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REACTIVE SILICA

XI. ACETYLENE, PROPYNE AND ALLENE SORPTION BY OXYGENATED REACTIVE SILICA*

By

M. J. D. Low***) and H. MARK**)

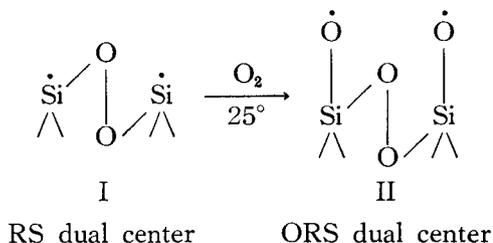
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Abstract

A variety of data indicates that unusual adsorption centers containing SiO radicals are formed when high surface area silicas are subjected to a sequence of steps involving methoxylation, pyrolysis of the methoxy layer, and high temperature degassing followed by the chemisorption of oxygen. Some aspects of the activity of this oxygenated reactive silica (ORS) were investigated by studying the sorption of acetylene, propyne and allene using infrared spectroscopic methods. Acetylene and propyne sorptions were similar in that, in addition to the formation of some olefinic species, dissociation to form $\equiv\text{Si-OH}$ and $\equiv\text{Si-O-C}\equiv\text{C-R}$ groups occurred; the latter rearranged upon heating to form $\equiv\text{Si}-\overset{\text{R}}{\underset{|}{\text{C}}}=\text{C}=\text{O}$ groups. Allene sorption led to extensive dehydrogenation and deactivation of the surface, silanol groups and a mixture of saturated hydrocarbon of variable composition being formed.

Introduction

The properties of reactive silica (RS)¹⁻¹²⁾ are thought to be imparted to ordinary high surface area silicas by the presence of unusual reaction sites, the properties of which are indicated schematically by structure I, *i. e.*, two closely-spaced silicon radicals associated with two



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unusually reactive oxygens. RS chemisorbs oxygen rapidly at room temperature, one oxygen molecule per RS center, the chemisorption being thought to lead to the schematic structure II.^{6,7} An RS sample which has been modified by such an oxygen chemisorption, termed ORS for brevity, is active in chemisorbing various gases but leads to reactions and products which are different than those found with RS.

Some surface species are simply modified by the presence of an additional oxygen atom, *e. g.*, H₂ chemisorption at room temperature results in ≡Si-OH groups with ORS; also, CH₄ chemisorption results in ≡Si-OCH₃ groups with ORS.⁷ With some adsorbates, however, completely different results are obtained with RS and ORS, *e. g.*, (CN)₂ sorption leads to ≡Si-CN species with RS but to a (CN)_n polymer with ORS⁷; also cyclopropane is dissociatively chemisorbed by RS, but apparently not chemisorbed by ORS.¹³ Some of the reactions of ORS are thus significantly different than those of RS. We have therefore studied the sorption of acetylene, propyne, and allene by ORS in order to obtain more information about the "activity" of the ORS center as well as to supplement our information about the reactions of those adsorbates with RS.¹¹ As significant differences in the nature of some of the surface species were found, we describe some aspects of the work.

Experimental

Most experimental procedures have been described elsewhere.^{2-7,11} The adsorbent samples used for much of the work were prepared by methoxylating Cab-O-Sil silica pellets¹⁴ with trimethoxymethane¹⁰, pyrolyzing in a kinetic vacuum at 850-900°, followed by degassing at 850-900° for 10-16 hrs. This treatment resulted in an RS sample which was then converted to ORS by exposure to O₂ (several tens of torr) at room temperature (nominally 25°) for several minutes; excess O₂ was then removed by degassing to 10⁻⁵ torr. The observed surface species of such samples were ≡Si-OH and =SiH₂.

Deuterated ORS having ≡Si-OD and =SiD₂ groups was prepared by treating a silica sample several times with D₂O vapor, in order to convert ≡Si-OH groups into ≡Si-OD groups, degassing, and then exposing the sample several times to CD₃OD vapor at 350°, so that the surface became covered with ≡Si-OCD₃ groups. The subsequent pyrolysis, degassing and O₂-treating steps were like those of other ORS samples.

C₂D₂ of 99.5% isotopic purity was used without further purification.¹⁵

To test the activity of ordinary silica toward the adsorbents, ordinary

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silica samples which had been degassed at high temperature but not subjected to the methoxylation/pyrolysis procedure were exposed to the adsorbents at room temperature and also at temperatures up to 200°. No reactions were observed, indicating that the effects described below can be attributed to the presence of the special reaction centers.

Results and Discussion

The spectral changes observed when ORS samples were exposed to acetylene or propyne and were then degassed are illustrated by the Figures; almost the entire spectral range was effected. Although the results were complex, by noting the appearance and disappearance of bands and the intimate relations between them it was possible to deduce the occurrence of several reactions, some occurring simultaneously, others sequentially. On viewing the entire data it becomes apparent that acetylene and propyne sorption involved the same general reactions in that sorption led to the formation of a mixture of fairly tightly- bound hydrocarbons which changed upon degassing, and of a species stable to 200-300° which was then supplanted by more stable species. Consequently, to simplify the presentation and interpretation of data, it is convenient to consider groups of bands indicative of certain reactions found with both adsorbates rather than lengthily

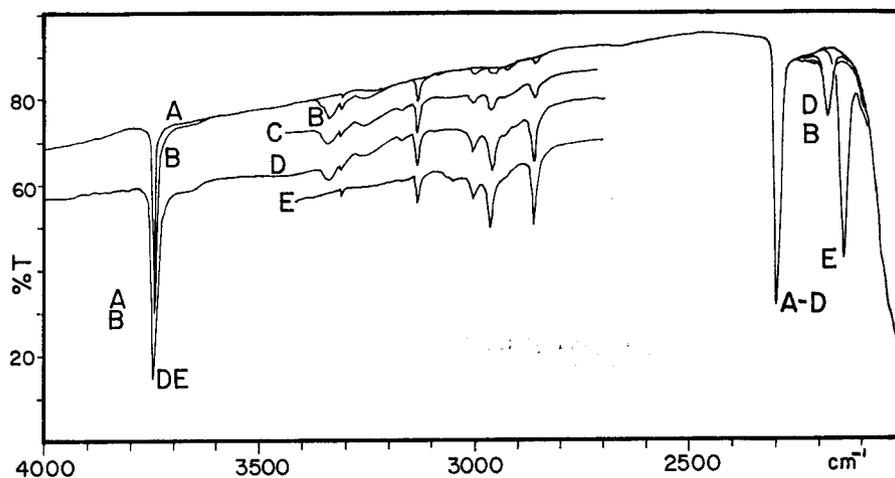


Fig. 1. Acetylene Sorption by ORS

After the background spectrum A of the ORS sample had been recorded, the sample was exposed to 7 torr of acetylene at 25° for 5 mins (B), 4 hrs (C), and 75 hrs (D). Spectrum E was recorded after degassing at 300° for 1 hr.

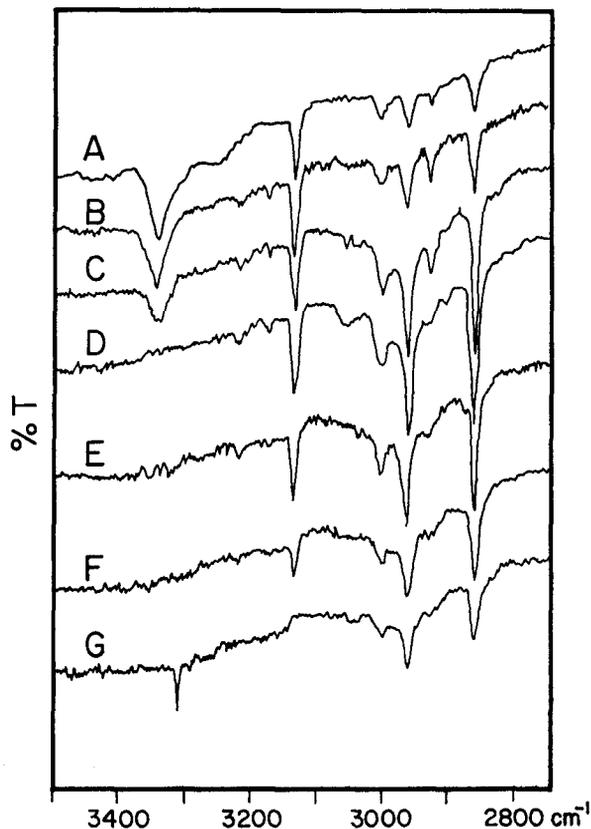


Fig. 2. Degassing Acetylene-Treated ORS

A: ORS after exposure to 5 torr acetylene for 16 hrs at 25°. The sample was degassed for 1/2 hr at 200° (B), 300° (C), 400° (D), 550° (E), 625° (F), and for 1 hr at 700° (G). The ordinates of the scale-expanded segments are displaced.

describing the spectral changes *in toto* for each adsorbate.

Immediately upon exposing an ORS sample to acetylene at 25° a weak band appeared in the C-H region near 3250 cm^{-1} , near the frequency of the 3287 cm^{-1} asymmetric C-H stretching band of gaseous acetylene (B, C, D, Fig. 1; A, Fig. 2). That band was easily removed by pumping for short times at 25° and was consequently caused by a very weakly-held species. Similar weak bands caused by species removable at room temperature were found with acetylene adsorbed on alumina and on porous glass and have been attributed to physically adsorbed acetylene; the topic was reviewed by Little.¹⁰ Similarly, the 3250 cm^{-1} band is attributed to acetylene physically

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adsorbed on the silica portion of the ORS. Weak bands in the 3300 cm^{-1} region attributable to physically adsorbed propyne were not observed.

The acetylene sorption also resulted in the immediate formation of a band at 3343 cm^{-1} (B, Fig. 1; A, Fig. 2), a band at 2185 cm^{-1} (B, Fig. 1), and an increase and broadening of the 3747 cm^{-1} $\equiv\text{Si-OH}$ band (B, Fig. 1). The change in the $\equiv\text{Si-OH}$ band was more clearly seen when C_2H_2 was sorbed by deuterated ORS (traces A, B, Fig. 3A).

There was a similar increase in the $\equiv\text{Si-OD}$ band when C_2D_2 was sorbed by deuterated ORS. Also, the 3343 cm^{-1} band found with ORS was replaced by another at 2625 cm^{-1} ($\nu_{\text{H}}/\nu_{\text{D}}=3343/2625=1.273$) and the 2185 cm^{-1} band by a weaker band at 1940 cm^{-1} ($\nu_{\text{H}}/\nu_{\text{D}}=1.126$).

The 3343 cm^{-1} band is in the range associated with the C-H stretching

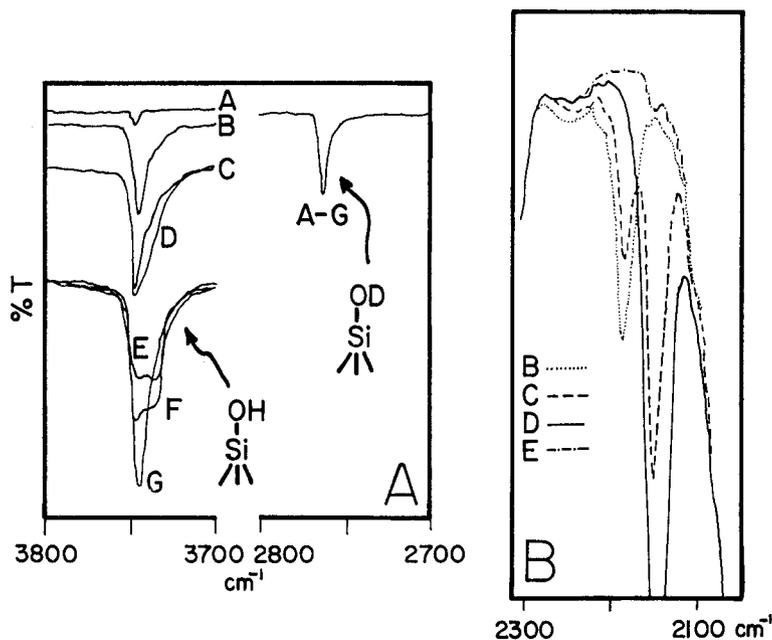


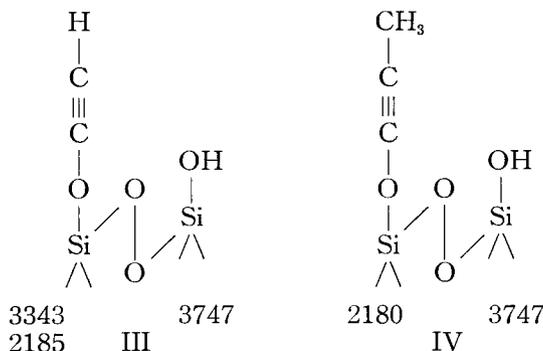
Fig. 3. Acetylene Sorption by ORS

Part A: C_2H_2 sorption on deuterated ORS; segments of the O-H and O-D regions of spectra. After the background spectrum A of the deuterated ORS sample had been recorded, the sample was exposed to 5 torr of C_2H_2 at 25° for 2 hrs (B) and 70 hrs (C). The sample was then degassed for 1 hr at 200° (D), 300° (E), 400° (F), and 500° (G).

Part B: C_2H_2 sorption on ORS. After exposure to C_2H_2 at 25° , the sample was degassed for 1 hr at 100° and 1/2 hr at 200° (B), 300° (C), 400° (D), and 550° (E).

mode of $\text{C}\equiv\text{C}-\text{H}$ groups and the 2185 cm^{-1} band falls in the range found for $\text{C}\equiv\text{C}$ stretchings.^{17,18)} Also, bands at 3311 cm^{-1} ($\nu_{\text{H}}/\nu_{\text{D}}=1.279$ and 2070 cm^{-1} ($\nu_{\text{H}}/\nu_{\text{D}}=1.069$) were attributed to the $\text{C}\equiv\text{C}-\text{H}$ and $\text{C}\equiv\text{C}$ modes of a surface $\equiv\text{Si}-\text{C}\equiv\text{C}-\text{H}$ structure respectively²⁾; bands in the same regions have been attributed to the same modes of surface $-\text{C}\equiv\text{C}-\text{H}$ structures.¹⁰⁾ It thus seems reasonable to attribute the 3343 and 2185 cm^{-1} bands to a $\equiv\text{Si}-\text{O}-\text{C}\equiv\text{CH}$ group.

The formation of such a surface acetylide implies the loss of one hydrogen from the adsorbate, and it is apparent that the formation of the acetylide is accompanied by the formation of surface silanols. The results thus suggest the formation of Structure III,



the acetylene dissociating upon reacting with the ORS center II, in analogy to the chemisorption of H_2 , H_2O , and of CH_4 on center II.⁷⁾ The intensity of the 2185 cm^{-1} band is high in relation to that of the 3343 cm^{-1} band, but the intensities of $\text{C}\equiv\text{C}$ bands are very variable and depend on the position of the triple bond within the absorbing structure, being progressively diminished as the structure becomes increasingly symmetric, and forbidden for a symmetric molecule.^{19,20)} The relatively high intensity of the 3343 cm^{-1} band may be attributed to the high degree of asymmetry of the $\equiv\text{Si}-\text{O}-\text{C}\equiv\text{C}-\text{H}$ portion of structure III.

Upon prolonged exposure to acetylene there were slight decreases in intensities of the 3343 and 2185 cm^{-1} bands (B, C, D, Fig. 1) accompanied by increases of intensities of bands in the C-H region. Apparently, structure III was slowly converted to something else.

Similar results were obtained with propyne sorption. The 3747 cm^{-1} silanol band increased (A, B, Fig. 4) and a weak band formed at 2180 cm^{-1} when ORS was exposed to propyne at 25° (B, Fig. 5, 6). There were no significant changes upon prolonged exposure to propyne or heating to 100° .

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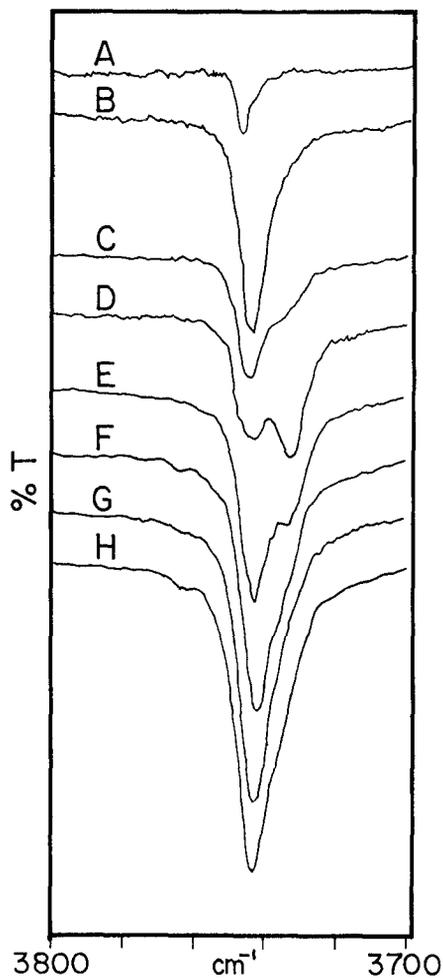


Fig. 4. Propyne Sorption by ORS

Segments of the OH region of spectra of propyne-treated ORS samples. After the background A of the fresh ORS sample had been recorded, the sample was exposed to 7 torr of propyne for 17 hrs, treated at 100° for 1 hr, and degassed for 1 hr at 100° subsequent to standing for 67 hrs in propyne. (B) The sample was then degassed for 1/2 hr at 250° (C), 1/2 hr at 400° (D), 1 hr at 500° (E), 1 hr at 600° (F), 1 1/2 hr at 620° (G) and heated in 30 torr H₂ at 350° for 1 hr (H). The ordinates are displaced. Other segments of the same series of spectra are shown in Fig. 5 and 6.

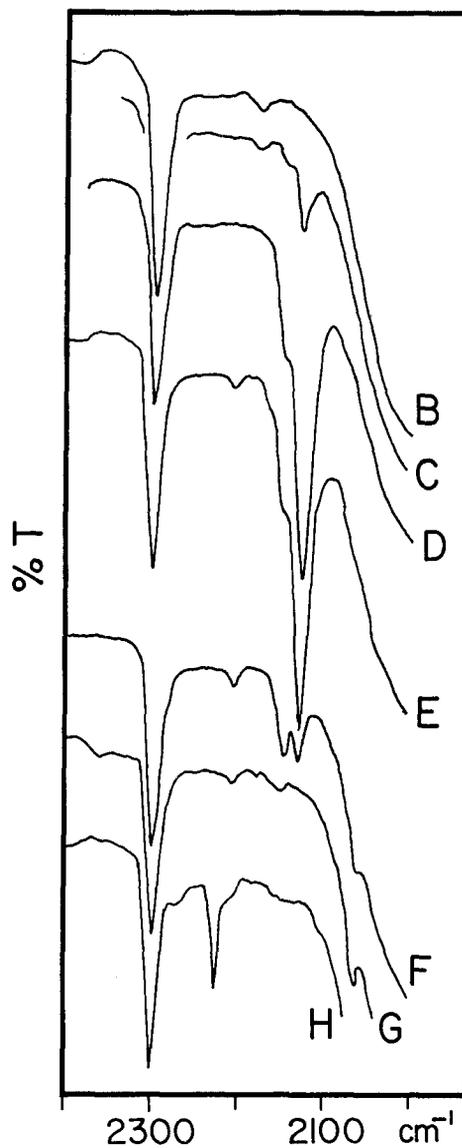


Fig. 5. Propyne Sorption of ORS

See the legend of Fig. 4.

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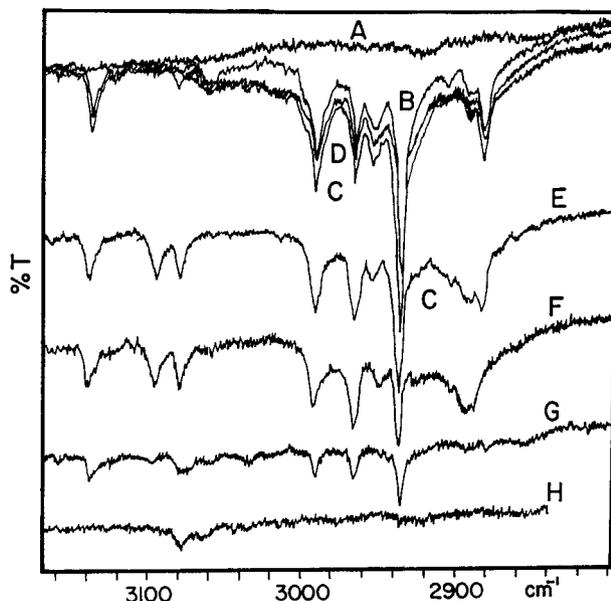


Fig. 6. Propyne sorption by ORS

Scale-expanded segments of spectra, the ordinates of some being displaced. After the background A had been recorded, the sample was exposed to 7 torr of propyne at 25° for 40 mins (B) and 17 hrs (C). After heating for 1 hr at 100°, standing for 67 hrs in propyne, and degassing for 1 hr at 100° (D), the sample was degassed for 1/2 hr at 250° (E), 1/2 hr at 100° (F), 1 hr at 500° and 1 hr at 600° (G), 1 1/2 hr at 620° and was heated in 30 torr H₂ at 350° for 1 hr (H).

In analogy to acetylene sorption, the 2180 cm⁻¹ band is attributed to the C≡C stretching of a ≡Si-O-C≡C-CH₃ grouping formed by reaction of a propyne molecule with the ORS center, resulting in structure IV. The hydrogen from the dissociative chemisorption would result in silanol groups. There is a weak absorption near 3000-2998 cm⁻¹, which disappeared when the 2180 cm⁻¹ band declined, close to the 2994 cm⁻¹ ν_{as}(CH₃) band of propyne; other C-H bands of the acetylenic portion of IV would be superimposed on other weak C-H bands, *e. g.*, B, Fig. 6. The small shift of the C≡C band with respect to that of the acetylenic structure III is attributed to the difference in the mass of the terminal group. Similar small shifts occur in monosubstituted and disubstituted acetylenes, *e. g.*, ν(C≡C) is at 2130 cm⁻¹ with H-C≡C-CH₃ and at 2120 cm⁻¹ with H-C≡C-C₆H₅.¹⁸⁾ It is pertinent to note that the acetylenic portion of structure IV is more symmetric than that of III, there being a pseudo-center of symmetry at or near the triple

suggest themselves. There was a very weak absorption near 3050 cm^{-1} which might account for the $-\text{CH}=\text{}$ group of VII. The extra hydrogen needed for VII or VIII would come from self-hydrogenation.

The sorption of either adsorbate at 25° led to the immediate formation of a number of weak and very weak absorption in the C-H region (Figs. 2, 6), *e. g.*, near 3195 , 3005 , 2963 , 2925 and 2859 cm^{-1} with acetylene, and near 3040 , 3005 , 2991 , 2967 , 2955 , 2939 , 2927 , 2910 , 2845 , 2885 and $2880\text{--}2860\text{ cm}^{-1}$ with propyne. These are attributable to olefinic and paraffinic C-H stretchings.^{17,18} The sorption of C_2D_2 by ORS led to some extremely weak absorptions in the C-D stretching region but the results were not useful. Upon degassing in the $100\text{--}300^\circ$ range there were only minor changes in these C-H bands, and the changes apparently were not connected with major changes occurring in other ranges. The cause of these minor bands is uncertain.

When C_2H_2 -treated ORS samples were degassed at temperatures above 200° , there was a rapid decline of the bands attributed to structure III accompanied by the formation of a new and very intense band at 2146 cm^{-1} (E, Fig. 1; Fig. 3B). The 2146 cm^{-1} band reached maximum intensity between 400° and 500° and decreased above 500° (Fig. 3B), and the changes in that band were accompanied by the changes in the $\equiv\text{Si-OH}$ region illustrated by Fig. 3A, *i. e.*, the 3747 cm^{-1} had first declined, a new absorption being formed on its low wavenumber side. The new absorption became a distinct band near 3737 cm^{-1} which increased and then decreased in intensity roughly paralleling the change in intensity of the 2146 cm^{-1} band. At the higher degassing temperature there was a continued increase of the $3747\text{--}3737\text{ cm}^{-1}$ absorption.

Similar effects were observed when propyne-treated ORS samples were degassed. A very intense band appeared at 2130 cm^{-1} having a shoulder on its high wavenumber side, reached maximum intensity between 400° and 500° , and then decreased in intensity. The intensity relations of the shoulder and 2130 cm^{-1} band changed, a distinct band forming near $2150\text{--}2146$ above 500° , so that two species were involved (Fig. 5). Simultaneously, the 3747 cm^{-1} band decreased, a distinct band appeared near 3733 cm^{-1} , the changes in that band (Fig. 4) roughly paralleling the changes in the $2146\text{--}2130\text{ cm}^{-1}$ bands, much as for C_2H_2 sorption.

C_2D_2 sorption on deuterated ORS and subsequent degassing similarly led to the formation of a very intense band, but at 2133 cm^{-1} , the growth of the band being much like that of the 2146 cm^{-1} band illustrated by the traces of Fig. 3B.

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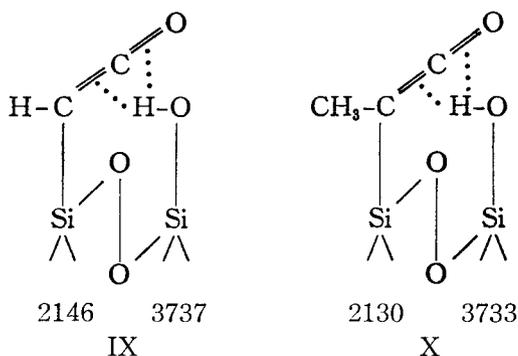
The surface hydride species of RS lead to "normal" isotopic shifts, *e. g.*, for =SiH_2 , $\nu_{\text{H}}/\nu_{\text{D}}=1.394$, while for ≡Si-H , $\nu_{\text{H}}/\nu_{\text{D}}=1.371$. Also, other silanes exhibit isotopic shifts close to the theoretical value.^{22,23)} * For the intense band, however, $\nu_{\text{H}}/\nu_{\text{D}}=2146/2133=1.006$. An attribution of the 2146 cm^{-1} band to an Si-H species thus seems unreasonable.

The intense 2146 and 2130 cm^{-1} bands fall in the spectral region associated with the stretching bands of acetylenes, cyanides, isocyanides, and of cumulated double bonds, *i. e.*, X=Y=Z structures where X, Y, or Z may be C, B, S or O, or to $\text{C}\equiv\text{O}$ complexes.^{17,18,20,22,24)} Many structures such as NCS can be eliminated because the necessary element is not present, leaving one with structures containing C, H, and possibly O, and of these, $\text{-C}\equiv\text{C-}$ seems likely if only because acetylenes were sorbed. However, the bands were very intense, implying that many molecules were present or that the extinction coefficient was high. The $\text{C}\equiv\text{C}$ absorption is strong, however, only if the structure is highly asymmetric, implying a fairly large structure which would give rise to fairly intense C-H absorptions. However, the C-H bands were weak and there were no significant changes in them, so that the presence of a large number of molecules or a relatively small number of large molecules cannot be substantiated. Terminal $\text{C}\equiv\text{C}$ or allenic groups present in fair number might lead to high band intensity, but terminal ≡C-H or =CH_2 groups were not observed. Coupling of $\nu(\text{C}\equiv\text{C})$ with another mode might lead to high intensity, but a reasonable structure containing a grouping with a vibration of the same symmetry as $\nu(\text{C}\equiv\text{C})$ cannot be reasonably established; in any event, the $\text{C}\equiv\text{C}$ group would have to be a part of a fairly large skeleton. It thus seems unlikely that the 2146 cm^{-1} band, and by analogy, the 2130 cm^{-1} band, can be attributed to an acetylene or allene or to a higher cumulene. Similarly, siliconcarbonyl complexes analogous to metal-carbonyl complexes^{22,24)} seem unlikely. Also, oxocarboxonium or acylonium ions seem unlikely. With CH_3CO^+ salts, absorption occurs in the 2229-2302 cm^{-1} range,¹⁸⁾ and various surface species, acylonium ions formed by adsorbing materials such as acetyl chloride or butyl chloride or AlCl_3 , also absorb above 2200 cm^{-1} (25) Similar bands have, however, been observed with another system.

Infrared spectra of acetic acid and of propionic acid sorbed by GeO_2 ²⁶⁾ showed that various surface esters were formed. When the samples were degassed above 300°, an intense band at 2150 cm^{-1} was formed with acetic acid-treated samples and an intense band at 2131 cm^{-1} was formed with propionic acid-treated samples. The bands reached maximum intensity

*) and refs. therein.

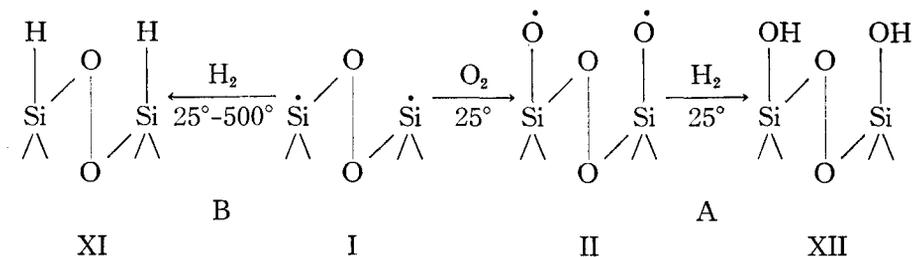
near 420° , and were observed after other surface species had disappeared. In general, the behavior of the intense bands observed with the carboxylic acid- GeO_2 system, which were ascribed to surface ketenes, was identical to the behavior of the 2146 and 2130 cm^{-1} bands. There is a strong absorption in the ketene spectrum at 2150 cm^{-1} assigned to $\nu(\text{C}=\text{C}=\text{O})$ and methyl ketene absorbs strongly at 2130 cm^{-1} ^(27,28). Also, the ketene $\nu(\text{C}=\text{C}=\text{O})$ absorption is an order of magnitude more intense than other ketene absorptions, and this difference in band intensities can readily explain the apparent absence of other bands associated with the intense bands. In analogy with the structures formed on GeO_2 , the 2146 and 2130 cm^{-1} bands are assigned to structures IX and X, respectively.



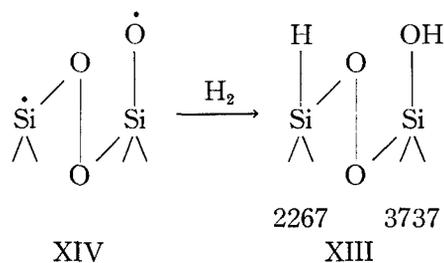
Differences in mass of the substituent on the $\equiv\text{Si}-\text{C}=\text{O}$ carbon accounts for small shifts of $\nu(\text{C}=\text{C}=\text{O})$. Also, an interaction between the $\equiv\text{Si}-\text{OH}$ groups of IX and X, indicated schematically by the dotted lines linking the hydroxyl and $\text{C}=\text{C}=\text{O}$ groups, accounts for the changes of the silanols (Figs. 3A, 5), the small differences in the $\text{C}=\text{C}=\text{O}$ bands leading to the small differences in the silanols (3737 vs 3733 cm^{-1}). Some support for such an interaction with a hydroxyl closely associated with what is considered to be the $\text{C}=\text{C}=\text{O}$ species is provided by the data of Fig. 3A: adsorption of C_2H_2 on a deuterated ORS produced $\equiv\text{Si}-\text{OH}$ groups; the $\equiv\text{Si}-\text{OD}$ groups surrounding the ORS center were not affected during the initial hydroxyl generation or during the changes resulting in the formation of species IX.

The mode of desorption of the ketenic species is not known, but desorption changes the ORS activity. Experiments were carried out in which the sample was heated in hydrogen subsequent to degassing, in order to test the activity of the degassed sample. A mild heating in H_2 would produce the hydride species XI absorbing at $2225\text{--}30\text{ cm}^{-1}$ ^(3,6,7) by reacting with the RS center I, or the hydroxyls of structure XII by

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reacting with the ORS center II.^{6,7)} The H₂-treatment caused a slight increase in the silanols (G, H, Fig. 4), *i. e.*, reaction A had occurred, indicating that the various desorption processes had led to the re-formation of some ORS centers II; and also caused a band at $\sim 2228 \text{ cm}^{-1}$ (H, Fig. 2), *i. e.*, reaction B had occurred, indicating that the various desorption processes had led to the re-formation of some RS centers I. In addition, a small band was formed at 2265 cm^{-1} (H, Fig. 5); it is not certain if a shoulder appeared near 3740 cm^{-1} . Pairs of bands near 3737 and 2265 cm^{-1} have been observed under various conditions and have been attributed to a structure XIII, arising from the reaction of



H₂ with a postulated structure XIV.⁸⁾ The results thus suggest that some of the same centers XIV had been formed, the ORS centers having been destroyed.

Deactivation is also implied by the continual increase of the silanol band upon desorption above 400° . The hydrogen required for the formation of the silanols can come from any of the sorbed species, but the oxygen can come only from the ORS or RS centers, *i. e.*, the integrity of the RS center was destroyed. The mechanism is uncertain.

Desorption at successively increasing temperatures caused decreases of the weak C-H bands of the unidentified species. With acetylene-treated ORS (Fig. 2), there were minor changes in that, for example, a band originally at 2859 cm^{-1} shifted to 2862 cm^{-1} (C, D, Fig. 2). Finally after several very weak bands had disappeared, absorptions were left near 3000 , 2962 , 2927 - 5 ,

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and 2860 cm^{-1} (G, Fig. 2). The frequencies, band pattern and high thermal stability suggest surface methoxy groups, $\equiv\text{Si}-\text{OCH}_3$ ^(2,29,30).

The cause of two bands at 3097 and 3080 cm^{-1} first formed when the ketene species were formed (C, Fig. 6) is uncertain. The bands seem unrelated to others. A highly stable, olefinic species is implied.

As with acetylene, the spectra of propyne-treated samples exhibited small changes in the C-H range upon progressive degassing. Residual material showing high thermal stability caused absorptions near 2991 , 2967 , and 2937 cm^{-1} (G, Fig. 6). The relatively high frequencies of the bands suggests alkoxy groups (other than methoxy), *e.g.*, ethoxy, *i*-propoxy, *sec.* butoxy groups.¹⁷⁾

The results obtained by exposing ORS samples to allene differed from those obtained with the acetylenes. There was an immediate increase in the $\equiv\text{Si}-\text{OH}$ band, much like that brought about by acetylene sorption shown in Fig. 1 by the change in traces A and B, and very weak absorptions appeared in the $3000\text{-}2800\text{ cm}^{-1}$ range, the intensities being of the same order, or less than, those of the bands of spectra B of Fig. 1. Increasing the allene pressure or heating had no effect in bringing about increased sorption. This general behavior was reproduced by eight ORS samples which were known to be active. In each case there was a generation of hydroxyls, indicating that allene sorption had occurred to an appreciable extent, but only very weak C-H bands, indicating that only very few aliphatic surface structures had been formed. Also, the frequencies and relative intensities of these very weak bands were not reproducible, *e.g.*, bands appeared variably near 2970 , 2920 , 2890 cm^{-1} , or near 2990 , 2980 , 2890 , and 2860 cm^{-1} , or near 2999 , 2960 , 2889 , 2858 cm^{-1} . Most of the bands were stable to degassing to 500° , but the intense bands observed upon degassing the acetylene or propyne-treated ORS samples were not observed.

The results indicate that most of the allene which had become sorbed was stripped of hydrogen, the hydroxyls of structure XII being formed, along with some re-arrangement and self-hydrogenation of the fragments into a mixture of saturated hydrocarbons of variable composition, simultaneously deactivating the surface.

Acknowledgement

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