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An unprecedented gas-phase condensation reaction mediated by a bissilylated chloronium ion intermediate⁺

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Gas-phase Cl₂Si(OH)⁺ and Si₂OCl_{4-n}(OH)_{n+1}⁺ (n = 0-4) ions are shown to undergo a novel condensation reaction with SiCl₄ that provides a potentially useful pathway for a variety of networks containing the –(Si-O-Si)- backbone. Theoretical calculations reveal that these reactions proceed via a bissilylated chloronium ion intermediate.

Silicon alkoxides, Si(OR)₄, and related alkoxysilanes have been extensively explored as molecular precursors of a large variety of silicon-containing glasses, gels, ceramics and nanomaterials via sol-gel chemistry.^{1,2} For these substrates, sol-gel processes are well known to be initiated by hydrolysis of the alkoxy groups followed by successive condensation reactions leading to the formation of $\equiv S_i - Q - S_i \equiv$ networks. While the kinetics and thermodynamics of the hydrolysis processes have been characterized,^{3,4} a full understanding of the initial processes is essential for the purpose of designing materials with well-defined properties.⁵ This has provided the impetus for: 1) theoretical studies addressing the mechanisms of the initial hydrolysis-condensation processes, 6-10 and 2) attempts to recreate some of these reactions in the gas-phase by mass spectrometric techniques in order to probe the intrinsic reactivity pathways of alkoxysilanes.¹¹⁻²⁰

Because chemical modifications of the alkoxide precursors allow for incorporation of organic functions and thus alter the functionality and nature of the end material,²¹⁻²⁴ there is considerable interest in unravelling new approaches to the hydrolysis-condensation reactions. In this communication, we present an unusual set of gas-phase condensation reactions between $Cl_{3-n}Si(OH)_n^+$ (n = 1-3) ions and $SiCl_4$ that provide a useful approach for a variety of $\equiv Si - Q - Si \equiv$ networks.

 $Cl_{3-n}Si(OH)_n^+$ (n = 1-3) ions (n = 1-3) ions were generated in an in-house built Fourier transform ion cyclotron resonance (FT-ICR) spectrometer by progressive hydrolysis of gas-phase $\rm SiCl_3^{*}$ ions as described in earlier studies. 25,26 The initial hydrolysed ions, the Cl_2Si(OH)^+ isotopologues, were selectively isolated in the icr cell using multiple ejections techniques^{25} and allowed to react with SiCl_4 at typical pressures of (3.5 \pm 0.5)×10⁻⁸ mbar. Under these conditions, reaction (1) was observed to proceed readily.

 $Cl_2Si(OH)^+ + SiCl_4 \rightarrow {}^+Cl_2SiOSiCl_3 + HCl$ (1)

The Cl₃SiOSiCl₂⁺ ions formed in (1) were then found to undergo rapid hydrolysis with the background water (used to generate Cl₂Si(OH)⁺ and related species) to yield a series of Si₂OCl₅₋ $_{n}(OH)_{n}^{+}$ (n =1 – 5) ions in analogous fashion to that described in our previous work.²⁵

$$Si_2OCl_{5-n}(OH)_n^+ + H_2O \rightarrow Si_2OCl_{4-n}(OH)_{n+1}^+ + HCl (n=0-4)$$
 (2)

The rate constant for reaction (1) was estimated from the successive half-lives taking into account the subsequent reactions (2). Correction for the ion gauge readings to obtain the absolute pressure of SiCl₄ leads to a rate constant of $(2.3\pm0.7)\times10^{-10}$ cm³ molecule⁻¹ s⁻¹ at a cell temperature of 333±5 K. This value is of the order of 10% of the calculated ion-neutral collision rate constant.

The fact that no equivalent reaction to (1) has been previously observed in the neutral chemistry of SiCl₄ and $Si_2Cl_6^{27-31}$ prompted us to investigate more thoroughly the mechanism of reaction (1). This is of considerable interest because of the important role that chlorosiloxane species play in the functionalization of silica particles.³²⁻³⁴ We therefore decided to explore mechanistic details for this reaction through computational chemistry. Theoretical calculations were carried out with the Gaussian 03 suite of $programs^{35}$ to address possible pathways, characterize intermediates and transition states and map out the energy profile of the reaction. Initial calculations for the structure and energy of reagents, products, intermediates and transition states were carried out at the B3LYP/6-311+G(d,p) level of theory with vibrational frequencies corrected by a factor of 0.9679 to estimate zero-point energies (ZPE).³⁶ For comparison purposes, calculations were also performed at the MP2/6-

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311+G(d,p) level with vibrational frequencies corrected by a factor of 0.9523,³⁷ and with the M05-2X functional with the 6-311+G (d,p) basis set. These different methods were useful for assessing the robustness of the calculated energies and structures in view of possible isomeric structures.³⁸ Transition states were identified by a single imaginary frequency and intrinsic reaction coordinate (IRC) calculations were carried out to characterize the connection between reaction intermediates and transition states.

(Scheme 1 about here)

Scheme 1. General view of the intermediates involved in the mechanism of reaction (1).

(Figure 1 about here)

Fig. 1 Calculated energy profile (including zero point energies) for reaction (1) at the MP2/6-311+G(d,p) level of theory.

(Figure 2 about here)

Fig. 2 Optimized geometries calculated at the MP2/6-311+G(d,p) level of theory for intermediates and transition states outlined in Scheme 1 and Figure 1. Distances are in Å and angles in degrees.

The results of these calculations indicate that reaction (1) proceeds by initial formation of a chloronium ion intermediate followed by an exchange of the bridging chlorine by an OH group as outlined in Scheme 1. The calculated energy profile for this multistep reaction (Figure 1) reveals that this pathway is very favourable with the two transition states lying well below the energy of the reagents. Furthermore, reaction (1) is predicted to be exothermic and thus consistent with the ease of the observed ion/molecule reaction. Figure 2 illustrates the calculated structures of the intermediates and transition states of the energy profile shown in Figure 1. Although the calculated values with the B3LYP method are considerably different from those obtained with the MP2 method and the M05-2X functional (see Table 1), the general features of the energy profile are the same.

Table 1 Calculated values for (E+ZPE) in kcal mol⁻¹ for the stationary points and transition states of Figure 1 using different computational chemistry models. Values are referenced to the energy of the reactants.

	B3LYP	MP2	M05-2X
RC	-18.3	-25.6	-25.4
TS1	-6.9	-14.6	-12.9
Int	-35.3	-47.8	-44.6
TS2	-12.1	-23.5	-19.9
PC	-26.3	-35.4	-34.1
Products	-9.0	-13.6	-10.5

The mechanism outlined for reaction (1) is particularly significant because it is found to proceed through a bissilylated halonium ion intermediate. These species have been recognized in recent years as important intermediates for carbon-halogen activation and as precursors of highly reactive Lewis acids.³⁹⁻⁴³ Similar type of species had been predicted to be stable

intermediates in some early theoretical modeling of the reaction between Si^+ and SiX_4 (X = F, Cl). 44

Several other aspects of reactions similar to (1) deserve further consideration. For example, the progressively hydrolyzed ions, $Si_2OCl_{4-n}(OH)_{n+1}^{*}$ (n = 0 - 4), can undergo further condensation reactions with SiCl₄ in an analogous fashion to reaction (1). These secondary reactions were not extensively investigated because they are considerably slower than (1) and the ionic products fall in a mass range above the useful range of our spectrometer.²⁵ Nevertheless, they do provide a convenient pathway for the formation of larger $\equiv Si - 0 - (SiCl_2 - 0 - Si(OH)Cl)_n - 0 - Si \equiv$ networks and

variations thereof as shown below.

Different ligands can also be introduced in the networks by making use of the ease with which ions such as $Cl_3SiOSiCl_2^+$ and $Si_2OCl_4(OH)^+$ can undergo gas-phase solvolysis type reactions by analogy to our previous work.²⁵ For example, reaction (3) is readily observed in experiments carried out in the presence of methanol at ~ 1.5×10^{-8} mbar,

$$Si_2OCl_4(OH)^+ + MeOH \rightarrow Si_2OCl_3(OH)(OMe)^+ + HCl$$
 (3)

These reactions are predicted to be considerably exothermic by our theoretical calculations. It should be noticed that further condensation reactions of the ionic product of reaction (3) with SiCl₄ pave the way for a variety of possible \equiv *Si* - *O* - (*SiCl*₂ - *O* - *Si*(*OH*)*R*)_{*n*} - *O* - *Si* \equiv motifs containing different organic groups *R*. On the other hand, a similar approach to these reactions using SiF₄ and the corresponding fluorinated ions is predicted to be unfavourable. In fact, the reaction of gaseous F₂Si(OH)⁺ with SiF₄, analogous to reaction (1), is estimated to be endothermic by 7.7 (B3LYP), 5.1 (MP2) and 6.9 (M05-2X) kcal mol⁻¹ and has not been observed in the earlier study of Speranza and coworkers.⁴⁵

In summary, we have shown that a new type of gas-phase reaction represents a novel approach for building up a variety of modified \equiv **Si** – **O** – **Si** \equiv networks. This type of reactions can be further pursued with ions obtained from siloxanol, siloxanediols⁴⁶ or oligomer diols containing the siloxane structure.⁴⁷ Furthermore, the mechanism of these reactions illustrates the important role that bissilylated chloronium ions can play in promoting condensation type reactions.

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Experimental

The experimental techniques and the FT-ICR spectrometer have has been previously described.²⁵ Cl₂Si(OH)⁺ ions were generated from the reaction of SiCl₃⁺ ions (formed inside the icr cell by electron ionization of SiCl₄) with H₂O maintained at a nominal pressure of 1.4 ± 10^{-8} mbar. The reaction and kinetics of Cl₂Si(OH)⁺ ions (isolated by removal of all other ions) with SiCl₄ maintained at a nominal pressure of Cl₂Si(OH)⁺ of $(3.5 \pm 0.5)\times10^{-8}$ mbar were followed through several half-lives periods up to 6 s. Nominal pressures measured by an ionization gauge were corrected to absolute pressures by a procedure similar to that previously used in this laboratory.⁴⁸ Nevertheless, we estimate that this procedure leads to an uncertainty of 30% in the actual values of the absolute

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pressures for the present case. The temperature of the cell heated by the filament used for electron ionization in these experiments has been previously measured with a thermocouple and is typically 333 ± 5 K.

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An unprecedented gas-phase condensation reaction mediated by a bissilylated *chloronium* ion intermediate

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Gas phase $Cl_2Si(OH)^+$ ions undergo an unusual condensation reaction with $SiCl_4$ to yield $Cl_3SiOSiCl_2^+$ ions that by progressive hydrolysis or solvolysis give rise to a large variety of siloxane type moieties.

