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Chemistry of Semiconductor Clusters: Reactions of Si_n^+ (n = 11-50) with C_2H_4 Show Evidence for Numerous Structural Isomers

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Abstract: The chemical reactions of Si_n^+ (n = 11-50) with C_2H_4 have been investigated at room temperature with use of injected ion drift tube techniques. The reaction kinetics for the addition of the first C_2H_4 molecule have been investigated in detail. The data suggest structural isomers, which react at widely different rates, are present for virtually all clusters in the size range investigated. Prior to this work isomers of atomic clusters have only been identified in a few specific cases. For Si_{20}^+ evidence is presented suggesting that the isomers interconvert slowly on the time scale of our experiments. All the other isomers appear to be stable at room temperature. There appears to be nothing unique about either Si_{39}^+ or Si_{45}^+ (which were found, by Smalley and co-workers, to be particularly unreactive with NH_3). The reactions with C_2H_4 appear to be much more sensitive to the cluster structure than the reactions with NH_3, suggesting that the reactions with C_2H_4 involve specific localized sites on the cluster.

While impressive progress has been made in studies of the chemistry of metal and semiconductor clusters,[1-29] we are still far from understanding the factors important in determining cluster reactivity. Probably the largest piece of information missing from the puzzle is the cluster's geometric structure. Though there have been numerous theoretical calculations of cluster geometry,[30-43] unambiguous experimental information for clusters containing more than three atoms is very limited.[44-46] Studies of cluster chemistry are providing some of the first clues about the structures of the larger clusters. For example, in recent publications Riley and co-workers proposed some plausible structures for several iron clusters based on studies of their reactivity.[2] Studies of cluster chemistry can also provide information about structural isomers. If two isomers react at significantly different rates, then their presence will be apparent from studies of the reaction kinetics. Examples have recently been reported for carbon (C_7^+, C_8^+, and C_9^+),[10,12] vanadium (V_9),[26] niobium (Nb_9, Nb_{11}, Nb_{12}, and Nb_{11}^+, Nb_{12}^+, Nb_{19}^+,[6,16,24] and silicon (Si_9^+, Si_{10}^+)[27] clusters.

In this paper we report the results of a study of the reactions of silicon clusters, Si_n^+ (n = 11-50), with C_2H_4. The reactions of silicon cluster ions have previously been investigated by several groups. Mandich, Reents, and Bondybey[9] and Creasy, O'Keefe, and McDonald[11] have investigated the reactions of small silicon clusters (n up to 8) with a range of simple reagents. Smalley and co-workers[15] have investigated the reactions of silicon clusters containing up to 65 atoms with NH_3 using FT-ICR and clusters injected from an external source. They found oscillations in the reactivity of the clusters, with the 39- and 45-atom clusters being particularly inert. Phillips[47] and George and co-workers[48] suggested that this reactivity pattern could be accounted for by a structural model in which the silicon clusters are a stack of six-membered rings.

More recently we described a study of the reactions of Si_n^+ (n = 3-24) with C_2H_4, where we found Si_{13}^+ to be remarkably inert.[27] Chelikowsky and Phillips[49] have developed an interatomic potential for silicon that reproduces the bulk phase diagram and predicts structures for small clusters in reasonable agreement with high-quality ab initio calculations.[30,31] Calculations for medium-sized clusters with this interatomic potential suggest that some of them have icosahedral structures. Chelikowsky and Phillips suggested that this might account for why Si_{13}^+ is so inert. In our earlier work[27] on the reactions of Si_n^+ with C_2H_4 we only investigated the reaction kinetics in detail for clusters containing 3-10 atoms. We found evidence that both Si_9^+ and Si_{10}^+ existed as at least two different structural isomers, in agreement with predictions of ab initio calculations.[31] Since it is likely that isomers exist for at least some of the larger clusters, and because of the interest

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in the 39- and 45-atom clusters generated by the work of Smalley and co-workers,[15] we have extended our previous measurements and investigated the detailed reaction kinetics of clusters containing up to 50 atoms.

Experimental Methods

The experimental methods employed were similar to those used in our previous work[27] and will only be briefly described here. Si_n^+ clusters were generated by pulsed laser vaporization[50] of a silicon rod in a continuous flow of helium buffer gas. An electron gun, used in some of our previous work to enhance the cluster ion abundance, was not employed in this work since enough cluster ions could be generated directly from the laser vaporization plasma. After exiting the source the cluster ions were focussed into a quadrupole mass spectrometer where a particular cluster size is selected. The mass-selected clusters were then focussed into a low-energy ion beam and injected through a 0.1-cm-diameter aperture into a miniature drift tube.[51] The entrance and exit plates of the drift tube have been modified since our previous work[27] to reduce temperature gradients, but since the reactions were not investigated as a function of temperature in this work the modifications will not be described in detail here. The drift tube is 2.5 cm long and contains 0.4 Torr of neon buffer gas that quickly thermalizes the clusters. They then drift across the drift tube under the influence of a weak electric field. Drift fields between 0.125 and 2.0 V/cm were used. Most of the work described here was performed with a drift field of 0.25 V/cm. As the clusters travel through the drift tube they may undergo chemical reactions with a reagent (in the present work C_2H_4) diluted in the buffer gas. As described below the drift field is sufficiently weak that any chemical reactions that occur take place under thermal energy conditions at a temperature characterized by the temperature of the drift tube walls (room temperature in these experiments). After travelling across the drift tube a small fraction of the product and reactant ions exit through a 0.1-cm-diameter aperture. These ions are focussed into a second quadrupole mass spectrometer where they are mass analyzed. In our previous work[27] a quadrupole with 5/8-in.-diameter rods was used. This had a mass range of 750 amu and so limited the cluster size that could be studied to $n < 25$. For this work a quadrupole with 3/8-in.-diameter rods was used. It has a mass range of 2000 amu so clusters up to $n = 70$ can be studied. After mass analysis the ions are detected by an off-axis collision dynode and dual microchannel plates.

Silicon has several naturally occurring isotopes (^{28}Si, 92.23%; ^{29}Si, 4.67%; and ^{30}Si, 3.10%) and the isotope distribution for the larger clusters studied is ~8 amu wide (fwhm). For most of the experiments reported here a portion of the isotope distribution around 4 amu wide was selected with the first quadrupole. The second quadrupole was usually operated with low resolving power so that the peaks in the mass spectrum where approximately flat-topped. Higher mass-resolving powers were used in experiments to determine the exact masses of the products.

In order to study the reaction kinetics it is necessary to know the neutral reagent pressure and the time the clusters spend in the drift tube. The reagent gas pressures were directly measured with a capacitance manometer. As discussed elsewhere[27] the measured pressures (which were recorded without the buffer gas in the drift tube) were corrected to account for transport of the reagent out of the drift tube by the buffer gas flow. The time that the clusters spend in the drift tube was determined by allowing a 40-μs pulse of cluster ions to enter the drift tube and measuring the arrival time distribution at the detector with a multichannel scaler. The measured time distributions were in good agreement with the distributions predicted by solution of the transport equation for ions traveling through the drift tube.[27,51]

Results

The only products observed from the reactions of Si_n^+ (n = 11-50) with C_2H_4 were a range of $Si_n(C_2H_4)_m^+$ adducts. Because of the broad isotope distribution of the silicon clusters it was difficult to determine the product masses with an accuracy better than 0.5 amu, so all the product assignments were confirmed with C_2D_4.

The reaction kinetics were followed by varying the reagent pressure in the drift tube. Under the conditions employed the reactions are expected to follow pseudo-first-order kinetics, and so

$$\ln \frac{I}{I_0} = -k[C_2H_4]t \qquad (1)$$

where I_0 is the initial Si_n^+ abundance (obtained by summing the intensities of the reactant and products in the mass spectrum), I is the final Si_n^+ abundance (also obtained from the mass spectrum), $[C_2H_4]$ is the C_2H_4 concentration, t is the average time the clusters spend in the drift tube, and k is the rate constant. A plot of ln (I/I_0) against $[C_2H_4]$ should yield a straight line with a slope $-kt$. Figure 1 shows plots of ln (I/I_0) against C_2H_4 pressure for a number of different clusters. The dashed lines show the results of a least-squares fit to the data where we have integrated over the time distribution that the clusters spend in the drift tube (the rather broad time distribution results in a slight departure from linearity that is only just discernable in the Figure). The experimental data are clearly often far from linear. Only clusters containing 11, 14, 18, and 19 atoms show close to linear behavior. The data for clusters containing 11 and 19 atoms is shown in the figure. The C_2H_4 partial pressure was kept below 6.0 mTorr in these experiments to ensure that the clusters undergo many collisions with the Ne buffer gas before encountering a C_2H_4 molecule. The 14-atom cluster is particularly inert and only around 7% of it reacts at the highest C_2H_4 pressure used, so it is possible that with this cluster we have not depleted enough of it to observe nonlinear behavior. Si_{13}^+ is even more inert than Si_{14}^+, and it was not feasible to investigate the reaction kinetics for Si_{13}^+ with the C_2H_4 pressures employed in these studies.

As can be seen from Figure 1 the shapes of the plots of ln (I/I_0) against C_2H_4 pressure in many cases suggest that there are two components of the silicon clusters that react at significantly different rates. Data presented in Figure 1 for clusters with 17, 24, and 26 atoms show this particularly clearly. The solid lines in the figure show the results of simulations where we assumed that there are two components for each cluster that react at different rates. A nonlinear least-squares procedure was used to fit this model to the experimental data. It is clear from Figure

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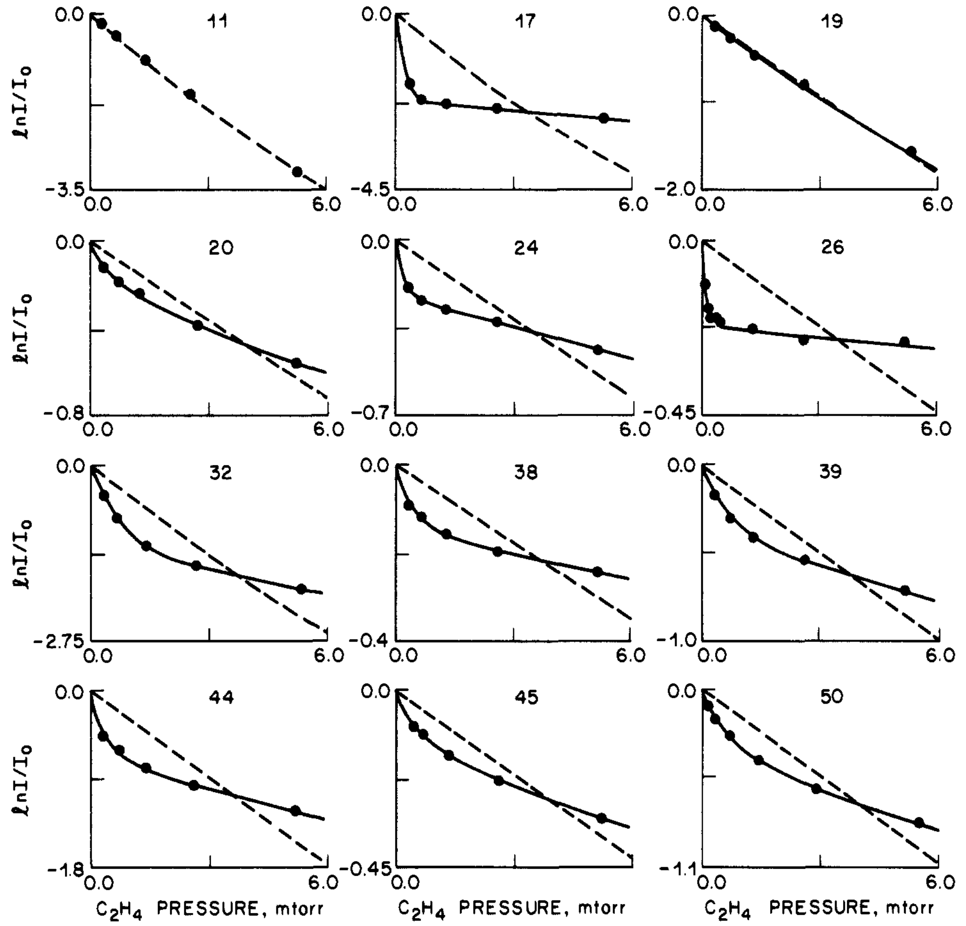

Figure 1. Kinetic data for the reactions of silicon cluster ions with C_2H_4. The figure shows plots of ln (I/I_0) against C_2H_4 pressure in the drift tube. For simple pseudo-first-order kinetics these plots are expected to be straight lines. Data are shown for clusters containing 11, 17, 19, 20, 24, 26, 32, 38, 39, 44, 45, and 50 atoms. The dashed line shows the result of a linear least-squares fit to the data. The solid line shows a least-squares fit of a two-component model discussed in the text. Note that the scale for the y axis (ln (I/I_0)) differs for each cluster.

1 that the two-component model fits the experimental data quite well. However, this should not be taken as indicating that there are *only* two different components present for each cluster.

Figure 2 shows plots of the rate constants obtained from the least-squares analysis with the two-component model. For each cluster a vertical line connects the rate constant obtained for the more reactive component with the rate constant obtained for the less reactive component. The uncertainty in these rate constants (assuming only two components are present) is generally a factor of 2 (somewhat larger uncertainties are expected for the less reactive clusters). We noted above that the kinetics for clusters with 11, 14, 18, and 19 atoms showed close to linear behavior. However, the data for Si_{18}^+ and Si_{19}^+ departed slightly from linear and we have included the results of the analysis with the two-component model for these clusters in Figure 2. The filled points in the figure show the average reactivity of the clusters that we define as

$$R = f_1k_1 + f_2k_2 \qquad (2)$$

where k_1 and k_2 are the rate constants for the two components and f_1 and f_2 are their relative abundances determined from the simulations. The dashed line shows the collision rate obtained from the Langevin–Gioumousis–Stevenson model[52]

$$k_L = 2\pi q\left(\frac{\alpha}{\mu}\right)^{1/2} \qquad (3)$$

where α is the polarizability of the neutral molecule, q is the electronic charge, and μ is the reduced mass. A histogram below the plot of the rate constants shows the fraction of the less reactive component present for each cluster size. The uncertainty in these values is 20% of the major component (assuming only two components are present). The data shown in the figure for clusters with 3–10 atoms were taken from our previous work.[27] The large changes in the reactivity of the smaller clusters are rapidly damped with increasing cluster size and only small oscillations in reactivity occur for the larger clusters. There is clearly nothing particularly unique about either Si_{39}^+ or Si_{45}^+. In the reactions with C_2H_4, Si_{13}^+ and Si_{14}^+ are the particularly inert clusters. As noted above, Si_{13}^+ is so inert that it was not possible to follow the detailed kinetics; the rate constant shown in the figure is an estimate obtained from measurements made with 5–6 mTorr of C_2H_4 in the drift tube (the highest C_2H_4 partial pressures used in these experiments).

It is clear from the results discussed above that for most of the clusters with 11–50 atoms there appear to be at least two components that react with C_2H_4 at different rates. Before proceeding, we should mention that there may be several different sites on the clusters that may react at different rates. However, this could not result in the observed nonlinear kinetics (the observed total rate constant would be the sum of the individual rate constants for reaction at the different sites). We have considered three possible explanations for the observed nonlinear kinetics: different structural isomers, hot clusters, and an equilibrium. In the case of an equilibrium there are, in fact, not two different components of the silicon clusters present, but an equilibrium

$$Si_n^+ + C_2H_4 \rightleftharpoons Si_nC_2H_4^+ \qquad (4)$$

is established where the reverse reaction is a thermally activated desorption of C_2H_4 from the cluster. The first component in the kinetic data then represents the approach to equilibrium. In the second component, where equilibrium has been established, ln (I/I_0) decreases as the increase in C_2H_4 pressure pushes the equilibrium to the right. We performed some simulations and found that we could not reproduce the shapes of the ln (I/I_0) versus C_2H_4 pressure plots for most of the clusters assuming an equi-

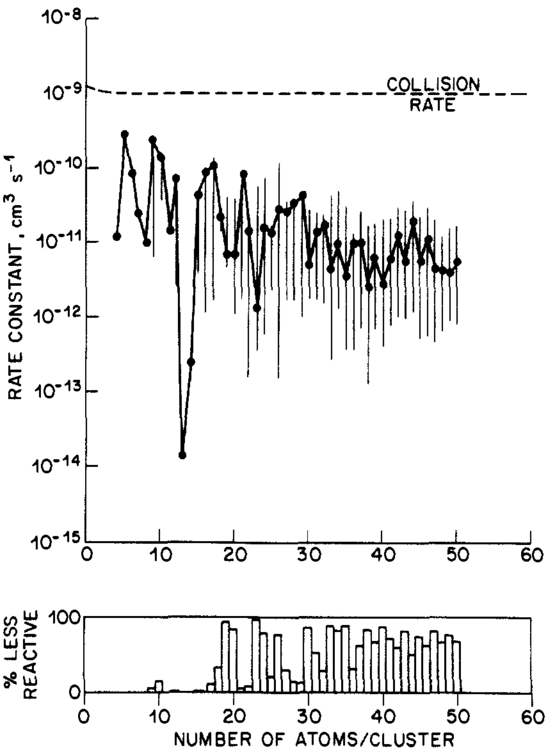

Figure 2. Plot of rate constants for the reactions of silicon cluster ions with C_2H_4. The vertical lines show the rate constants obtained with the two-component model discussed in the text. The vertical line connects the rate constant obtained for the more reactive component with that obtained for the less reactive component. The histogram below the rate constants shows the relative abundance of the less-reactive component. The solid points show the average reactivity of the clusters (as defined in the text). The dashed line shows the collision rate obtained from the Langevin–Gioumousis–Stevenson model.[52]

librium. Below we will describe experimental data that rule out an equilibrium except possibly in the case of Si_{14}^+.

Chemisorption of C_2H_4 onto the silicon clusters is an association reaction that at least for the smaller clusters probably occurs by a two-step mechanism. First the C_2H_4 chemisorbs on the silicon cluster to form a metastable adduct:

$$Si_n^+ + C_2H_4 \rightleftarrows Si_nC_2H_4^{+*} \qquad (5)$$

The metastable adduct then either dissociates back to reagents or is stabilized by collisions with the Ne buffer gas to give products:

$$Si_nC_2H_4^{+*} + Ne \rightarrow Si_nC_2H_4^+ + Ne \qquad (6)$$

If the silicon clusters are hot, if they have not been thermalized to the buffer gas temperature and contain extra internal energy, then this will have a dramatic effect on the lifetime of the $Si_nC_2H_4^{+*}$ metastable adduct and reduce the overall reaction rate. Clearly hot clusters might be responsible for at least some of the complicated kinetic behavior that we observe. A rather obvious place where the clusters could become excited is as they are injected into the drift tube. Injection energies of 5 eV were used in most of the work described here. We found that the results were insensitive to the injection energy for small injection energies (<15 eV), but for some of the clusters checked the reactivity decreased sharply for injection energies >20 eV. We will discuss these results in more detail below; the main point we wish to make at the moment is that the injection energies employed are sufficiently low that they do not appear to influence the reactivity of the clusters. These results, however, do not prove that all the clusters are thermalized.

A much more rigorous test for the presence of hot clusters is obtained by varying the time the clusters spend in the drift tube by varying the drift voltage. In these experiments we vary the time and C_2H_4 pressure together, keeping their product approximately constant so that the reactivity should also remain constant. If hot clusters are present the reactivity will decrease at shorter times because there is less time available for thermalization by collisions with the buffer gas. If an equilibrium is responsible for the complicated kinetic behavior then the apparent reactivity will increase at shorter times as the equilibrium is pushed to the right by the higher C_2H_4 pressure. Figure 3 shows plots of the apparent reactivity of a selection of clusters against (drift voltage)$^{-1}$. The time the clusters spend in the drift tube increases (and the C_2H_4 pressure decreases) to the right in these plots. These experiments were performed for all clusters with 11–50 atoms (except for Si_{13}^+).

We will now briefly discuss the measurements of the average time spent in the drift tube. The drift velocity is expected to vary linearly with drift field under the low field conditions employed in these experiments.[51] However, we found slight deviations from linearity that appear to be consistent with a 0.12-V offset in the drift voltage scale. The drift velocity was found to vary linearly with the drift field in our previous work,[27] and we believe that the apparent offset in the drift voltage scale may be related to contact potentials or surface potentials introduced by the modifications we have made to reduce the temperature gradients in the drift tube (see Experimental Section). Since all the times were directly measured in this work the slight departure from linearity is not important. For Si_{11}^+ the measured average time spent in the drift tube varies from 0.20 to 2.30 ms, and for Si_{50}^+ the average time varies from 0.45 to 5.19 ms with the drift voltages employed (5 to 0.3125 V). Note that the average time spent in the drift tube is not simply related to the drift velocity (which must be determined from analysis of the arrival time distribution with the transport equation for ions in the drift tube[51]). A referee noted that the drift times appear to show a nearly exact correlation with $m^{-0.5}$, but theoretically the mobilities depend on $\mu^{-0.5}$. However, on going from Si_{11}^+ to Si_{50}^+ we are changing more than just the mass of the cluster. In addition to possible changes in the Si_n^+–Ne interaction potential, the physical size of the cluster has changed dramatically and the collision cross section also enters into theoretical expressions for the mobility[51] (also see ref 52).

As can be seen from the data shown in Figure 3, a significant dependence of the apparent reactivity on time was only observed for Si_{14}^+ and Si_{20}^+. For Si_{14}^+ the apparent reactivity increases at short times (or high C_2H_4 pressures). As discussed above this is the signature of an equilibrium, where thermally activated desorption of the C_2H_4 from the $Si_{14}C_2H_4^+$ product occurs on the time scale of our experiments. In our previous work[27] on the reactions of silicon clusters with C_2H_4, we argued that the lifetime of the $Si_nC_2H_4^{+*}$ metastable adduct (see eq 5 and 6) determines the apparent reactivity of the clusters. Two main factors are expected to influence the lifetime: the number of internal degrees of freedom and the binding energy of the C_2H_4 molecule to the cluster. Since the number of internal degrees of freedom increases steadily with cluster size, we argued that variations in the binding energy are responsible for the large oscillations in reactivity observed with the smaller clusters. As can be seen from Figure 2, Si_{14}^+ is particularly inert, suggesting that C_2H_4 is particularly weakly bound to this cluster. It is not surprising then to find that thermally activated desorption of C_2H_4 from the $Si_{14}C_2H_4^+$ product occurs on the time scale of our experiments. As mentioned above these experiments were not performed for Si_{13}^+ because it is so inert. Thermally activated desorption of C_2H_4 is clearly also expected to be important for this cluster. On the other hand, our results suggest that thermally activated desorption of C_2H_4

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[52] Gioumousis, G.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *29*, 294. The Langevin–Gioumousis–Stevenson model begins to fail for the larger clusters. This model uses the point charge-induced dipole potential. A rough estimate of the average capture cross section for this potential can be obtained from

$$\sigma_L = \frac{k_L}{(2k_BT/\mu)^{1/2}}$$

For clusters with ~50 atoms the capture cross section estimated from the above expression approximately equals the hard sphere collision cross section estimated with the bulk density of silicon. However, it is unlikely that the collision rates estimated with the Langevin–Gioumousis–Stevenson model are in error by more than a factor of 2 even for Si_{50}^+.

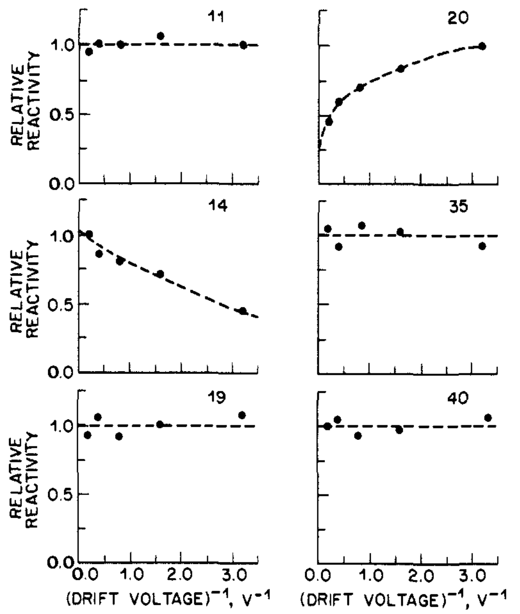

Figure 3. Plots of the relative reactivity against (drift voltage)$^{-1}$. In these experiments the time the clusters spend in the drift tube and the C_2H_4 pressure are varied together and their product kept approximately constant. The time the clusters spend in the drift tube increases (and the C_2H_4 pressure decreases) to the right in these plots. The points are the experiment data and the dashed lines are guides.

from the $Si_nC_2H_4^+$ products is not important for any of the other clusters in the size range studied.

As can be seen from Figure 3, the apparent reactivity of Si_{20}^+ increases with time, the signature of a hot cluster. However, for all the other clusters studied the apparent reactivity is independent of time, which provides strong evidence that all the clusters are thermalized. If Si_{19}^+ and Si_{21}^+ are thermalized we naturally expect Si_{20}^+ to be thermalized as well. We discuss below another possible explanation for why the apparent reactivity of Si_{20}^+ depends on time. The point we would like to stress at the moment is that the clusters appear to be thermalized. The time they spend in the drift tube has been changed by over an order of magnitude in these experiments. If there were any hot clusters, increasing the number of collisions they experience with the buffer gas by a factor of 10 would surely have an effect. Since the clusters are thermalized and thermally activated desorption of C_2H_4 from the $Si_nC_2H_4^+$ products is not important (except for Si_{14}^+ and possibly Si_{13}^+), it appears that the only reasonable explanation of our results is that structural isomers exist for virtually all silicon cluster ions containing 11–50 atoms.

With this knowledge we will now reconsider the unique behavior of Si_{20}^+. If the activation barrier for isomerization is small so that the isomers rapidly interconvert at room temperature, then clearly it will not be possible to distinguish structural isomers on the basis of their differing reactivity. A possible explanation for the behavior observed with Si_{20}^+ is that the isomers are in equilibrium, and at room temperature they interconvert at a rate comparable with the time scale of our experiments. The reaction with C_2H_4 depletes the (less abundant) more reactive isomer. To re-establish equilibrium some of the less reactive isomer will be converted into the more reactive one. As the clusters spend longer in the drift tube more of the less reactive isomer will be converted and the apparent reactivity will increase.

We noted above that for some clusters the reactivity declined sharply as the injection energy was raised above 20 eV. As the injection energy is increased the average time the clusters spend in the drift tube decreases slightly (by ~10% when the injection energy is increased from 2.5 to 30 eV) because at the higher injection energies the clusters penetrate further into the drift tube before they are thermalized. This is not responsible for the observed decrease in reactivity because the small difference in the time that the clusters spend in the drift tube is measured and taken into account. Increasing the injection energy will increase the amount of collisional excitation of the clusters as they enter the drift tube. This could influence the reactivity of the clusters in two ways. First, as discussed above, if the internal excitation is only removed slowly the extra internal energy will make the clusters appear less reactive. Second, the extra internal energy could cause the clusters to isomerize to a lower energy structure. In other words the clusters would be annealed. Because of the difficulty of distinguishing between these two possibilities we have not pursued this point further at present, though clearly the ability to collisionally anneal the clusters warrants further investigation.

Discussion

Influence of Drift Field on Reactivity. Before proceeding to discuss the experimental results we will briefly consider the effect the drift field may have on the reactivity of the ions. The average kinetic energy of ions in the drift tube is given approximately by[53]

$$\langle KE_{lab} \rangle = \tfrac{1}{2}m_i v_D^2 + \tfrac{1}{2}m_b v_D^2 + \tfrac{3}{2}k_B T \qquad (7)$$

where m_i and m_b are the masses of the ion and buffer gas, respectively, and v_D is the drift velocity. With use of eq 7 it is straightforward to estimate the influence of the drift field as

$$\Delta T_{eff} = \frac{m_r}{2k_B} v_D^2 \frac{m_i + m_b}{m_r + m_i} \qquad (8)$$

where ΔT_{eff} is the increase in the effective temperature caused by the drift field and m_r is the mass of the neutral reagent. The increase in the effective temperature estimated by using this expression for drift fields of 0.25 V/cm (where most of our work was done) is <1 K. At 2 V/cm the estimated effective temperature increase is significant, particularly for the smaller clusters (26.5 K for Si_{11}^+ and 5.0 K for Si_{50}^+). However, Bohringer and Arnold[54] have shown experimentally that eq 8 significantly overestimates the effective temperature increase. In our previous work[27] we showed that the reactivity of the smaller clusters decreased sharply with increasing temperature. It is apparent from Figure 3 that the reactivity of Si_{11}^+ is unaffected by increasing the drift voltage from 0.3125 to 5 V. Clearly eq 8 significantly overestimates the effective temperature increase due to the drift field and the drift field does not influence the reactivity of the clusters.

Isomers and Cluster Generation. Prior to this work, evidence for structural isomers had only been found in the few isolated cases mentioned in the Introduction.[6,10,12,24,26,27] An obvious question that we should address is whether there is anything particularly unique about the way the clusters were generated in this study, which might enhance the occurrence of structural isomers. Compared with more conventional laser vaporization sources our source uses a continuous flow of buffer gas rather than a pulsed flow. The pressures in our source are lower and the time the clusters spend in the source correspondingly longer. In other words, the cooling rate is considerably slower than in sources using a pulsed valve. However, it is the faster cooling rate that would be expected to freeze out the less stable cluster structures. A rather obvious difference between this work and the previous studies of cluster chemistry is that most of the previous work has been performed with metal clusters. Bonding in metals is not strongly directional so that close-packed structures are preferred. Crystalline silicon has a more open diamond structure with strongly directional sp^3 bonds. With metals it is quite possible that a large number of different structures have close to the same energy and that the activation barriers for interconversion between these structures is so low that the isomers interconvert rapidly at room temperature. Structure, meaning the precise location of all the atoms, may not be a useful concept for metal clusters. But for silicon clusters with stronger directional bonding, the activation barriers for isomerization are probably larger so that the isomers do not generally interconvert at room temperature.

Mechanism of the Reactions. In our previous work[27] on the reactions of silicon clusters with C_2H_4 we applied statistical phase

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(53) Wannier, G. H. *Phys. Rev.* **1951**, *83*, 281.

(54) Bohringer, H.; Arnold, F. *J. Chem. Phys.* **1982**, *77*, 5534.

space theory[55] to the reactions of clusters containing 4–10 atoms. We assumed that the reactions occur through the two-step mechanism shown in eq 4 and 5 and outlined in the Results section. Here a $Si_nC_2H_4^{+*}$ metastable adduct is generated at the ion–molecule collision rate (probability of chemisorption equal to 1), and products are formed if the adduct survives long enough to be collisionally stabilized. The reactivity of the clusters is thus controlled by the lifetime of the $Si_nC_2H_4^+$ metastable adduct, which is in turn determined by the number of internal degrees of freedom in the adduct and the Si_n^+–C_2H_4 binding energy. This model appears to be valid for the small clusters (n = 4–10), the predicted temperature dependences of the reaction rates were in good agreement with experiment,[27] and we found evidence suggesting C_2H_4 is only weakly bound to Si_{14}^+, which is a particularly inert cluster. The larger clusters studied here have many internal degrees of freedom so that the metastable adduct will have a long lifetime and the observed sticking probability should approach 1, unless the Si_n^+–C_2H_4 binding energy is very small. We found no experimental evidence for thermally activated desorption of C_2H_4 from the reaction products (except as discussed for Si_{14}^+), suggesting that C_2H_4 is quite strongly bound to the larger clusters. However, as can be seen from Figure 2 the sticking probabilities for the larger clusters are small, ~0.01–0.001. These low sticking probabilities could be accounted for by either a small activation barrier associated with chemisorption of C_2H_4 onto the clusters or a tight restrictive transition state, possibly involving only a few active sites on the cluster surface. Studies of the temperature dependence of the reaction rates would help to discriminate between these possibilities, but such studies would be complicated by the presence of the isomers.

It is clear from the preceeding discussion that the reaction mechanism appears to change with cluster size. For the smaller clusters, initial chemisorption of C_2H_4 occurs at the collision rate, but the reactivity (sticking probability) is determined by the probability that the adduct survives long enough to be stabilized. For the larger clusters, if the C_2H_4 chemisorbs it will stay on the cluster (the stabilization efficiency is close to unity), but the reaction is slow and there appears to be a tight transition state associated with chemisorption of C_2H_4 onto the cluster. This change in reaction mechanism may be explained by the weakening of the charge-induced dipole interaction caused by increased delocalization of the charge over the cluster. Ion–molecule reactions often proceed without an activation barrier because of the strongly attractive ion-induced dipole interaction. This interaction reduces the energy of the tight transition state, which exists in corresponding neutral systems, to below the energy of the reactants. Thus the transition state in ion–molecule reactions moves out to the centrifugal barrier and ion–molecule reactions often occur at the collision rate. With increasing cluster size the charge becomes more delocalized and the charge-induced dipole interaction becomes weaker. The energy of the tight transition state increases and ultimately controls the rate of reaction.

Comparison with Bulk Silicon. The reactions of C_2H_4 with silicon surfaces has not been widely investigated. C_2H_4 appears to bind to Si(111) by a strong π-bonding interaction.[56] From the data shown in ref 56 we estimate a sticking probability of ~0.004 for C_2H_4 on Si(111) at room temperature. This is within the range of sticking probabilities observed for the larger clusters (~0.01–0.001).

Comparison with Other Reactions of Silicon Clusters. The only other data on the reactivity of the larger silicon clusters is the work performed by Smalley and co-workers[15] on the reactions with NH_3. They found Si_{39}^+ and Si_{45}^+ to be particularly inert. In their recent studies[57] of these reactions they have not observed evidence for large numbers of isomers as found in the present work (though evidence for some isomers was found). The implication is that the reactions with NH_3 are much less sensitive to cluster structure that the reactions with C_2H_4. We have recently started to investigate the reactions of silicon clusters with oxygen, and while our results are still preliminary, it is clear that the reactions with oxygen also appear to be much less sensitive to cluster structure. So what makes the reactions with C_2H_4 so sensitive to cluster structure? One possible explanation is that the reaction with C_2H_4 occurs at specific sites on the clusters. Isomers with one or more of these sites are reactive isomers, and isomers with fewer or none of these sites are the inert ones.

Cluster Size Dependence of Reaction Rates. The large differences in reactivity observed for the different structural isomers make it difficult to draw any firm conclusions about how the reactivity varies with cluster size. It appears from the data shown in Figure 2 that the large oscillations in reactivity observed for the smaller clusters are rapidly damped with increasing cluster size. For clusters with more than 30 atoms the changes in reactivity with cluster size are usually quite small, and much smaller than the differences in reactivity observed for the different isomers. Si_{13}^+ is by far the most unreactive cluster. Since the reactions with C_2H_4 appear to be very sensitive to cluster structure it is natural to wonder if the inert nature of Si_{13}^+ is in some way related to its structure. Chelikowsky and Phillips[49] have obtained an icosahedral structure for Si_{13} from their calculations. However, recent preliminary ab initio calculations (employing an effective core potential) by Raghavachari suggest that the icosahedral structure is not the most stable structure for Si_{13}.[58] Chelikowsky and Phillips noted that somewhat lowered reactivity is also observed at other magic numbers in the icosahedral-pentagonal growth sequence, at n = 19 and 23. The next magic number in this sequence occurs at n = 25, which corresponds to capping opposite ends of an icosahedron (above n = 25 there are many possible packing combinations until the second shell is closed at n = 55). As can be seen from Figure 2 there does not appear to be anything unique about the reaction of Si_{25}^+ with C_2H_4. At the moment the data base is too small for further speculation. More reactions must be investigated in order to establish whether the observed reactivity trends reflect the intrinsic properties of the clusters or something unique to the individual reactions.

Conclusions

We have described a detailed study of the kinetics of the reactions of Si_n^+ (n = 11–50) with C_2H_4. Except for clusters with n = 11, 14, 18, and 19, the reactions do not show simple pseudo-first-order kinetics. Several possible explanations for these observations were examined. The most reasonable explanation is that structural isomers are present for virtually all clusters in the size range studied. Previously isomers of atomic clusters have only been identified in a few specific cases. For Si_{20}^+ evidence is presented suggesting that the isomers interconvert slowly on the time scale of our experiments.

It appears that the reactions of silicon clusters with C_2H_4 are uniquely sensitive to the cluster's structure. Large numbers of isomers were not observed by Smalley and co-workers in their studies of the reactions with NH_3,[57] and preliminary results obtained by us suggest that the reactions with oxygen are much less structure sensitive. These results suggest that the reactions with C_2H_4 occur at specific localized sites on the cluster.

The phase space theory model used to analyze and interpret data on the reactions of the smaller clusters[27] predicts that the sticking probability should approach 1 for the larger clusters studied here, but the measured sticking probabilities are ~ 0.01–0.001. It appears that the reaction mechanism must change with increasing cluster size. The low reactivity of the large clusters is probably associated with either a small activation barrier for chemisorption of C_2H_4 onto the clusters or a tight restrictive transition state (possibly involving only a few sites on the cluster).

Registry No. C_2H_4, 74-85-1.

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