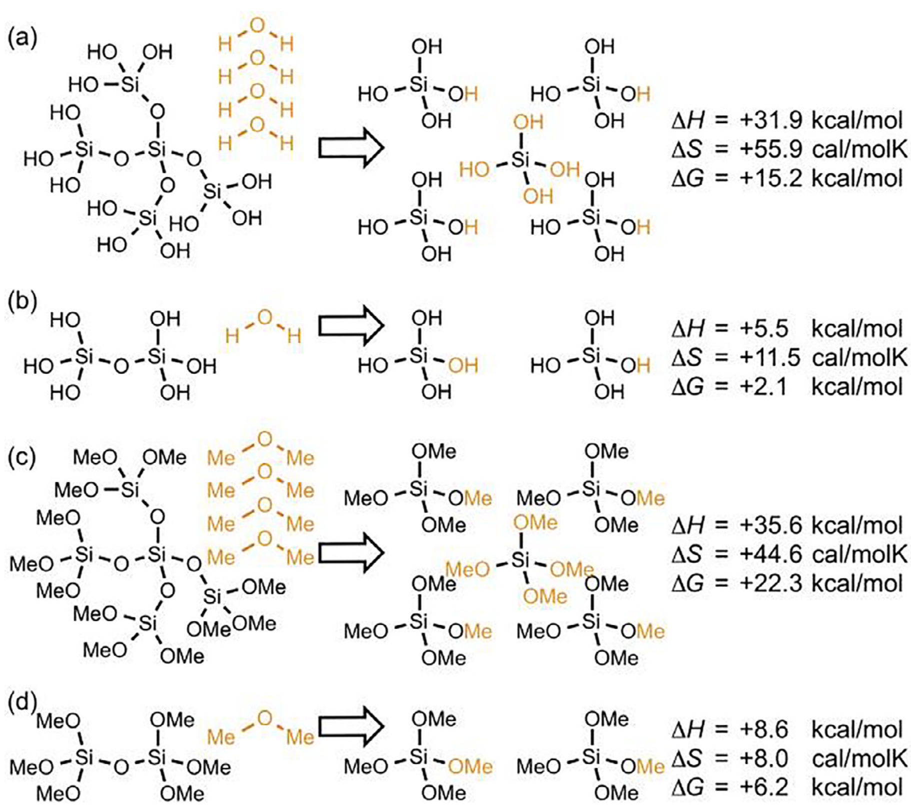

Fig. 2. (a) Depolymerization of silica is modeled by the isodesmic hydrolysis or etherolysis reactions: (a) $Si[OSi(OH)_3]_4$ to $Si(OH)_4$; (b) $(HO)_3SiOSi(OH)_3$ to $Si(OH)_4$; (c) $Si[OSi(OMe)_3]_4$ to $Si(OMe)_4$; and (d) $(MeO)_3SiOSi(OMe)_3$ to $Si(OMe)_4$ (DFT/B3LYP/6–31+G*/vacuum at 298.15 K).

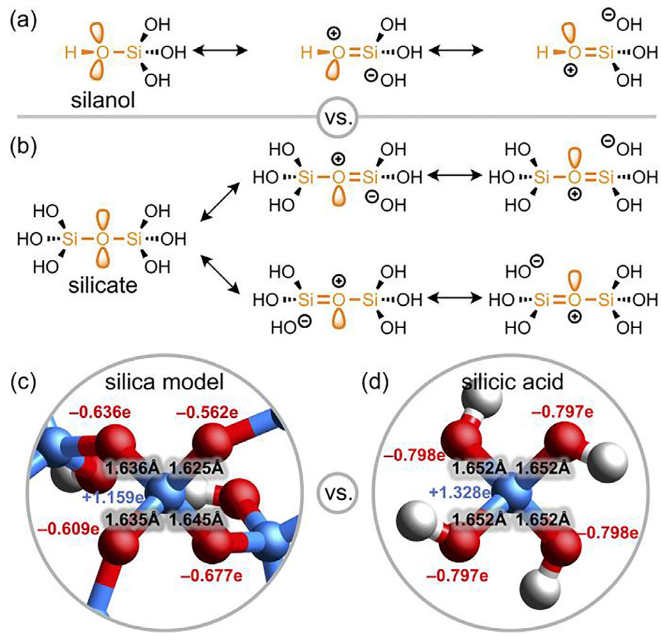

Fig. 3. (a) Resonance delocalization of oxygen lone pair electrons is limited for the Si-O-H silanol linkage, but (b) more extensive for the Si-O-Si silicate linkage. Computed electrostatic charges (red and blue) show less charge separation for the silica model (c, $Si[OSi(OH)_3]_4$) and more charge separation for silicic acid (d, $Si(OH)_4$). Bond lengths (black) are also shorter for the silica model, indicating stronger Si-O bonds. ((Colour online.))

of this stabilization is the delocalization of oxygen lone pair electrons. Fig. 3a depicts this delocalization for one silanol linkage in $Si(OH)_4$ with a *no-bond resonance* formalism [17,18]. Each lone pair of electrons from oxygen can delocalize into a σ^* orbital of an anti-coplanar Si-O bond. This O $n \rightarrow$ Si-O σ^* interaction [19–21] is the silicon analogue of the anomeric/hyperconjugative stabilization energy [22] found in carbon-based acetals [23]. For the model compound pyrosilicic acid, $(HO)_3SiOSi(OH)_3$, depicted in Fig. 3b, *additional* resonance delocalization is possible when oxygen is flanked by *two* silicon atoms. This additional stabilization of about 8.0 kcal/mol is the resonance energy of the Si-O-Si silicate linkage, since it accounts for the difference in energy between an actual molecule and its lowest energy canonical form [24]. Stoichiometrically, silica possesses two Si-O-Si linkages per SiO_2 unit and thus, an estimated resonance energy of about 16.0 kcal/mol of SiO_2—at least based on the model compounds of Fig. 2 [25]. Indeed, this effect can be likened to the resonance energy described for many species, such as organic benzene [26] or inorganic graphite [27].

Fig. 3c shows the computed electrostatic charges for the core $Si(O)_4$ atoms of the silica model compound $Si[OSi(OH)_3]_4$ (from Fig. 2a) and Fig. 3d shows this for the same core atoms after their hydrolytic release in the form of $Si(OH)_4$. In the silica analogue, the silicon atom bears a +1.159e charge and the oxygen atoms bear an average charge of −0.621e; hence the average Si-O charge difference computes to $\Delta_{Si\text{-}O}$ = 1.780e. In silicic acid, the silicon atoms bears a +1.328e charge and the oxygen atoms bear an average charge of −0.798e; hence the average charge difference computes to $\Delta_{Si\text{-}O}$ = 2.126e. Clearly, electronic charge is more evenly distributed in the silica model (less polar), whereas charge is more separated in the free monomer, silicic acid (more polar). Furthermore, a resonance delocalization effect is suggested by the computed Si-O bond lengths. These are shorter (average = 1.635 Å) for the stronger Si-O bonds in the silica model (Fig. 3c) and these are longer (average = 1.652 Å) for the weaker Si-O bonds in silicic acid (Fig. 3d). For comparison, silica, in its quartz crystal, has an average Si-O bond length of 1.610 Å [28].

2.2. Silicic acid to alkylorthosilicates

Fig. 4 describes the thermodynamics (Gibbs free energy) of exchanging the –OH groups of silicic acid for the -OR groups of methanol, ethylene glycol (EG), or 1,3-propanediol (PD). Note that each -OR group installment liberates one equivalent of water. For methanol (Fig. 4a), all four steps are similarly endergonic in each medium: vacuum, acetone, and ethanol (via the SM8 solvent correction model). The overall reaction entropy (ΔS_{rxn}) is consistently unfavorable in all three media (−19.0 to −20.8 cal/molK) and not compensated by the slightly favorable enthalpy in the two solvents (−1.4 kcal/mol in acetone or −4.5 kcal/mol in ethanol). In vacuum, the reaction enthalpy (ΔH_{rxn}) is unfavorable at +1.8 kcal/mol, probably because favorable hydrogen bonding within the silicic acid (intramolecular) is lost when the produced water is treated computationally in a vacuum. In short, the conversion of silicic acid to alkylorthosilicates with simple mono-alcohols, such as methanol, seems thermodynamically prohibited even in the most favorable (polar) media.

For ethylene glycol (EG), the overall thermodynamics of producing the 5,5-silaspirocycle alkylorthosilicate (Fig. 4b) are very medium-dependent. In vacuum, the ΔH_{rxn} of +7.9 kcal/mol is similar to that of silicon methoxide production (+7.5 kcal/mol). The first chelation step is quite entropically favorable with ΔS = +36.9 cal/molK. But the enthalpy is quite unfavorable with ΔH = +15.1 kcal/mol. So, ΔG for this step is substantially endergonic at +4.1 kcal/mol. Interestingly, the second chelation step is also quite entropically favorable with ΔS = +37.3 cal/molK; but, its enthalpy is much less penalizing at ΔH = +10.9 kcal/mol. Hence, this final chelation step is slightly exergonic at ΔG = −0.2 kcal/mol. Compared to vacuum, the first chelation enthalpy is more favorable in polar solvents: ΔH = +10.0 kcal/mol in acetone and ΔH = +8.0 kcal/mol in ethanol. The second chelation enthalpy is even more favorable: ΔH = +6.5 kcal/mol in acetone and ΔH = +4.9 kcal/mol in ethanol. Hence, in polar solvents, production of the 5,5-silaspirocycle from silicic acid is considerably exergonic: ΔG = −2.5 kcal/mol in acetone and ΔG = −6.1 kcal/mol in ethanol.

For production of the 6,6-silaspirocycle alkylorthosilicate from 1,3-propanediol (PD), the ΔG_{rxn} values are also very medium-dependent and each value is more favorable (Fig. 4c) than that for the corresponding 5,5-silaspirocycle (Fig. 4b). The origin of this difference is the comparatively more favorable enthalpy of the two chelation steps: in vacuum, ΔH = +7.9 and +7.8 kcal/mol; in acetone, ΔH = +3.1 and +4.0 kcal/mol; in ethanol, ΔH = +1.3 and +2.0 kcal/mol. Hence, in polar solvents, production of the 6,6-silaspirocycle from silicic acid is even more exergonic than for the 5,5-spirocycle: ΔG = −6.8 kcal/mol in acetone and ΔG = −11.5 kcal/mol in ethanol.

Overall, the entropic benefit of chelation is clear. For the production of silicon methoxide (Fig. 4a), the reaction entropy is negative in all three media (−19.0 to −20.8 cal/molK). But for the silaspirocycles, the entropy is positive since the overall reaction generates five molecules from three: +52.3 to +53.8 cal/molK for the 5,5 silaspirocycle (Fig. 4b) and +50.2 to +50.7 cal/molK for the 6,6 silaspirocycle (Fig. 4c).

2.3. Alkylorthosilicate metathesis (AOSM)

We have previously demonstrated silicon acetal metathesis (SAMP) and applied this to the synthesis of polysilicon acetals [29]. This metathesis reaction occurs very slowly without added catalyst; but Brønsted acids, such as *para*-toluenesulfonic acid (*p*-TSA), serve to establish equilibrium between $MeOSiMe_2OMe$

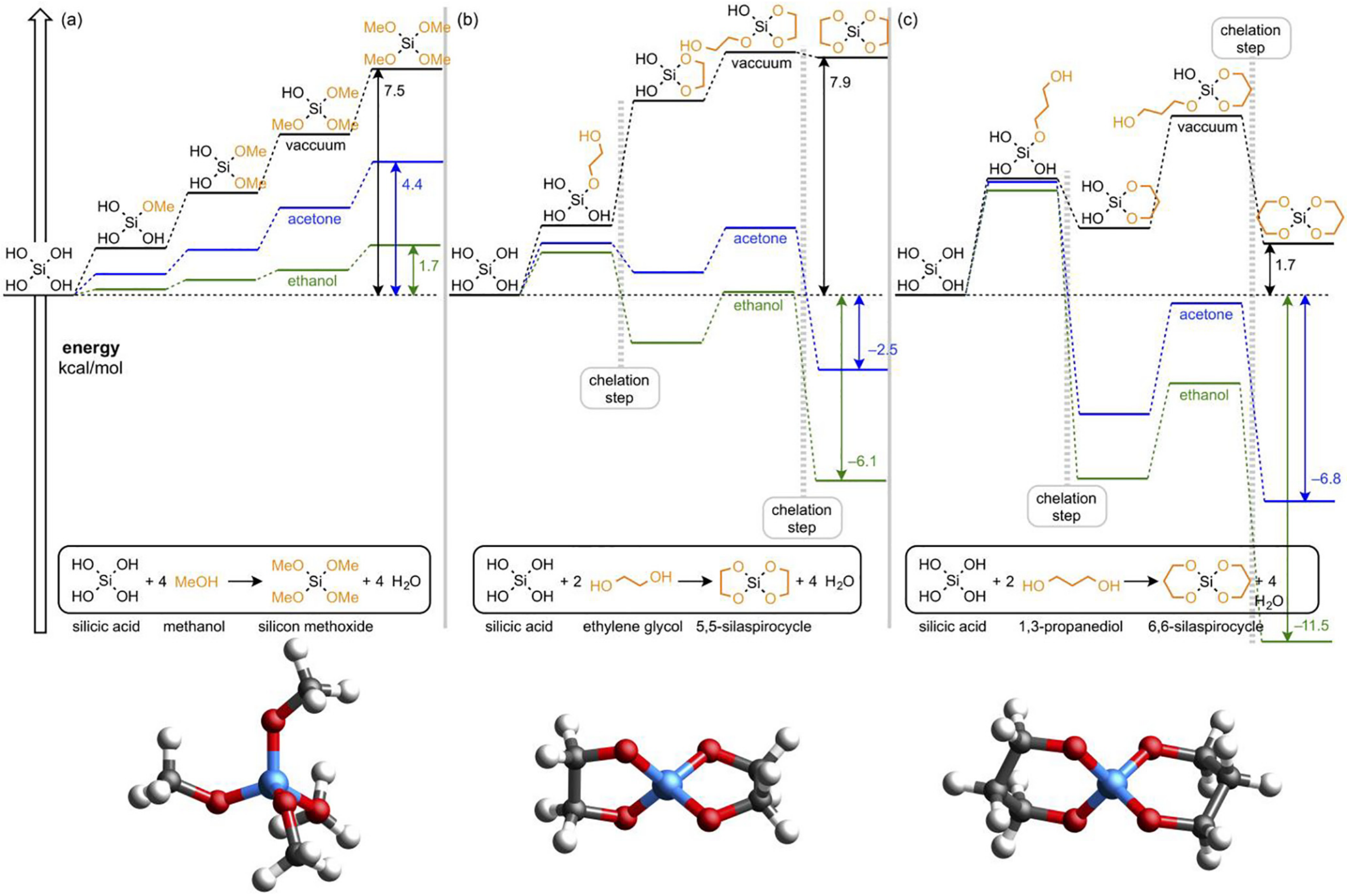

Fig. 4. Calculated (DFT/B3LYP/6–31+G*) thermodynamics (Gibbs free energy @ 298.15 K) of silicic acid conversion to alkylorthosilicates with (a) methanol, (b) ethylene glycol (EG), or (c) 1,3-propanediol (PD). Isodesmic reactions show that the 6,6-silaspirocycle is more stable than silicon methoxide by (1.7–(7.5)) = –5.8 kcal/mol in vacuum, (–6.8–(4.4)) = –11.2 kcal/mol in acetone, and (–11.5–(1.7)) = –13.2 kcal/mol in ethanol.

and $EtOSiMe_2OEt$ in 5 h at room temperature, yielding a statistical amount of $MeOSiMe_2OEt$. Recently, we have demonstrated that alkylorthosilicate metathesis (AOSM) is also acid-catalyzed and equilibrium can be established in minutes at room temperature [30]. Here, we employ AOSM to investigate the relative thermodynamic stability of silicon methoxide, the 5,5-silaspirocycle, and the 6,6-silaspirocycle. Fig. 5 describes the fate of silicon methoxide when combined with 1.99 equivalents of ethylene glycol (blue circles) or 1.75 equivalents of 1,3-propanediol (orange squares) and *p*-TSA as catalyst (~0.02 mol%) in acetone d_6 at room temperature. The two silaspirocylces are formed, as quantified by ^{1}H NMR (see the Supplementary Data). Equilibrium is established in several hours; the final conversion to the 5,5-silaspirocycle from ethylene glycol is 74.6% and that to the 6,6-silaspirocycle from 1,3-propanediol is comparable at 66.2%. Conversions above 50% reflect the greater thermodynamic stability of both silaspirocycles versus silicon methoxide, as suggested by the entropically favored chelation steps computed in Fig. 4. The greater conversion measured for the 5,5-silaspirocycle might suggest that it is thermodynamically more stable than the 6,6-silaspirocycle. But note that initial diol equivalents are not the same and that precipitation phenomena may skew the ^{1}H NMR analysis, which only observes species in solution.

2.4. Factors dictating alkylorthosilicate stability

The atomic structure of $Si(OMe)_4$ is not known from single crystal X-ray crystallography, although it reportedly crystallizes in the

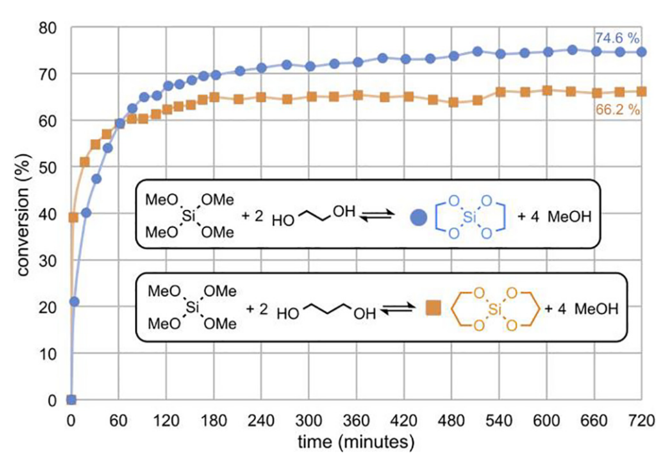

Fig. 5. With acid catalyst, silicon methoxide ($Si(OMe)_4$) exchanges its methoxy groups for ethylene glycol or 1,3-propanediol, yielding the 5,5-silaspirocycle (blue circles) or the 6,6-silaspirocycle (orange squares), respectively. ((Colour online.))

*P*23 cubic space group [31]. An X-ray crystal structure for the analogous tetravalent $Si(OiPr)_4$ is known [32] and metrics from that study match the parameters well for $Si(OMe)_4$ computed herein (DFT/B3LYP/6-31+G*/vacuum) and depicted in Fig. 6a. For example: (1) both assume the molecular point group S_4; (2) both have large (115.1°, 114.9°) and small (106.7°, 106.8°) O-Si-O bond

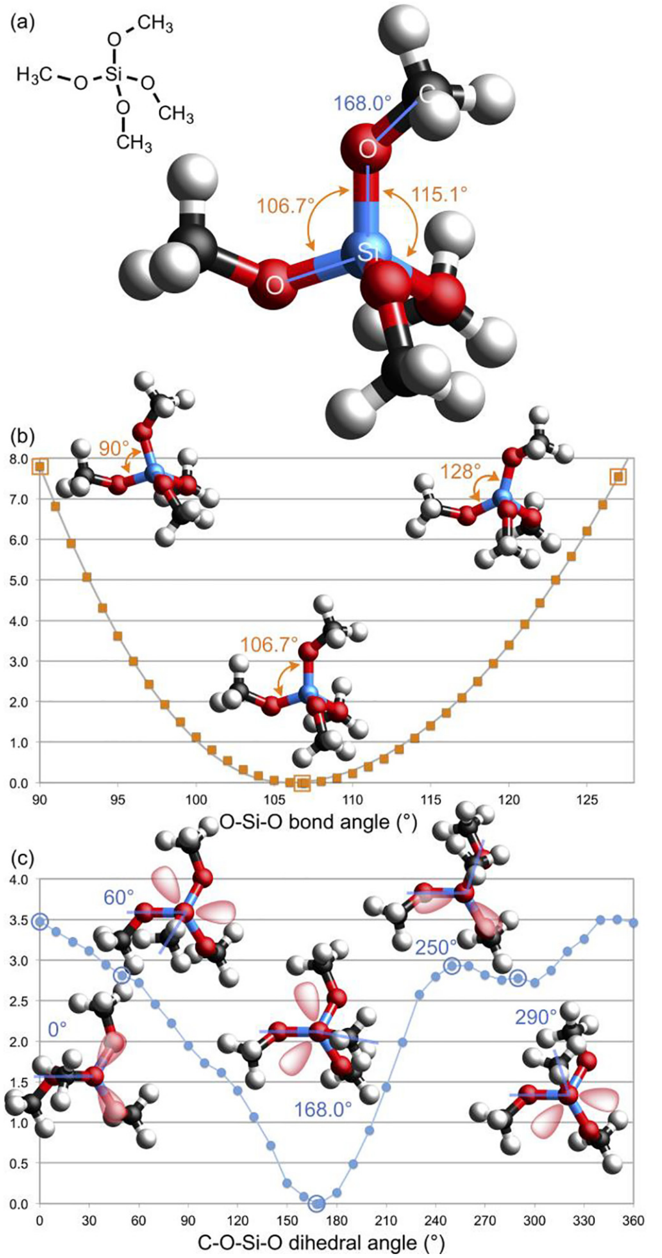

Fig. 6. (a) Calculated (DFT/B3LYP/6–31+G*/vacuum) structural parameters for $Si(OMe)_4$ show four O-Si-O bond angles of 106.7° and two of 115.1°, along with four C-O-Si-O dihedral angles of 168.0°. (b) Calculated energetic deviations from the 106.7° O-Si-O bond angle of $Si(OMe)_4$. The gray line represents $\Delta E = k_\Theta(\Delta\theta)^2$ with a larger compressive (0.0315 (kcal/mol)(degree)$^{-2}$) and smaller expansive (0.0167 (kcal/mol)(degree)$^{-2}$) force constant (k_Θ). (c) Conformational analysis of the C-O-Si-O dihedral angle shows energy minima at 168° and 290°, for which O $n \rightarrow$ Si-O σ^* anomeric interactions are maximally engaged.

angles; and (3) both have singular C-O-Si-O dihedral angles that are close in value (168.0° and 162.7°).

Fig. 6b shows the computed potential energy diagram for O-Si-O bond angle deviations from the idealized 106.7°. Compression of this angle by 10° costs 2.5 kcal/mol. Compression another 4° doubles the energy penalty to 5.0 kcal/mol. Expansion of this angle by 10° costs 2.0 kcal/mol. Expansion another 4° also doubles the energy penalty, to 4.0 kcal/mol. For bond angle distortions, $\Delta E = k_\Theta(\Delta\theta)^2$ and typical hydrocarbon C-C-C bond angle distortions have a force constant k_Θ = 0.0175 (kcal/mol)(degree)$^{-2}$ [33,34]. For Fig. 6b the O-Si-O force constant computes to $k_{\Theta\text{-comp}}$ = 0.0315 (kcal/mol)(degree)$^{-2}$ for compression and $k_{\Theta\text{-exp}}$ = 0.0167 (kcal/mol)(degree)$^{-2}$ for expansion (gray curves). So, compared to the C-C-C bond angle of hydrocarbons, the O-Si-O bond angle of $Si(OMe)_4$ has a substantially greater (stiffer) force constant for compression and a lower (softer) force constant for expansion. The large compression force constant can explain the computed instability of the 5,5-silaspirocycle relative to the 6,6-silaspirocycle. The ring O-Si-O bond angle (DFT/B3LYP/6–31+G*) for the smaller silaspirocycle is 97.8°, whereas that for the larger silaspirocycle is 107.1°. According to $\Delta E = k_\Theta(\Delta\theta)^2$, the *two* compressed rings of the 5,5-silaspirocycle add $2\Delta E$ = 2[0.0315 (kcal/mol)(degree)$^{-2}$][106.7°–97.8°]^2 = 5.0 kcal/mol of angle strain. There is negligible (0.01 kcal/mol) angle strain for the rings of the 6,6-silaspirocycle since [107.1°–106.7°]^2 is small. This difference in angle strain largely accounts for the overall energy differences of the small and large silaspirocycles found in Fig. 4: [7.9–1.7] = 6.2 kcal/mol in vacuum; [−2.5–(−6.8)] = 4.3 kcal/mol in acetone; and [−6.1–(−11.5)] = 5.4 kcal/mol in ethanol.

Fig. 6c shows the potential energy diagram computed for conformational analysis of the C-O-Si-O dihedral angle in $Si(OMe)_4$. The global minimum exists at 168.0° because this conformer (1) has minimal methoxy-methoxy steric interactions and (2) allows for significant anomeric stabilization/ hyperconjugation of the oxygen lone pairs (red lobes) as they donate into anti-coplanar Si-O σ^* orbitals (when the [lone pair]-O-Si-O dihedral angle is 180°). Anomeric interactions are also fully engaged when the C-O-Si-O dihedral angle is 290°, although this is only a local minimum because of penalizing methoxy-methoxy steric interactions. Near a C-O-Si-O dihedral angle of 60°, the anomeric interactions would be also be fully engaged; however, a torsional energy minimum is not observed here because of the very close methoxy-methoxy contact. The global energetic maximum of Fig. 6c exists near 0°; at this dihedral angle, anomeric stabilization is minimized and methoxy-methoxy steric repulsion is maximized.

Absent steric influences, the anomeric stabilization would maximize at C-O-Si-O dihedral angles of 60°, 180°, and 300° and minimize at 0°, 120°, and 240°. Table 1 shows the relevant dihedral angles in the optimized (DFT/B3LYP/6–31+G*/vacuum) structures of $Si(OMe)_4$, the 5,5-silaspirocycle, the 6,6-silaspirocycle, and quartz (from X-ray crystallography) [28]. The value of Δ° is tabulated and represents the deviation (in degrees) from the nearest anomeric stabilization angle of 60°, 180°, or 300°. This deviation could range from 0° (maximum stabilization) to 60° (minimum stabilization). $Si(OMe)_4$ enjoys a small average Δ° of 13.7° and thus has considerable anomeric stabilization. This is expected since there are essentially no conformational restrictions prohibiting this stabilization. However, the silaspirocycles (Fig. 4) have conformational and angular limitations that restrict full anomeric engagement. The 6,6-silaspirocycle, with average Δ° = 45.6°, enjoys slightly more anomeric stabilization compared to the 5,5-silaspirocycle, with average Δ° = 50.6°. Since these average Δ° dihedral angle values are so similar, it is likely that the thermodynamic preference of the 6,6-silaspirocycle versus the 5,5-silaspirocycle is mostly attributable to the negligible O-Si-O angle strain of the former and the substantial O-Si-O angle strain of the latter, as noted in the previous discussion in reference to Fig. 6b. Note that quartz [28], the most stable form of silica with average Δ° = 38.3°, seems to sacrifice some anomeric stabilization in order to minimize O-Si-O bond angle strain; it has only small deviations from the ideal O-Si-O angle of 106.7°: 109.2°, 108.8°, 110.5°, 110.5°, 108.8°, and 109.0°.

2.5. Silica to alkylorthosilicate thermodynamics

The net depolymerization thermodynamics of silica with alcohols to $Si(OMe)_4$, the 5,5-silaspirocycle, or the 6,6-silaspirocycle

Table 1
Calculated[a] C-O-Si-O dihedral angles (°) for $Si(OMe)_4$, the 5,5-silaspirocycle, the 6,6-silaspirocycle, and quartz (Si-O-Si-O, by X-ray diffraction[b]), along with Δ°, the angular deviation from the nearest anomeric stabilization angle of 60°, 180°, or 300° [c].

$Si(OR)_4$	Δ°	5,5	Δ°	6,6	Δ°	quartz	Δ°
44.5	15.5	114.1	54.1	107.4	47.4	12.3	47.7
168.0	12.0	227.5	47.5	225.4	45.4	131.9	48.1
286.3	13.7	350.7	50.7	345.5	45.5	252.6	47.4
44.5	15.5	113.0	53.0	−105.8	45.8	31.0	29.0
168.0	12.0	226.3	46.3	−224.9	44.9	151.5	28.5
286.3	13.7	349.7	49.7	−344.7	44.7	271.1	28.9
−44.5	15.5	−113.3	53.3	−105.8	45.8	12.3	47.7
−168.0	12.0	−226.7	46.7	−224.9	44.9	131.9	48.1
−286.3	13.7	−350.0	50.0	−344.7	44.7	252.6	47.4
−44.5	15.5	−114.3	54.3	107.4	47.4	31.0	29.0
−168.0	12.0	−227.5	47.5	225.4	45.4	151.5	28.5
−286.3	13.7	−350.9	50.9	345.5	45.5	271.1	28.9
AVE:[d]	13.7		50.6		45.6		38.3

[a] Calculated according to DFT/B3LYP/6-31+G* in vacuum.
[b]Si-O-Si-O dihedral angle measured from the reported single X-ray crystal structure of quartz [28].
[c]The factor Δ° ranges from 0 to 60° and smaller values imply greater anomeric stabilization. [d]The average value of Δ°.

can be approximated computationally. The idealized reactions with silica are:

$$(SiO_2)_n + 4\ MeOH \rightarrow Si(OMe)_4 + 2\ H_2O + (SiO_2)_{n-1}$$

$$(SiO_2)_n + 2\ HOCH_2CH_2OH \rightarrow Si(OCH_2CH_2O)_2 + 2\ H_2O + (SiO_2)_{n-1}$$

$$(SiO_2)_n + 2\ HOCH_2CH_2CH_2OH \rightarrow Si(OCH_2CH_2CH_2O)_2 + 2\ H_2O + (SiO_2)_{n-1}$$

Importantly, the methanol reaction converts five molecules to four molecules, but the diol reactions convert three molecules to four molecules. An apt depolymerization model must match this stoichiometry or else the entropy parameters will be irrelevant. The excision of SiO_2 from an unstrained ring approximates the depolymerization of silica since quartz is an endless array of unstrained 12-membered rings. It is reported that 8-membered siloxane rings (*cyclic*-$[SiOMe_2]_4$) are also devoid of ring strain [35]; hence, a viable model reaction is as follows [36]:

$$cyclic\text{-}[SiO(OH)_2]_4 + 4\,ROH \rightarrow Si(OR)_4 + 2\,H_2O + HO[SiO(OH)_2]_3H$$

Fig. 7 shows the model reaction of the 8-membered Si4 ring *cyclic*-$[SiO(OH)_2]_4$ with methanol, ethylene glycol, or 1,3-propanediol. The computed reaction enthalpies (Δ*H*), entropies (Δ*S*), and free energies (Δ*G*, at both 25 and 100 °C) are listed in Table 2 (DFT/B3LYP/6–31+G*/SM8 solvent correction model).

The Δ*G* of each reaction is plotted in Fig. 7 versus temperature in vacuum (dotted lines), ethanol (dashed lines), or water (solid lines) as the computational solvent medium. The reaction with methanol is never favorable (never exergonic) because the reaction enthalpy is positive (+2.2 to +6.3 kcal/mol) and the reaction entropy is negative (–41.9 to –46.6 cal/molK), on account of the reaction stoichiometry noted above (five molecules to four). The reactions with the diols also have positive enthalpies (ethylene glycol: +28.4 to +15.7 kcal/mol; 1,3-propane diol: +21.3 to +9.5 kcal/mol), but positive entropies (ethylene glycol: +30.8 to +26.4 cal/molK; 1,3-propane diol: +27.8 to +24.3 cal/molK), indicating that there is a temperature above which the reaction is exergonic. This thermoneutral temperature (ΔG_{rxn} = 0) for the ethylene glycol reaction is 314 °C in the most favorable reaction medium, water. However, the thermoneutral temperature for the 1,3-propanediol reaction is much lower because of the greater stability computed for the 6,6-silaspirocycle versus the 5,5-silaspirocycle. In ethanol as the computational solvent medium, the reaction is exergonic above 171 °C (Fig. 7, dashed orange line); but in water, the reaction is favorable above 99 °C (Fig. 7, solid orange line). Solvation markedly improves the reaction thermodynamics with the diols (versus vacuum) because one additional molecule is solvated on the products side of the reaction. Note, the net reaction parameters for an acetone medium were also calculated and fall predictably between those of vacuum and ethanol (Table 2). For comparison, the bulky mono-alcohol isopropanol forms a markedly less stable $Si(OiPr)_4$ compared to $Si(OMe)_4$ (see Table 2), probably for steric reasons.

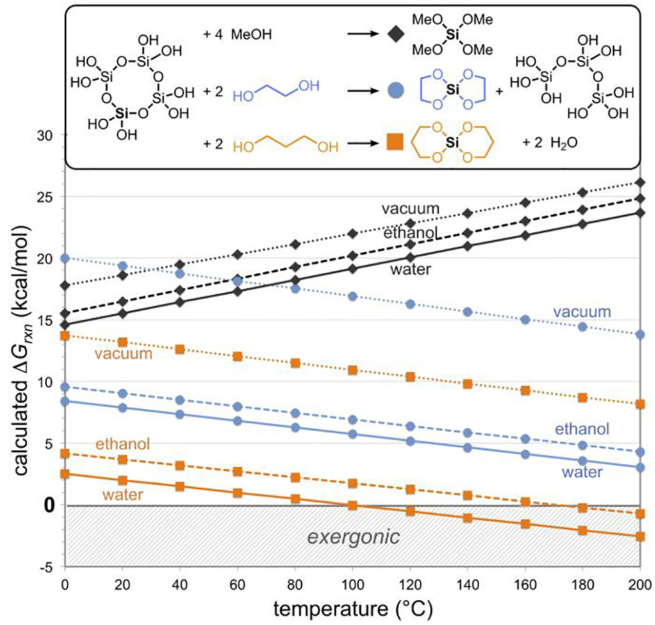

Fig. 7. Calculated silica depolymerization thermodynamics as a function of temperature, as modeled by alcoholysis of *cyclic*-$[SiO(OH)_2]_4$. Reactions with mono-alcohols (such as methanol, black diamonds) are never thermodynamically viable since ΔH_{rxn} is positive and ΔS_{rxn} is negative. Reactions with diols (such as ethylene glycol, blue circles or 1,3-propanediol, orange squares) have an exergonic temperature range since ΔH_{rxn} and ΔS_{rxn} are both positive. With 1,3-propanediol, the depolymerization of silica is calculated to be exergonic above 171 °C in ethanol or above 99 °C in water. ((Colour online.))

Table 2
Calculated[a] thermodynamic parameters for silica depolymerization, modeled by the alcoholysis reactions of Fig. 7.

alcohol	medium	Δ*H* (kcal/mol)	Δ*S* (cal/molK)	$\Delta G_{25°C}$ (kcal/mol)	$\Delta G_{100°C}$ (kcal/mol)
MeOH	vacuum	+6.3	−41.9	+18.8	+22.0
	acetone	+3.6	−44.5	+16.8	+20.2
	ethanol	+2.8	−46.6	+16.7	+20.2
	water	+2.2	−45.4	+15.7	+19.1
ethylene glycol	vacuum	+28.4	+30.8	+19.2	+16.9
	acetone	+18.4	+28.4	+9.9	+7.8
	ethanol	+16.8	+26.4	+8.9	+6.9
	water	+15.7	+26.8	+7.8	+5.7
1,3-propane-diol	vacuum	+21.3	+27.8	+13.0	+11.0
	acetone	+13.3	+25.7	+5.6	+3.7
	ethanol	+10.8	+24.3	+3.6	+1.7
	water	+9.5	+25.4	+1.9	−0.02
*i*PrOH	vacuum	+7.7	−67.2	+27.8	+32.8

[a] Calculated according to DFT/B3LYP/6-31+G* with the SM8 solvent correction model.

3. Conclusions

The resonance energy of silica (polymeric SiO_2) has been estimated via model compounds and explains the thermodynamic stability of this enormously abundant material. The Si-O-Si silicate linkage is stabilized by about 8.0 kcal/mol versus Si-O-R species, since the latter sacrifices oxygen electron hyperconjugation/delocalization described by O $n \rightarrow$ Si-O σ^*. Silica possesses two oxygen atoms per silicon atom and thus, an estimated resonance energy of 16.0 kcal per mol of SiO_2. The actual resonance energy might be attenuated because of non-ideal Si-O-Si-O dihedral angles in the crystal lattice (see Table 1). This effect will be reported elsewhere [25]. Despite silica's resonance energy stabilization, its conversion to molecular alkylorthosilicates with alcohols is thermodynamically feasible if the entropic benefit of chelation is exploited. Computationally, silica depolymerization with methanol—and presumably any mono-alcohol—is never exergonic. The enthalpy is slightly unfavorable and the entropy term (five molecules to four) is unfavorable at all temperatures. However, silica depolymerization with diols can be exergonic. The unfavorable enthalpy term is offset by a favorable entropy term (three molecules to four) above the thermoneutral temperature. For example, silica depolymerization with ethylene glycol or 1,3-propanediol is calculated to be exergonic above 314 °C or 99 °C in water, respectively. Two factors have been described that dictate the stability of the formed alkylorthosilicates. The O-Si-O bond angle is minimally strained at 106.7° and the C-O-Si-O dihedral angle maximizes anomeric interactions at 168°. Silicon methoxide, $Si(OMe)_4$, reacts with ethylene glycol or 1,3-propanediol to yield the silaspirocycles $Si(OCH_2CH_2O)_2$ and $Si(OCH_2CH_2CH_2O)_2$, respectively, via acid-catalyzed alkylorthosilicate metathesis (AOSM). The silaspirocycles are enthalpically less stable than $Si(OMe)_4$ since their bond and dihedral angles are farther from ideal. Still, they are favored at equilibrium because of favorable entropy. Therefore, it is conceivable that other chelating diols exist that would form more thermodynamically stable alkylorthosilicates and behave as superior silica depolymerization agents. Finally, note that silica gel, diatomaceous earth, and rice husk silica are all hydrated forms of silica and hence, partially depolymerized according to the thermodynamic schemes of Fig. 2. Therefore, their depolymerization should occur at lower temperatures versus those necessary for bulk silica itself.

4. Experimental section

4.1. Materials and methods

Ethylene glycol (98+%, Fisher Scientific), tetramethylorthosilicate (99%, Acros), 1,3-propanediol (98+%, Tokyo Chemical Industry), and *para*-toluenesulfonic acid (98%, Sigma-Aldrich), were purchased and used as received. NMR solvents, including deuterated acetone (acetone d_6, without tetramethylsilane, TMS), were purchased from Cambridge Isotope Laboratories. All other chemicals, unless otherwise described, were utilized as received.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Bruker 600 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to residual proton in the specified solvent. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; br, broad.

4.2. NMR metathesis experimental details

All NMR metathesis experiments were conducted in acetone d_6 using eight scans and a 30 s relaxation delay. Time-evolved plots were made by obtaining spectra every 15 min for three hours and then every 30 min for nine hours. Two additional spectra were taken at 24 and 48 h. All components were measured using a P1000 micropipette.

4.2.1. Metathesis of tetramethylorthosilicate and ethylene glycol

In an NMR tube, tetramethylorthosilicate (0.208 g, 1.37 mmol), ethylene glycol (0.161 g, 2.60 mmol), and *p*-toluenesulfonic acid (15 µL of a 0.0168 M solution in acetone d_6, 2.52×10^{-4} mmol) were combined. Equilibrium was reached after about 12 h, giving 74.6% conversion to the 5,5-silaspirocycle. ^{1}H NMR (600 MHz, acetone d_6, 25 °C) δ: 3.90 (s, 8H, CH_2).

4.2.2. Metathesis of tetramethylorthosilicate and 1,3-propanediol

In an NMR tube, tetramethylorthosilicate (0.208 g, 1.37 mmol), 1,3-propanediol (0.1910 g, 2.50 mmol), and *p*-toluenesulfonic acid (15 µL of 0.0168 M solution in acetone d_6, 2.52×10^{-4} mmol) were combined. Equilibrium was reached after about 12 h, giving 66.2% conversion to the 6,6-silaspirocycle. ^{1}H NMR (600 MHz, acetone d_6, 25 °C) δ: 3.86 (t, 8H, CH_2O), 1.63 (quint, 4H, –CH_2–).

4.3. Computational studies

Computational results were obtained with Spartan '10 for Macintosh. Geometry optimizations and thermodynamic calculations were performed at the DFT B3LYP/6-31+G* level of theory. Enthalpic energies were taken as the optimized electronic energy (E), while entropic energies were the sum of the computed vibrational, translational, and rotational entropies. The SM8 solvent correction model provided these thermodynamic parameters in the solvents acetone, ethanol, or water.

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Appendix A. Supplementary data

Supplementary data is available providing dimensional analysis, NMR spectra and conversions, and computational protocols and results. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2020.114562.

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