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REACTIVE SILICA

IX. Sorption of Acetylene, Propyne and Allene^{*)}

By

M. J. D. LOW^{**) and H. MARK^{**)}}}}

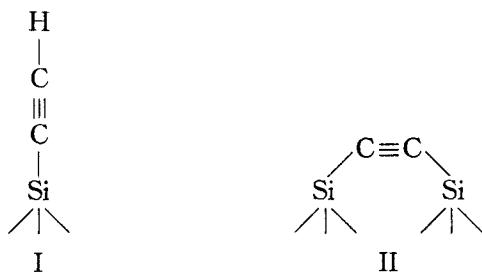
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Abstract

The sorption of acetylene, propyne and allene by reactive silica (RS) (MORTERRA and LOW, Ann. N.Y. Acad. Sci. 220(4), 133 (1973)) was studied by infrared spectroscopic techniques. There were similarities in that with each adsorbent a weakly-bound species, a mixture of more strongly-bound, as well as a very strongly-bound species, were formed. The acetylene apparently dimerized. Each sorption was accompanied by self-hydrogenation. The data suggest that the weakly-bound species have similar overall structure, being bound by adjacent carbon atoms to the two sites of each RS dual center; the unidentified intermediate species contained methyl and methylene groups; the strongly-bound species were surface methoxy groups. The sorption-desorption cycle deactivated the RS, some of the centers responsible for the activity of RS being destroyed. Also, surface "carbide," formed because of self-hydrogenation leading to the more strongly-bound species, was probably associated with the RS centers and suppressed the sorptions.

Introduction

The infrared spectrum of reactive silica (RS)^{1~10} frequently shows sharp but weak absorptions at 3311 and 2070 cm⁻¹ which have been attributed²⁾ to the C-H and C≡C stretchings of a very stable surface acetylidyne, I, and the behavior of the postulated species I, described in



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detail elsewhere², led to the postulate of the existence of a species II. The latter is, essentially, a "surface carbide" which, under certain conditions, may convert to species I. It is not known how or from what reactant the species I is formed; as RS is prepared by pyrolyzing methoxylated silica and then degassing at high temperatures, it seems likely that the centers responsible for the activity of RS sorbed some hydrocarbon produced by the thermal collapse of the surface methoxy groups. It was then of interest to determine if the bands attributed to species I might be formed directly by exposing RS to acetylene, but preliminary work⁷ showed that although RS did chemisorb acetylene, species I apparently was not formed under the conditions of the experiments; some olefinic surface species were produced. Consequently, in order to obtain more information about the nature of the RS reaction center, the olefinic surface species, and the possible existence of doubly-bound species such as structure II, we have examined the sorption of acetylene, and also that of propyne and allene, by RS and describe some of the results.

Experimental

Most experimental procedures have been described elsewhere.^{2~7} RS was prepared by methoxylating Cab-O-Sil silica¹⁰ with methyl orthoformate^{9,10} and pyrolyzing and degassing at 900~950°C overnight. Acetylene and propyne¹² were degassed at liquid nitrogen temperature, and then distilled several times.

Preliminary experiments showed that the adsorbates did not react with ordinary silica pellets which had been degassed at 900~950°C, so that the effects described later are attributed to the reaction of adsorbate with the RS reaction centers.

Experiments and Results

Acetylene Sorption. Upon exposing RS to acetylene at room temperature (nominally 25°C), two sharp bands at 3065 and 3047 cm⁻¹ were observed. That spectrum, and other spectra obtained after an initial exposure to gas, were recorded within 5~10 min, *i.e.*, a short period needed to remove the cell from the vacuum system, place it in the spectrometer, and scan to the C-H region. These bands attained full intensity in 1~2 hr. The intensities of the bands relative to the $\equiv\text{Si}-\text{OH}$ are shown by trace E, Fig. 1; scale-expanded segments of spectra are shown in Fig. 2. Weaker bands were observed near 2997, 2962, 2945, 2927, and 2860 cm⁻¹, and these bands grew slowly over a period of two days (A~C, Fig. 2). The $\equiv\text{Si}-\text{OH}$

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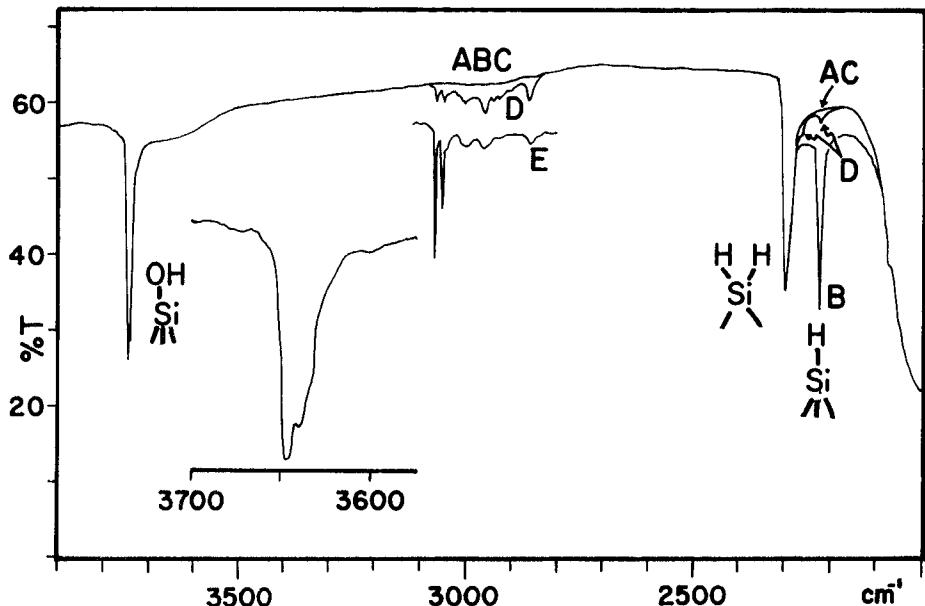


Fig. 1. Acetylene Sorption at 250°C.

- A: "background" sample of fresh RS sample.
- B: after exposure to H_2 at 350°C for 1 hr.
- C: after degassing at 700°C for 1 hr.
- D: after exposure to 19 torr acetylene for 1 hr and degassing for 1 hr at 250°C.
- E: segment of a spectrum recorded after exposing an RS sample to 12 torr acetylene at 25°C for 2 hr.

It is not feasible to show in the figure the slight increase and broadening of the $\equiv Si-OH$ band which occurred upon degassing above 200°C. The insert is an example of a scale-expanded segment of the $\equiv Si-OH$ band of a sample.

band remained unaffected; there were no new bands in the Si-H region.

On degassing, the sharp 3065 and 3047 cm^{-1} bands declined abruptly above 200°C (D, E, Fig. 2). An absorption which was an indistinct shoulder in the 3070~3080 cm^{-1} region (C, D, Fig. 2) became a distinct band at 3077 cm^{-1} (E, Fig. 2), declined in the 300~500°C region and disappeared upon degassing at 600°C (E, F, Fig. 2). A minor absorption was also formed near 3030 cm^{-1} (E, Fig. 2). The 2997, 2962, and 2860 cm^{-1} bands remained constant until 500°C and then decreased in intensity. However, a shoulder on the high wave number side of the 2962 cm^{-1} band disappeared in the 200~300°C region. Also, a broadish band near 2927 cm^{-1} which was observed at low temperature (A~C, Fig. 2) disappeared (D, E, Fig. 2) but

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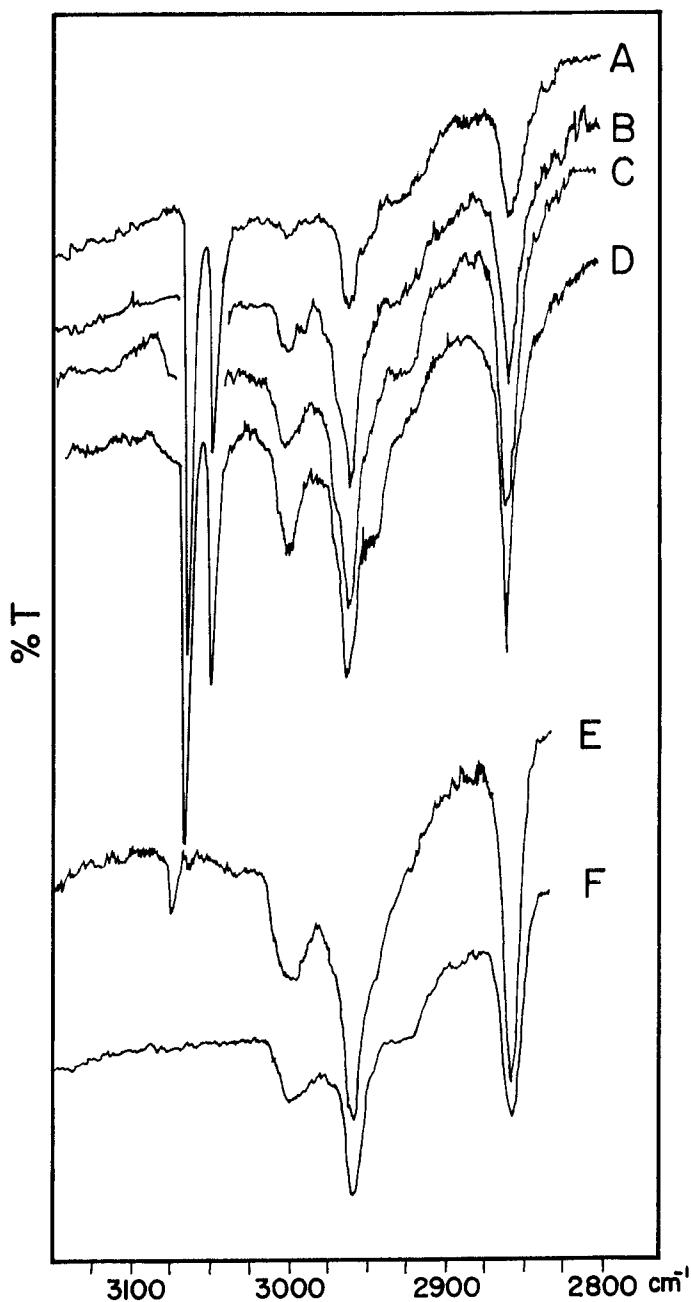


Fig. 2. Acetylene Sorption-Desorption.

The sample was exposed to 7 torr acetylene at 25°C for 1 hr (A), 18 hr (B), and 56 hr (C), and was then degassed for 1 hr at 200°C (D), 300°C (E), and 400°, 500°, and 600°C (F). The scale-expanded ordinates are displaced to avoid overlapping of traces.

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reappeared upon degassing in the 400~500°C range (F, Fig. 2). The $\equiv\text{Si}-\text{OH}$ band increased and broadened slightly upon degassing above 200°C.

Exposure of the sample to H_2 at 350°C subsequent to a 600°C degassing, when most of the sorbed acetylene had been removed and the $\equiv\text{Si}-\text{OH}$ band had grown, led to the formation of a weak $\equiv\text{Si}-\text{H}$ band.³⁾ The intensity of the $\equiv\text{Si}-\text{H}$ band formed after such a H_2 treatment is a measure of the activity of the RS.^{6,7)} Consequently, the weak $\equiv\text{Si}-\text{H}$ band as well as the increase of the $\equiv\text{Si}-\text{OH}$ band indicated that the acetylene sorption-desorption cycle had partially deactivated the RS.^{6,7)}

Heating an RS sample in 5 torr acetylene at 150°C caused no significant changes in the spectra except that the sharp 3063 and 3047 cm^{-1} bands increased slightly, reaching maximum intensity after about 90 min, and then decreased. Also, after about 20 hr, a slight increase in the intensity of the $\equiv\text{Si}-\text{OH}$ band became noticeable.

Slightly larger changes were observed at 250°C. After exposing RS samples to 12 or 19 torr of acetylene for 1 to 2 hr and degassing for 1 hr at 250°C, the spectra in the C-H region (D, Fig. 1) were much like those recorded after a room-temperature sorption, e.g., spectra D, Fig. 2, except that the 3063 and 3047 cm^{-1} bands were greatly diminished. After degassing at 300°C or higher, the spectra were much like spectra E and F, Fig. 2. However, minor bands formed near 2223 and 2267 cm^{-1} (D, Fig. 1) and the $\equiv\text{Si}-\text{OH}$ band increased slightly in intensity and breadth, and became split. The insert in Fig. 1 shows this more clearly, a second absorption appearing near 3737 cm^{-1} in the scale-expanded spectrum. Upon prolonged heating in acetylene, and also after degassing in the 300~500°C range, the weak 3737 and 2267 cm^{-1} bands became less distinct and disappeared while the $\equiv\text{Si}-\text{OH}$ band thickened and increased.

Propyne Sorption. When an RS sample was exposed to propyne at 25°C, there were immediate changes in the spectra in that new weak bands were observed in the C-H region near 3040, 2969, 2927, and 2864 cm^{-1} , and in the Si-H region at 2230 cm^{-1} (B, Fig. 3). The C-H bands, as in the case of acetylene, were weak. There were no apparent changes in these bands for periods up to 20 hr. Upon degassing, the changes shown by the sequence of the spectra of Fig. 3 were observed. The 3040 cm^{-1} band decreased at 200°C and then disappeared (B, C, D, Fig. 3). A minor new band appeared near 3000 cm^{-1} at 200°C, increased slightly in intensity, and was retained at 500°C. The 2864 cm^{-1} band increased at 200°C (B, C, Fig. 3) and then shifted to 2860 cm^{-1} and decreased (C~F, Fig. 3), while the 2969 cm^{-1} band remained roughly constant in intensity in the 200~300°C

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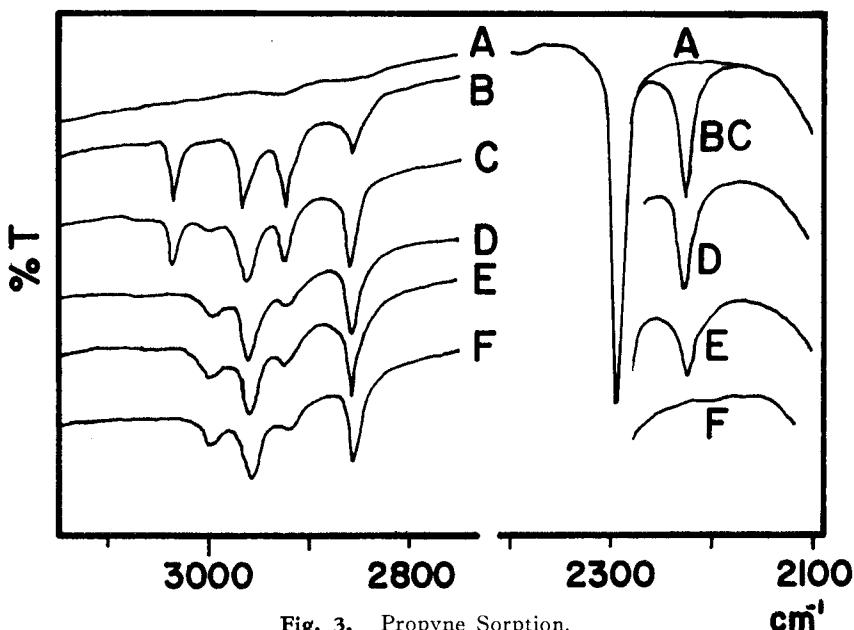


Fig. 3. Propyne Sorption.

After the background spectrum A of a fresh RS spectrum had been recorded, the sample was exposed to 8 torr propyne at 25°C for periods up to 20 hr (B). The sample was then degassed for 1 hr at 100°C and 200°C (C), 300°C (D), 400°C (E), and 500°C (F). The ordinates are displaced.

range but shifted to 2960 cm⁻¹, decreasing slightly in intensity, at higher temperatures. The 2230 cm⁻¹ band decreased above 200°C and disappeared above 400°C. The \equiv Si-OH band, which had remained unaffected during the sorption and desorption up to 300°C, increased slightly above 300°C. Heating RS in propyne at 100°C had no effect; the spectrum was like B, Fig. 3.

Allene Sorption. The major spectral change produced on exposing RS to allene at 25°C was the formation of two sharp bands at 3066 and 2981 cm⁻¹ (Fig. 4) which reached their full intensities in 1~2 hr and then decreased slightly. Simultaneously, a series of minor absorptions appeared in the C-H region and also a minor absorption near 2225 cm⁻¹ (B, C, D, Fig. 4). The sharp bands decreased slightly upon degassing at 100°C and were removed at 200°C (C, D, Fig. 4). The residual bands in the C-H region, and their changes upon degassing, are seen more clearly in the scale-expanded segments of spectra shown in Fig. 5. Degassing at 200°C caused a band at 2862 cm⁻¹ to increase (C, D, Fig. 4); at higher temperatures the band

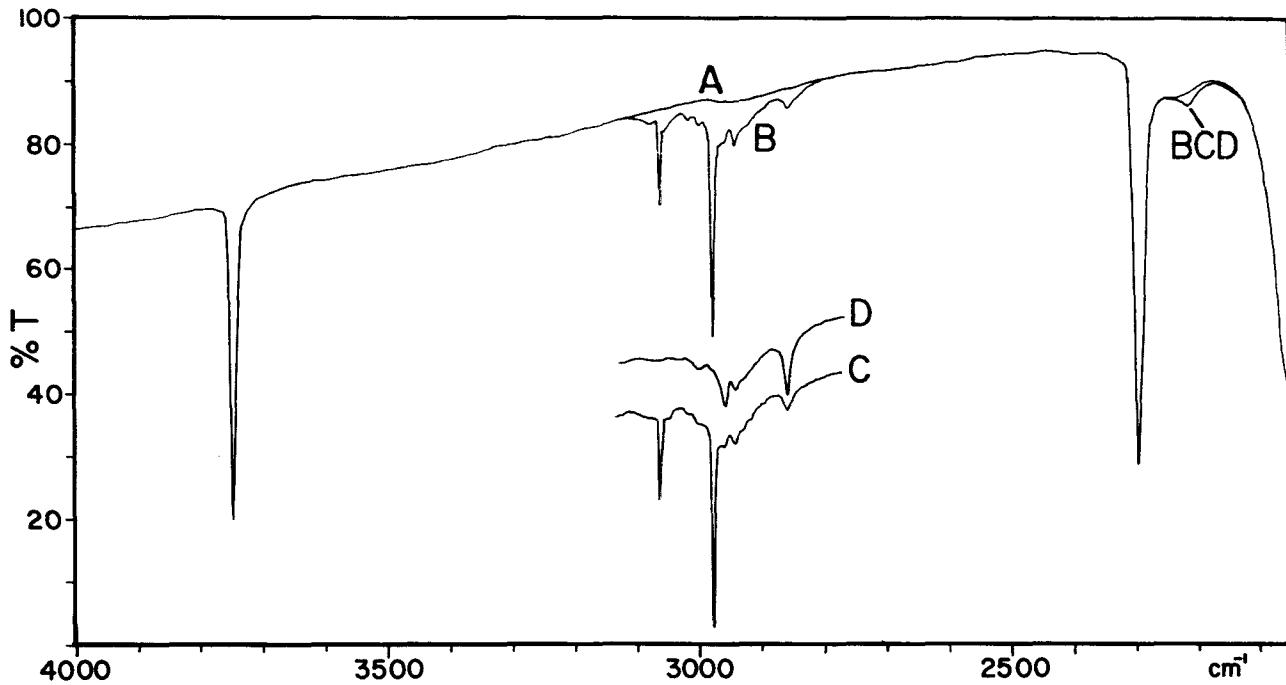


Fig. 4. Allene Sorption.

After the background spectrum A of a fresh RS sample had been recorded, the sample was exposed to 9 torr allene at 25°C for 20 hr (B) and 40 hr followed by 1 hr degassing at 25°C (C), and was then degassed for 1 hr at 200°C (D).

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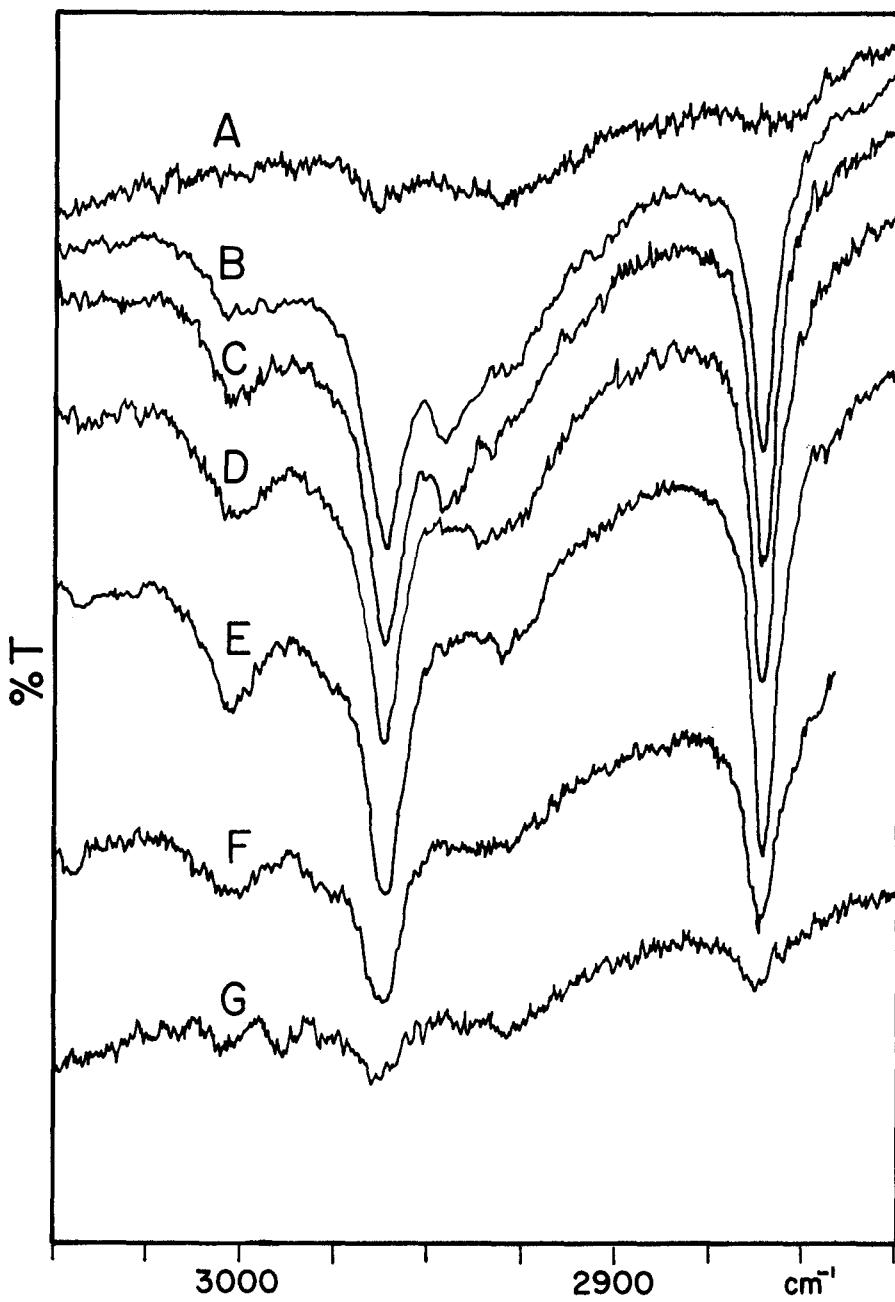


Fig. 5. Allene Desorption.

Scale-expanded segments of spectra, the ordinates being displaced. A: background. B: after exposure to 8 torr allene at 25°C for 20 hr and degassing 1 hr at 200°C. Subsequent degassing occurred for 1 hr at 300°C (C), 400°C (D), 500°C (E), 600°C (F), and 700°C (G).

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decreased and shifted to $\sim 2860 \text{ cm}^{-1}$ (Fig. 5). A minor band near 2950 cm^{-1} disappeared in the $300\text{--}400^\circ\text{C}$ range and was replaced by a minor band near 2927 cm^{-1} (B~E, Fig. 5). Other bands initially near 3003 and 2966 cm^{-1} decreased slightly and shifted to 3000 cm^{-1} and 2962 cm^{-1} , respectively. The minor band near 2225 cm^{-1} was unaffected until degassing temperatures exceeded 500°C , when it disappeared. The $\equiv\text{Si-OH}$ band was not affected by sorption and desorption up to 300°C , but increased slightly in intensity upon desorption in the $300\text{--}500^\circ\text{C}$ range.

Discussion

The changes of the spectra observed on sorbing and desorbing the three adsorbates bear some similarity, as follows: (a) There was the rapid formation of surface species giving rise to sharp and relatively intense bands (3063 , 3047 cm^{-1} with acetylene, 3066 , 2981 cm^{-1} with allene) except for propyne, the 3040 cm^{-1} band being relatively weak. These "weak species" could be easily destroyed by desorption or by conversion into other more tightly-bound species. (b) A series of minor bands point to the existence of more tightly-bonded "intermediate species" containing methylene and methyl groups, as well as olefinic ones, stable in the 25°C to $300\text{--}400^\circ\text{C}$ range. (c) The intermediate species were removed and/or converted to "stable species" absorbing at 3000 , 2962 , 2927 , and 2860 cm^{-1} . (d) The $\equiv\text{Si-OH}$ bands increased slightly at the same time the "intermediate species" changed. (e) The amounts of more or less strongly-bound surface species, judging by the small intensities of the bands in the C-H region, *e.g.*, D, Fig. 1 and D, Fig. 4, were never large, although the RS samples were known to be "active." For example, prior to exposing the RS sample to the acetylene treatment resulting in some of the data of Fig. 1, the freshly prepared RS sample (its background spectrum is trace A of Fig. 1) was heated in H_2 at 350°C for 1 hr. H_2 was chemisorbed, resulting in the formation of the prominent $\equiv\text{Si-H}$ band^{2,4} of trace B, thus indicating that the RS sample contained numerous active centers. The sample was then restored to its initial condition (C, Fig. 1), the low-temperature H_2 adsorption being reversible.^{2,3,6,7} Also, increasing the adsorbent pressure had no significant effect on the band intensities. It is thus possible to seek explanation for the various observations in terms of the nature of the weak species, the formation of tightly-bound species, and the deactivation of the adsorbent.

The easy removal of what has been termed the weak species at first suggests physical adsorption. However, there is no reasonable relation between the observed bands of the gaseous adsorbates and the surface species,

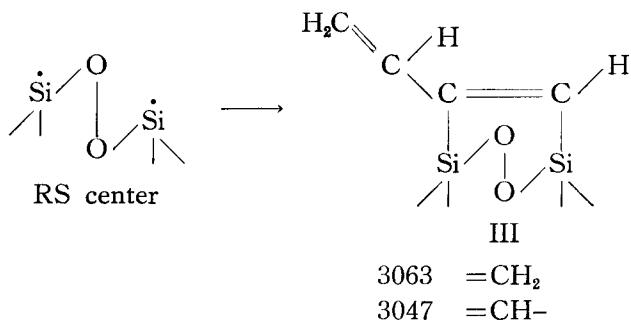
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taking into account the usual shifts in band frequencies and intensities which occur when adsorbate molecules become physically adsorbed. The most obvious case is that of acetylene, olefinic C-H bands rather than the characteristic acetylenic $\text{C}\equiv\text{C}-\text{H}$ band being observed. Similarly, the normally intense 3337 cm^{-1} C-H stretching band of $\text{C}\equiv\text{C}-\text{H}$ associated with propyne, or the very intense 1952 cm^{-1} $\text{C}=\text{C}=\text{C}$ allene band, was never observed. Although the lack of a band is not a very satisfactory criterion for making assignments, the combination of the bands which were observed, along with those which were not observed, suggests that chemisorption was involved with each of the three adsorbates.

Of the two sharp bands at 3063 and 3047 cm^{-1} produced by sorbing acetylene, the 3063 cm^{-1} band falls near the $3095\sim3075 \text{ cm}^{-1}$ region usually characteristic for the terminal $=\text{CH}_2$ group, and the 3047 cm^{-1} band falls near the $3040\sim3010 \text{ cm}^{-1}$ region usually characteristic for $-\text{CH}=\text{CH}-$ or $\text{CR}_1\text{R}_2=\text{CR}_3$ group.¹³ These bands cannot be attributed to acetylene *per se*. However, acetylene is known to dimerize or undergo "self-vinylation,"



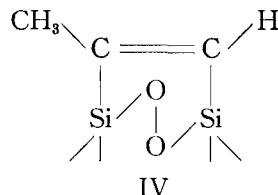
to vinylacetylene¹⁴, suggesting the formation of species III,



The RS center^{6,7} is shown schematically, and that formulation summarizes the properties of a center consisting of a pair of closely-spaced silicones associated with two anomalously reactive oxygen atoms, but implies little about the geometry and structure beyond the requirement that the two silicones be closely spaced. The postulated structure III would not have an acetylenic C-H absorption (none was observed) and the $=\text{CH}_2$ group and $=\text{CH}-$ groups can account for the 3063 and 3047 cm^{-1} bands, respectively.

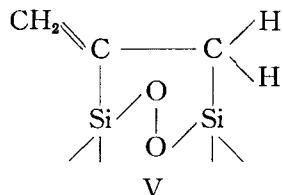
Structures IV and V are suggested for weakly adsorbed propyne and allene, respectively. The 3040 cm^{-1} band of adsorbed propyne is attributed

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weakly adsorbed propyne

3040	=CH-
2962	-CH ₃
2864	



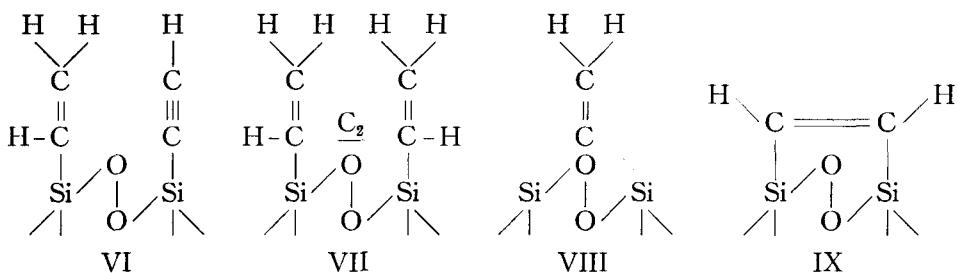
weakly adsorbed allene

3066	=CH ₂
2981	-CH ₂ -

to the C-H stretching of =CH— of structure IV. Absorption near 2962 and 2864 cm⁻¹ would be expected¹³⁾ for the —CH₃ group of structure IV, but these would fall near and merge with the absorptions of other surface hydrocarbon species (B, C, Fig. 3). The 3066 cm⁻¹ band of adsorbed allene falls near the 3095~3075 cm⁻¹ region normally encountered for =CH₂ groups and is attributed to the =CH₂ group of structure V. The 2981 cm⁻¹ band of adsorbed allene is somewhat high for a "normal" paraffinic —CH₂— asymmetric stretching band (usually at 2926±10 cm⁻¹), but falls in the 2999~2977 cm⁻¹ region for CH₂ in cyclobutanes¹⁵⁾, *i.e.*, the band is somewhat high in frequency because of strain. A four-membered ring is apparent in structure V, disregarding the two oxygens associated with the silicones, strain apparently causing the increase in frequency, so that the assignment of the 2981 cm⁻¹ band to the —CH₂— group of structure V may be appropriate.

The small changes in band frequencies, intensities and relative intensities occurring upon degassing indicate that what has been termed the intermediate species were mixtures of several species. Judging from group frequencies^{13,15)}, various species containing —CH₂— and —CH₃ groupings and, in the case of acetylene, a species containing an olefinic species absorbing near 3077 and 3030 cm⁻¹ were present. These bands, characteristic of =CH₂ and =C-H groups, appeared together, apparently were not related to other bands, and may be attributed to ≡Si-CH=CH₂ groups. The simultaneous adsorption and rearrangement of two acetylene molecules or the scission of one vinylacetylene molecule would lead one to expect a structure VI which should, however, also give rise to an acetylenic C-H band near 3330 cm⁻¹ and a C≡C stretching band near 2100 cm⁻¹, *i.e.*, the right-hand portion of VI is equivalent to structure I. Weak bands were observed, on occasion. However, as spectra of fresh RS frequently exhibit very weak bands characteristic of structure I, the formation of such bands upon treat-

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ing RS with acetylene, and consequently of structure VI, cannot be clearly established. As self-hydrogenation probably occurred when some of the acetylene became sorbed, it may be possible that the symmetrically vinylated structure VII may have formed, a third acetylene molecule supplying the necessary hydrogen, the stripped skeleton forming the "carbide" schematically shown as C_2 . Absorptions suggesting the formation of structures VIII or IX analogous to structures formed with acetylene on metals²³, each of which would give rise to a single band, were never observed.

Other species are not identified because the bands were quite weak and some intensity changes are uncertain and the valuable spectral region containing information about deformations was not useful because of the weakness of the bands and the opacity of the adsorbent. However, comparison of the spectra of Figs. 2, 3, and 5 shows that the mixtures were similar although not identical upon degassing at the lower temperatures, but became identical at the highest degassing temperatures, when the "stable species" were formed.

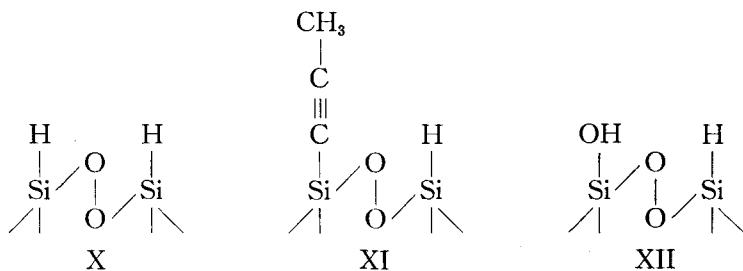
The stable species absorbing near 3000, 2962, 2927, and 2860 cm^{-1} exhibit the band frequencies, band pattern and high thermal stability of surface $\equiv Si-OCH_3$ groups.^{2,7,10~18} In view of this, the stable species are thought to be surface methoxy groups. The oxygen necessary for such groups could come either from the normal silica network, *i.e.*, by the reaction of a carbonaceous fragment with a normal or strained siloxane bridge, or from the RS center itself, *i.e.*, the fragment reacting with the oxygen of the center and thus destroying the integrity of the RS center. Such a reaction would deactivate the adsorbent, and might in part be responsible for the deactivation which was observed.

The weak bands observed near 2267 and 2225 cm^{-1} when acetylene-treated samples were heated, the weak 2225 cm^{-1} band formed when allene was sorbed, and the weak band at 2230 cm^{-1} formed when propyne was sorbed, are all attributed to surface $\equiv Si-H$ stretchings.^{3,6,7} However, the differences in frequencies, thermal stabilities, and circumstances under which

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the bands were produced, suggest that different species and mechanisms were involved.

With propyne sorption it is pertinent to note that the 2230 cm^{-1} band formed right away, remained stable in frequency, was observed after the weakly-bound species had been removed (D, E, Fig. 3), but declined on degassing in the $300\sim400^\circ\text{C}$ range and was completely removed by degassing at 500°C (D~F, Fig. 3). In contrast, the silane band of species X (which is formed by the dissociative chemisorption of H_2 by the RS dual center in



the $25\sim500^\circ\text{C}$ range^{3,6,7)} is usually observed in the lower part of the $2230\sim2225\text{ cm}^{-1}$ range^{3,7)}, and species X does not begin to decompose until $500\sim550^\circ\text{C}$ is reached.^{3,7)} The results suggest the formation of a species XI through the dissociative chemisorption of propyne, the $\equiv\text{Si}-\text{H}$ portion absorbing at 2230 cm^{-1} . The absorption of the $-\text{CH}_3$ grouping would fall within the absorptions of the other carbonaceous surface species and would not be distinguished. The acetylenic portion of XI has a pseudo-center of symmetry at the $\text{C}\equiv\text{C}$ group, so that the $\text{C}\equiv\text{C}$ stretching would be expected to be extremely weak.¹⁹⁾ In contrast to the propyne Si-H band, the weak bands near 2225 cm^{-1} formed with acetylene and allene sorption were stable to 500°C , and are attributed to small numbers of structure X. Such groupings probably formed when weakly-bound or intermediate species rearranged and became dehydrogenated. The occurrence of a 2225 cm^{-1} band with allene sorption makes it tempting to postulate a structure similar to XI but containing a $\text{Si}-\text{CH}=\text{C}=\text{CH}_2$ grouping, in analogy to propyne sorption. However, the terminal $=\text{CH}_2$ of the allenic species would be expected to absorb above 3100 cm^{-1} (*e.g.*, with $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ it is at 3115 cm^{-1} (Ref. 20), and no absorption was observed).

The formation of the weak 2267 cm^{-1} band, which is also attributed to a Si-H stretching, was accompanied by the splitting of the $\equiv\text{Si}-\text{OH}$ band, a distinct band being observed at 3737 cm^{-1} (insert, Fig. 1). Such a 3737 , 2267 cm^{-1} pair has been attributed to a structure XII which may

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be formed during several reactions which are described in detail elsewhere.^{7,8} It is thought that such structures, as well as methoxy groups, and the silanols formed during the degassing, came about as a result of the degeneration of the RS dual center, *i.e.*, tentatively, hydrogen atoms or protons released directly at the RS dual center, because of some rearrangement of the species sorbed at the center, attack and react with one or both of the anomalously reactive oxygen atoms of the center, thus forming methoxy and hydroxyl groups. The latter, or possibly water formed from hydroxyls and additional hydrogen, would then lead to structure XII. In any event, some fraction of the RS centers were destroyed, leading to the observed lowered activity of samples after a sorption-desorption cycle. However, an additional deactivation mechanism may be suggested.

It is apparent, judging from the intensities of the C-H bands even keeping in mind that the intensities of bands of adsorbed C-H species are lower than those of "free" species²³, that the amounts of observed adsorbed species were always small, even though the samples were "active" as judged by the criterion of H₂ chemisorption, and heating and/or increasing the adsorbate pressure had no marked effect in increasing the amount of observed adsorbed species. Also, in order to obtain the species which were detected, self-hydrogenations must have occurred in some cases. The situation is analogous to those found when light hydrocarbons chemisorbed on supported metals, *e.g.*, acetylene chemisorption on Ni led to the formation of surface ethyl groups, the self-hydrogenation also leading to the formation of a "surface carbide."²⁴ Similarly, propyne chemisorption on silica supported Pt led to surface species containing some olefinic and some saturated CH groups.²² The surface carbide is, essentially, the carbon skeleton of the adsorbate, stripped of hydrogen, and multiply-bound to the surface metal atoms; treating a carbided sample hydrogenated at least some of the carbide; the topic is reviewed by LITTLE.²⁵ In view of the effects observed with RS, it seems likely that a similar "carbiding" occurred, *i.e.*, a portion of the RS centers became rapidly covered with "carbide" when first exposed to adsorbate vapor, so that the formation of large numbers of species such as III, IV, V, or XI was suppressed. The gradual accumulation of intermediate species might then occur in part on the carbided sites.

Acknowledgment

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