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The Reaction of Ammonia with $\equiv$Si—O—SiHCl$_2$ Monolayers on Silica

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High surface area silica was completely dehydroxylated by reaction with HSiCl$_3$. The $\equiv$Si—O—SiHCl$_2$ (I) monolayer was then exposed to NH$_3$ at 22°C, the surface reactions being followed by infrared spectroscopy using the perturbation of the Si—H band as probe of the otherwise unobservable reactions occurring at the Si—Cl bond. NH$_3$ was taken up at quite low pressures to form a mixture of surface species. I reacted to form a species II which was then converted to a species III. Degassing at 22°C reversed the processes, almost all I being re-formed. Successive sorption–degassing cycles caused the formation or at least three other species. The spectra suggest that reversible ammonolysis of I occurred, the Si—H mode being perturbed by the reversible formation of $\equiv$Si—NH$_2 \cdots$ NH$_4$Cl. The complex results suggest that reactions on halogenated surfaces are more involved than has so far been suspected.

INTRODUCTION

Silica surfaces have been studied extensively, especially by infrared techniques, and many of the reactions of surface silanols with a large number of adsorbates, as well as the properties of the chemisorbed layer, have been described; Kiselev and Lygin (*1*) give an extensive summary, as does Little (*2*). However, the nature and properties of halogenated silica surfaces still seem obscure.

It is known that silica can react with halogen-bearing adsorbates so that the surface will incorporate halogen after reaction. For example, Boehm and Schneider (*3*) reacted SOCl$_2$ with silica and found by chemical analysis that, for each surface silanol, the surface retained one chlorine atom. Similarly, Folman recorded the infrared spectra of porous glass and found the $\equiv$Si—OH absorption band to decrease when the solid was reacted with SOCl$_2$, thus suggesting the formation of surface chloride (*4*). More recently, Hair and Hertl (*5*) used a combination of infrared spectroscopic data and chemical analyses to study the chlorination of silica surfaces with a variety of adsorbates. However, information about surface halogen obtained in these and similar studies (*6–8*) is indirect in that chemical analyses may quantitatively confirm the presence of halogen but give little specific information about the structure of the halogen-containing surface species. Infrared spectroscopic information is similarly indirect because the Si–Halogen bands fall in a spectral region where adsorbent samples of usable thickness are opaque, so that the pertinent surface species cannot be observed; information is deduced from the behavior of other surface species such as silanols. Parenthetically, Morrow recently reported being unable to detect surface $\equiv$Si—Cl by laser-Raman techniques (*9*).

That halogens can modify the reactivity of silica surfaces has been shown. For example, it was thought that the presence of the electronegative fluorine atom next to a silanol shifted the electron density to the vicinal atoms so that the bond of the hydroxyl was weakened, resulting in an increased protonic acidity (*10*). Also, the reactions of chlorosilanes with silica show unusual kinetics (*11, 12*) thought to be brought about through the formation of $\equiv$Si—Cl groups, and the chemisorption of

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certain halogenated adsorbates apparently caused autocatalysis (*12*). It would thus seem useful to obtain more information about halogen-containing surface species. We have attempted to do so by using infrared spectroscopy to study the interactions of several adsorbates with surface $\equiv$Si—O—SiHCl$_2$ groups. The Si—Cl absorptions of the latter are, as usual, not detectable because of the opacity of the adsorbent. However, the frequency of the Si—H stretching band is known to be affected in a predictable manner by the electronegativity of the other atoms bonded to the silicon (*13–17*), so that adsorbate–adsorbent interactions involving the Si—Cl linkages would make themselves felt as variations of the frequency of the Si—H band. Somewhat less indirect observation of the halogen-containing surface species would thus be obtainable. As the Si—H group is relatively stable (*18*) it is useful to compare the reactions of the Si—Cl groups of Si—HCl$_2$ structures with those of the Si—Cl group of chlorided silica. With this in mind, we have studied the reactions of HSiCl$_3$-treated silica with NH$_3$, using the Si—H band as "probe."

EXPERIMENTAL

Many experimental procedures have been described elsewhere (*18*). Samples for spectroscopic study were prepared by compressing approximately 85 mg of Cab-O-Sil M-5 silica (*19*) in a steel die at 30–40 kg/cm^2. The resulting pellet (approximately 40 mg/cm^2) was mounted in an infrared cell (*18*) and subjected to various treatments. Spectra were recorded at 22°C using Perkin-Elmer Model 621 or Digilab Model FTS-14 spectrometers. Anhydrous NH$_3$ (*20*) was used without further purification. HSiCl$_3$ (*21*) was subjected to several freeze–pump–thaw cycles prior to use. Silica samples were exposed to the NH$_3$ and spectra recorded at room temperature (22°C).

The following procedure was used to prepare samples for study. A fresh silica disc was heated in O$_2$ for 3–6 hr at 500–600°C to remove the adsorbed hydrocarbons and other impurities normally found on such samples. The sample was then degassed at 700–800°C for 2–4 hr to dehydroxylate the surface and to remove most of the interstitial hydroxyls. The sample was then exposed to 10–20 Torr of HSiCl$_3$ vapor at 300°C and degassed at 300°C for 1 hr. This procedure brought about the complete dehydroxylation of the surface, the dominant feature of spectra of such samples being a strong band at 2270 cm^{-1} attributable to the Si—H stretching of surface $\equiv$Si—O—SiHCl$_2$ groups, as observed by Chuiko *et al.* (*22*). As they pointed out, the mean distance between free hydroxyls on aerosil calcined at 400°C is 5.9–6.5 Å, the Si—Cl bond length in HSiCl$_3$ is 2.02 Å, the Cl—Si—Cl angle is approximately 109°, and the distance between the two Cl atoms in HSiCl$_3$ is approximately 3.30 Å, so that the simultaneous participation of two Cl atoms from one silane molecule in a surface reaction with the free silanols is improbable for geometric reasons. It is thus reasonable to assume the HSiCl$_3$-treated silica surface to consist predominantly of $\equiv$Si—O—SiHCl$_2$ groups. It is probable that some $\equiv$Si—Cl groups were also formed, in analogy to the $\equiv$Si—Cl species and reactions postulated to account for the peculiar kinetics of reactions of chlorosilanes with silicas (*11, 12*). However, a study of the decomposition of the chemisorbed layer at high temperatures suggests that the number of $\equiv$Si—Cl groups is relatively small (*23*). It is thus reasonable to ascribe the effects observed predominantly to the reactions of $\equiv$Si—O—SiHCl$_2$ groups.

RESULTS

Room Temperature NH$_3$ Sorption

Figure 1 shows a typical spectrum of an HSiCl$_3$-treated sample. The sample had been completely dehydroxylated and the only pertinent spectral feature is the prominent Si—H stretching band at 2270 cm^{-1} of surface $\equiv$Si—O—SiHCl$_2$ groups (for brevity, termed Band I). The absorptions below

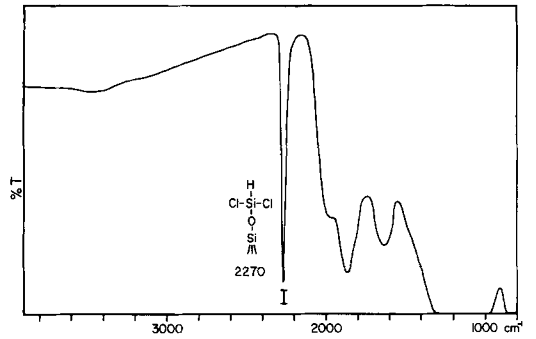


FIG. 1. Spectrum of silica dehydroxylated by reaction with $HSiCl_3$.

2100 cm^{-1} are caused by the silica. The 1000–850 cm^{-1} "window" showed no absorptions, indicating the absence of special adsorption sites described by Morrow *et al.* (*24–26*). When such a sample was exposed to even quite low pressures of NH_3 at 22°C, two additional bands II and III appeared on the low-frequency side of band I (Fig. 2). As the NH_3 pressure was increased bands II and III became more prominent (Fig. 3) but then band II also declined while band III kept increasing (Fig. 4). The build-up and decline of band II (2240 cm^{-1}) are shown more clearly in Fig. 5.

It is known that, when NH_3 was adsorbed on silica-bearing surface silane groups, the Si—H stretching bands of the silica showed only a slight tailing and remained largely unperturbed, i.e., there is very little direct interaction between adsorbed NH_3 and the Si—H group (*18*). Consequently, the change in the Si—H stretching band I of the surface $\equiv$Si—O—$SiHCl_2$ groups is unlikely to have been caused by Si—H · · · NH_3 interactions. In view of the reactants, the band sequences of Fig. 5 suggest that the main reaction at room temperature was the sequential conversion of the chemisorbed layer into two products,

$\equiv$Si—O—$SiHCl_2$ →	$\equiv$Si—O—SiHClX →	$\equiv$Si—O—SiHXX
Species I	Species II	Species III
band I	band II	band III
2270 cm^{-1}	2240 cm^{-1}	2190 cm^{-1}

where the X is the grouping causing the Si—H mode to become perturbed.

Other changes which occurred along with those in the Si—H region can be summarized as follows. (a) Strong bands appeared at 3160 and 3060 cm^{-1}, seen clearly only in Fig. 1, a weaker band at 2925 cm^{-1}, a strong band at 1410 cm^{-1}, and a weak band near 1775 cm^{-1}. These bands are attributed to the various modes of NH_4^+ formed by reaction of NH_3 with the chlorided surface and will be termed "the NH_4^+ bands" (*27*–

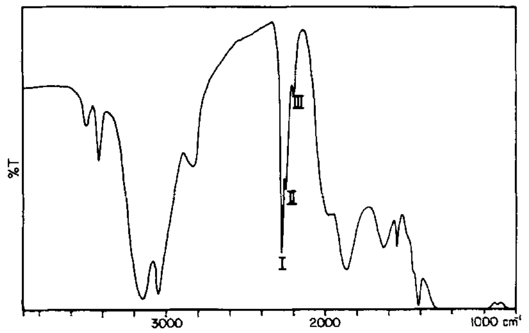


FIG. 2. NH_3 sorption. The sample of Fig. 1 had been exposed to 0.3 Torr NH_3 at 22°C.

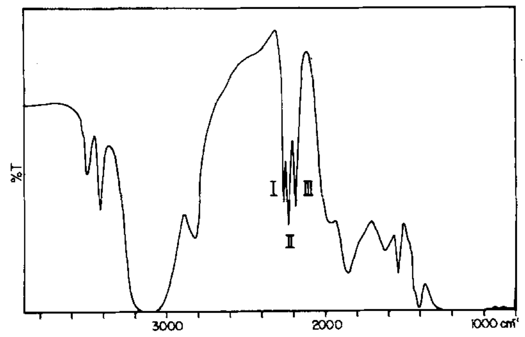


FIG. 3. NH_3 sorption. The sample of Fig. 1 had been exposed to 0.6 Torr NH_3 at 22°C.

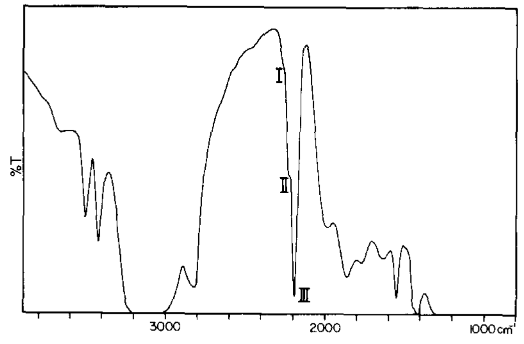


FIG. 4. NH$_3$ sorption. The sample of Fig. 1 had been exposed to 5.6 Torr NH$_3$ at 22°C.

30). The same bands were observed when NH$_4$Cl was sublimed onto a sample; under those conditions there was no perturbation of the Si—H band. (b) A pair of bands appeared at 3510 and 3425 cm^{-1}. The bands' intensities increased progressively but the relative band intensities and frequencies were not changed significantly. Simultaneously, a band appeared at 1550 cm^{-1}. The bands' frequencies are too high to be brought about by molecular NH$_3$ physically adsorbed by or coordinated to the surface but are close to those of NH$_3$ chemisorbed on silica, i.e., those of surface primary amine (*1, 2, 18*), and are termed "the NH$_2$ bands." In addition, an absorption appeared at 920 cm^{-1} (Figs. 2 and 3), close to the 932 cm^{-1} band due to the Si—N stretching band of ≡Si—NH$_2$ groups (*26*). (c) The various changes occurred rapidly, i.e., within the few minutes required to treat a sample and record the spectrum;

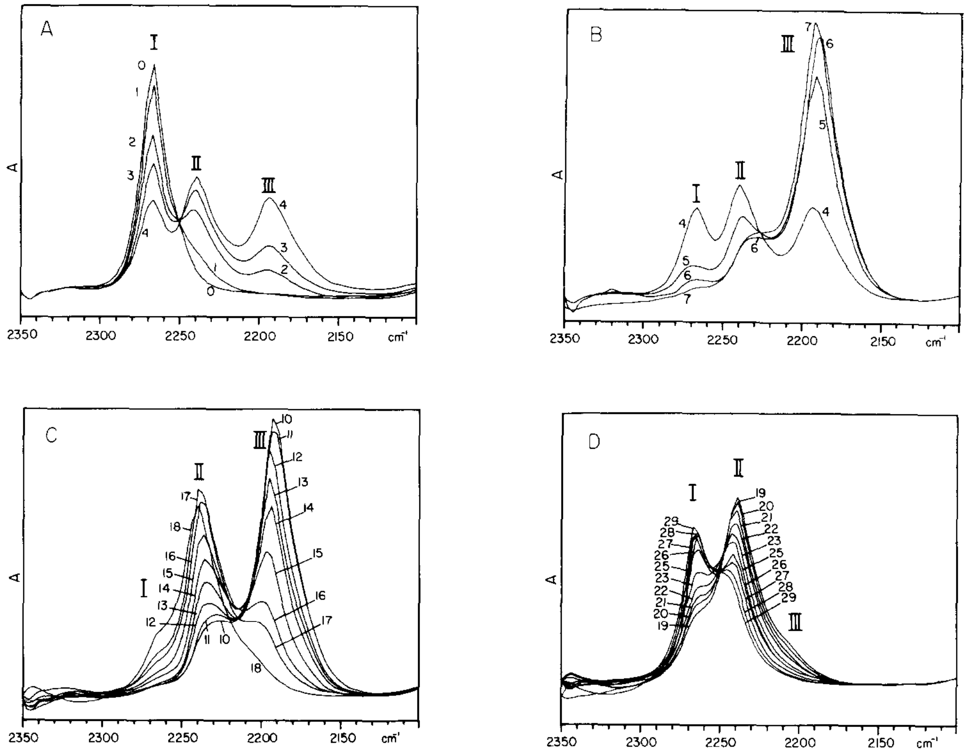


FIG. 5. NH$_3$ sorption at 22°C and low-temperature degassing. The fresh sample (trace 0) was exposed to NH$_3$ at successively increasing pressures in Torr, 1, 0.18; 2, 0.3; 3, 0.4; 4, 0.6; 5, 1.0; 6, 1.8; 7, 3.4; 8, 5.6; 9, 8. The sample was then degassed at 22°C for the following cumulative time periods: 10, 30 sec; 11, 3 min; 12, 13 min; 13, 35 min; 14, 65 min; 15, 125 min; 16, 4.5 hr; 17, 6.5 hr; 18, 21.5 hr. The sample was then degassed at slightly higher temperature: 19, 50°C, 15 min; 20, 50°C, 45 min; 21, 60°C, 15 min; 22, 60°C, 45 min; 23, 60°C, 105 min; 22, 60°C, 3 hr 45 min; 25, 70°C, 25 min; 26, 75°C, 45 min plus 80°C, 15 min; 27, 85°C, 30 min; 28, 95°C, 20 min; 29, 100°C, 40 min.

there were no changes upon letting a treated sample stand. (d) The changes occurred progressively, but to a decreasing extent, as the NH_3 pressure was increased; there were no significant changes above 1 Torr. (e) The formation of surface silanols was not observed.

Degassing at Low Temperature

If a sample which had been exposed to NH_3 at 22°C was degassed at 22°C, the changes caused by the NH_3 sorption as shown in Figs. 2–4 gradually appeared to reverse. To summarize: (a) As shown by the sequence of Fig. 5C, band III diminished continuously and band II built up, but it was not until band III had almost disappeared that significant amounts of the band I absorption reappeared, i.e., the band III material was mostly converted into band II material, reinforcing the suggestion that three distinct species were involved. When the degassing temperature was varied slightly (Fig. 5D) the band II absorption declined and band I grew. However, a shoulder remained near 2250 cm^{-1} (trace 29) and band I was not restored to its initial intensity. (b) The NH_4^+ bands decreased progressively, e.g., the increase of the 1775 cm^{-1} band roughly mirrored its decrease. The NH_4^+ bands disappeared after degassing at 100°C, showing that there was no connection between the presence of NH_4^+ and the residual perturbation of band I (i.e., the 2250 cm^{-1} shoulder). (c) The NH_2 bands declined progressively. Initially there were no significant changes in the relative intensities of the 3510 and 3425 cm^{-1} bands, but on degassing at temperatures above room temperature the 3510 cm^{-1} band declined faster than the other band. The latter became less symmetric and moved to higher frequencies by approximately 10 cm^{-1}.

Taken together, the results indicate that degassing under relatively mild conditions caused most of the products of the NH_3 sorption to be decomposed or altered. The conversion of band III to band II to band I occurred readily, indicating that species II and III were weakly bound. The NH_4^+ bands and the NH_2 bands also disappeared readily, also indicating that these bands were caused by groupings which could easily be altered by pumping.

Sorption–Desorption Cycles

A series of experiments was carried out during which a sample was exposed to numerous sorption–desorption cycles. The Si—H regions of some of the spectra of one sequence are shown in Fig. 6. It is apparent that the pattern of three Si—H bands persisted throughout the course of 13 cycles, but there were significant changes in band intensities, frequencies, and stabilities of the surface species.

The results of the first cycle (A,B, Fig. 6) are entirely like those described earlier; bands II and III could be removed readily, leaving a residual shoulder near 2250 cm^{-1}. At cycle 4, a distinct band rather than shoulder had been built up which, at cycle 9 (spectrum G) was the dominant band at 2245 cm^{-1}. This band could not be reduced by degassing at 500°C (spectrum J) and consequently was not caused by the same species causing the original band II. The 2245 cm^{-1} band, termed band IV, is conse-

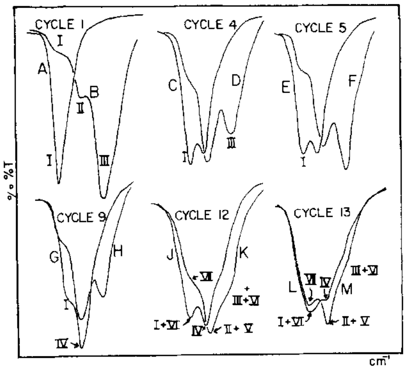


FIG. 6. Sorption–desorption cycles. A fresh sample (A) was exposed to NH_3 (B) and then subjected to 12 additional degassing–sorption cycles. Degassing was carried out from room temperature up to 200°C (C, E, G), to 500°C (J, K), and 600°C (L); other traces were recorded after exposing the degassed sample to 5–10 Torr NH_3 at 22°C. The roman numerals identify the bands mentioned in the text.

quently attributed to a relatively stable species IV.

As the sequence progressed, the band I absorption progressively declined; it was still a well-defined band at cycle 5 (E) but only a shoulder at cycle 9 (G). Also, when NH_3 was sorbed, the changes in the bands, i.e., the decrease of band I and the accompanying increases of the other two bands, occurred to smaller and smaller extents. The changes of band I are such as to suggest that another absorption "grew up" under band I; that this is so is supported by the observation that the shoulder on the high-frequency side of band II or band IV increased upon degassing at 500°C (it is labeled VII on trace K) and became a distinct band at 2277 cm^{-1} upon degassing at 600°C (cycle 13). The observations that, at intermediate stages, band IV decreased when NH_3 became sorbed, e.g., cycle 9, along with a shift of the third band to 2200 cm^{-1}, suggest that species IV was also able to react with NH_3 to yield other species. If we tentatively assume that, like species I, species IV is able to react in two stages to yield species V and species VI, their respective bands overlapping those of species II and III would lead to the labeling of the three absorptions as shown for cycles 12 and 13.

Observations in the N—H stretching region tend to support the multiplicity of structures. (i) Throughout the sorption–degassing sequence, when the degassed sample was exposed to NH_3, the 3510 and 3425 cm^{-1} bands of weakly bound NH_2 species were formed, much as in Figs. 2–4, but with gradually increasing intensities and a gradual shift to 3515 and 3430 cm^{-1}, and the latter band exhibited "tailing." Both bands could be diminished by degassing at 100°C. (ii) Bands remained after degassing below as well as above 100°C. A minor band formed and grew at 3530 cm^{-1}; a second, somewhat more intense, asymmetric band formed at 3450 cm^{-1}. Both bands decreased slightly upon degassing at 500°C, but the intensity of the 3450 cm^{-1} band declined more than that of the 3530 cm^{-1} band. The behavior suggests that there were two overlapping bands absorbing near 3450 cm^{-1} and another at 3530 cm^{-1}, i.e., a pair of bands at 3530 and approximately 3450 cm^{-1} attributed to —NH_2 groups (*1, 2, 18, 31*) and a single band near 3450 cm^{-1} attributed to —NH— groups, both these groups being more stable than the —NH_2 groups formed immediately upon exposing the sample to NH_3. (iii) the 3160 and 3060 cm^{-1} "NH_4^+ bands" became progressively weaker as the sorption–degassing sequence progressed, e.g., after 10 cycles their intensities were similar to those shown in Fig. 2.

DISCUSSION

The various results indiate that the main reaction of NH_3 with the "chlorided" surface was not simply,

$$\equiv Si—Cl + 2NH_3 \rightarrow \equiv Si—NH_2 + NH_4Cl \quad (A)$$

as might be expected from other work (*1, 2, 31–33*). "Normal" $\equiv$Si—NH_2 groups formed in this way on silicas or by the chemisorption of NH_3 on silica (*1, 2, 18*) are quite stable. Peri, for example, noted that when silica, from which OH groups had been removed by reaction with Cl_2 or CCl_4, was exposed to NH_3, strong bands indicating NH_4Cl formation were produced; heating at 400–600°C sublimed the NH_4Cl, leaving a surface covered with NH_2 groups. The NH_2 groups were as difficult to remove by degassing at high temperatures as the OH groups which they had replaced (*31*). In contrast, the main reaction of NH_3 with $\equiv$Si—O—Si—HCl_2 led to relatively unstable species and the surface layer consisted of a mixture which progressively changed when subjected to sorption–desorption cycles. The mechanism scheme of Fig. 7 suggests itself, which summarizes the observations outlined earlier that the first sorption occurred in two stages with the formation of NH_4^+ and unstable —NH_2 species; most of the spe-

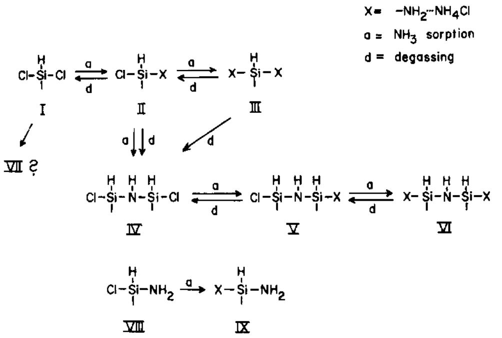


FIG. 7. Reaction scheme.

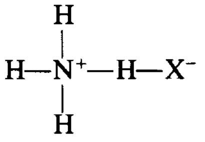
cies first formed were removed or destroyed readily leaving on the surface small amounts of species containing fairly stable secondary amine groups and perturbed Si—H groups; and that reexposure to NH_3 after degassing led to further perturbation of Si—H groups and the build-up of additional stable species.

The main problem in arriving at reasonable mechanisms and surface structures involves reconciling the easy "reversibility" and the simultaneous formation of NH_4^+ and unstable —NH_2 groups. The —NH_2 groups formed by Reaction (A) above might have been removed by a condensation of neighboring groups,

$$\equiv Si—Cl + NH_2—Si\equiv \rightarrow \equiv Si—NH—Si\equiv + HCl \quad (B)$$

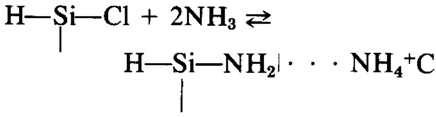
and such condensation reactions probably occurred to some extent, e.g., the conversions II → IV and III → IV of Fig. 7. The conversion of I into II into III would thus not be reversible. However, if Reaction (B) were to be the only means of removing —NH_2 groups, band I should not have reappeared at all, an =NH band of significant intensity should have appeared, and the reactivity of the surface should have been greatly diminished and changed. As band I did reappear, the =NH band was slight, and the surface still very reactive, an additional mechanism is needed.

It is suggested that the reactions I → II and II → III were indeed reversible and that the groupings X causing the perturbation of the Si—H mode involved both —NH_2 and NH_4^+, i.e., that a reaction formally written as Reaction (A) occurred, yielding both $\equiv Si—NH_2$ and NH_4Cl, but that the two products remained associated (shown as —$NH_2 \cdots NH_4Cl$ in Fig. 7). Some support for this comes from the observation that NH_3 and NH_4Cl reversibly form the adduct $NH_4Cl \cdot 3NH_3$ (*34*); also, that the reaction of the silicon-halogen bond with water, alcohols, and amines is actually reversible, although for most of the chlorides, bromides, and iodides the equilibrium is essentially completely displaced toward the hydrolysis product (*35*). Also, studying adsorption of NH_4Cl in sintered porous glass, Hair (*36*) observed bands at 3170 and 3070 cm^{-1} attributable, as in the present case, to the ν_3 and $(\nu_2 + \nu_4)$ modes of NH_4^+. The intensity of the 3070 cm^{-1} band seemed surprisingly high for a combination based, as also in the present case, causing the suggestion that this band was due to the normally inactive ν_1, vibration becoming active because of a change in symmetry of the NH_4^+, i.e., perhaps the formation of an "ion pair,"



$$\begin{array}{c} H \\ | \\ H—N^+—H—X^- \\ | \\ H \end{array}$$

Thus the generalized Reaction (C),



$$H—\underset{|}{Si}—Cl + 2NH_3 \rightleftarrows H—\underset{|}{Si}—NH_2 \cdots NH_4^+Cl^- \quad (C)$$

occurring reversibly, can explain the formation of species such as II to IV and their removal without extensive build-up of stable—NH_2 groups.

The change of band II to band IV along with the formation of a band due to stable =NH groups suggests the formation of groups such as IV (as well as Cl—(=SiH—NH—)$_n$—Cl polymer) which could react reversibly to yield species V and VI. As aminosilanes show some tendency to condense (*35*), some (—NH_2)-

containing species formed by Reaction (A), or from species II, or by Reaction (B), might form a species such as IV, but only to a limited extent at room temperature because the =NH band was small after degassing at room temperature. The gradual build-up of the =NH band and the formation of band IV suggest that the condensation or Reaction (B) occurred on degassing and was probably accelerated during the cycling process by using degassing temperatures above room temperature. Also, the formation of bands due to stable (—NH$_2$)-containing species indicates that other side reactions occurred leading to more stable species such as the schematic structure VIII (which might then react to form IX) and to numerous similar silazanes not included in the skeletal reaction scheme. However, the low intensity of the bands indicates that these reactions were not extensive. The nature of the structures responsible for band VII is uncertain. Degassing of NH$_3$-treated samples as well as fresh, untreated samples at temperatures above 600°C accelerated the formation of band VII, so that it seems likely that a rearrangement of the surface layer not involving ammonia-containing species was involved.

Taken together, the results indicate that the NH$_3$ sorption, which might have been expected to be fairly simple mechanistically on the basis of other work with chorided surfaces, was unexpectedly complex. This suggests, then, that reactions on halogenated surfaces are probably not as straightforward as suspected; their complexity has simply not yet been observed.

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