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Reactive Silica

XVI. Reaction with Cyclopropane, Benzene, and Toluene[1]

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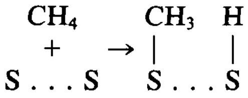
Infrared spectroscopy was used to follow the sorptions of relatively stable adsorbates by reactive silica. Dissociative chemisorption occurred in each case. With cyclopropane, the ring was disrupted and at least three distinct surface species were formed. The main surface product resulting from cyclopropane sorption was also formed when propene was adsorbed. Ring disruption also occurred with benzene, leading to the formation of silanols and some coke-like hydrocarbons, but surface aryls were not observed. However, two surface aryl species were formed with toluene.

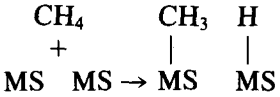
INTRODUCTION

The novel adsorbent termed "reactive silica" (RS, prepared by pyrolyzing methoxylated silica and degassing (*1, 2*) is not merely very "active" but is capable of chemisorption reactions completely unlike those found with ordinary silicas. One of these unusual reactions involves the chemisorption of methane. Methane, like other alkanes, is singularly unreactive as far as most organic reactions are concerned and is thermally stable in the presence of nonmetallic surfaces until quite high temperatures are reached, but it was dissociated and chemisorbed by RS at 60°C (*1*). On the basis of infrared spectroscopic studies, the reaction is thought to involve dissociative chemisorption on the two adsorption sites S . . . S of the RS center to form $\equiv$Si—H and $\equiv$Si—CH_3 species,



$$\begin{array}{c} CH_4 \\ + \\ S\ldots S \end{array} \rightarrow \begin{array}{ccc} CH_3 & & H \\ | & & | \\ S & \ldots & S \end{array}$$

Methane chemisorption does occur on a variety of transitional metal surfaces and exchange occurs with D_2 at relatively low temperatures (*3–5*), a possible rate-limiting step being the dissociative chemisorption on two adjacent sites MS on the metal surface,



$$\begin{array}{cc} CH_4 & \\ + & \\ MS & MS \end{array} \rightarrow \begin{array}{cc} CH_3 & H \\ | & | \\ MS & MS \end{array}$$

The chemisorption on RS and on metals thus bear some similarity in that apparently pairs of sites are involved and similar surface species are produced; of greater interest is the similarity of the "activity" of the sites. Apparently, the RS center can impart to the normally unreactive silica some of the activity associated with metal surfaces. It is consequently pertinent to inquire about the behavior of RS toward other molecules which, like methane, are relatively inactive and stable, and we have studied some of the aspects of the reaction of RS with cyclopropane, and with benzene and toluene. Cyclopropane is relatively stable, its thermal decomposition starting near 450°C although the total ring strain renders it more reactive than open-chain alkanes (*6*). Similarly, benzene is relatively stable, the condensation to biphenyl beginning near 500°C (*7*), and chemically unreactive as far as ring breakage is concerned, as is toluene, the characteristic reactions of benzene involving substitutions.

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[1] See Ref. (*2*) for Part XV.

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EXPERIMENTAL

Most experimental procedures have been described (*1*). Cab-O-Sil M-5 silica (*8*) was methoxylated by reaction with trimethoxymethane (*9*), followed by pyrolysis and a 16-h degassing at 900°C. Spectroscopic grade benzene and toluene, and cyclopropane and propene were purified by freeze–pump–thaw cycles and vacuum distillations prior to use.

EXPERIMENTS AND RESULTS

Cyclopropane

When RS was exposed to cyclopropane vapor at 25°C, a series of bands appeared in the C—H region and a minor absorption appeared near 2250 cm^{-1} (A, Fig. 1). Prolonged exposure for up to 4 days caused the bands to increase only very slightly. Heating up to 150°C caused a slight increase in a band at 2937 cm^{-1}.

Upon degassing for short periods at 25°C, bands at 3125, 3104, 3048, and 3023 cm^{-1} disappeared (B, Fig. 1). These bands closely match the bands of gaseous cyclopropane observed at 3125, 3103, 3050, and 3023 cm^{-1}, and are attributed to physically adsorbed cyclopropane.

The slight growth of the 2937-cm^{-1} band, and the changes observed upon degassing (Fig. 2) indicate that the sorbed layer consisted of a mixture of fairly tightly bonded species. Upon degassing at room temperatures all bands decreased slightly in intensity, some more rapidly than others, and small frequency changes occurred; further changes occurred at higher temperatures.

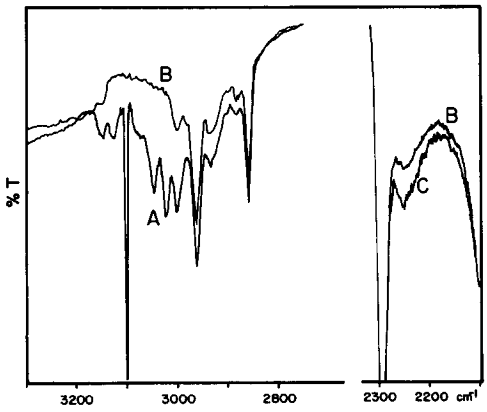


FIG. 1. Cyclopropane sorption at 25°C. (A) RS after exposure to 5 Torr cyclopropane at 25°C for 40 min, (B) after degassing at 25°C for 15 min, (C) after heating in 5 Torr cyclopropane at 150°C for 2 h.

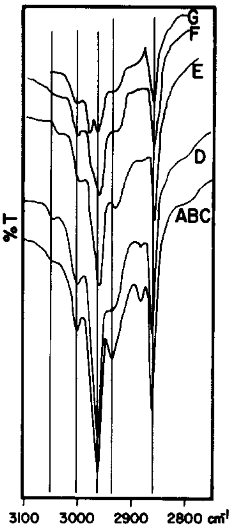


FIG. 2. Cyclopropane desorption. After RS was heated in 5 Torr of cyclopropane at 150°C for 2 h and degassed at 25°C for 15 min (A), the sample was degassed for 0.5 h at: 200°C (B), 300°C (C), 400°C (D), 500°C (E), 550°C (F), and 600°C (G).

Of the residual absorptions observed near 3050–3040, 3003, 2964, 2937, 2882, 2862, and 2250 cm^{-1}, after physically adsorbed cyclopropane had been removed (A, Fig. 2), (a) the 2882-cm^{-1} band decreased and disappeared above 500°C, these changes being accompanied by a change in the 2964-cm^{-1} band, which shifted to 2960 cm^{-1} and became asymmetric, and by a decline and shift of the 2862-cm^{-1} band to 2857 cm^{-1}; (b) a broad but weak absorption in the region 3050–3040 cm^{-1} became indistinct as the degassing temperature approached 500°C; (c) the 2937-cm^{-1} band decreased and shifted its center to 2930 cm^{-1} and then became an ill-defined absorption in the region 2950–2900 cm^{-1}. This absorption and another ill-defined one in the region 3020–2900 cm^{-1} remained after degassing at 600°C; (d) the 2250-cm^{-1} band was replaced by another near 2210 cm^{-1} in the 400–500°C range; (e) the appearance of the 2210-cm^{-1} band approximately followed the increasing asymmetry of the 2964-cm^{-1} band and, at the highest temperature, the latter split into bands near 2980 and 2960 cm^{-1} (E, Fig. 2).

Apparently, the major absorptions near 2964 and 2862 cm^{-1}, and also the less prominent one near 2937 cm^{-1}, were composed of several overlapping bands, the contribution of which changed with degassing. Consideration of all of the data, including frequencies and relative band intensities, the appearance and disappearance of bands and the relations between them, indicates that the bands be grouped as listed in Fig. 3, which also summarizes the reactions and data, and indicates some assignments based on group frequencies (*10–13*).

Exposure of RS to cyclopropane for prolonged periods, or heating to 150°C, caused no change in the Si—OH band. However, upon degassing at temperatures above 200°C, there was a progressive increase in that band, indicating that silanols had formed. It thus seems likely that the destruction of some of the surface species led to attack of the RS center (the anomalously reactive oxygen atoms associated with the center providing the oxygen required for the formation of silanols (*1*)).

The properties of RS can be changed by exposing it to O_2, which becomes chemisorbed (*1*). The modified adsorbent (ORS) was prepared and then exposed to 5 Torr cyclopropane at 25°C for up to 41 h. In distinct contrast to the reaction observed with RS, there was no chemisorption. Only the physical adsorption of cyclopropane was found with ORS.

Cyclopropane can isomerize to propene, which might then become adsorbed. Consequently, several experiments were carried out in which RS was exposed to propene. It was found that (a) exposing RS to 50–100 Torr of propene at 25°C for periods ranging from 5 to 60 min led to the formation of very weak bands at 2964, 2937, and 2882 cm^{-1}, i.e., the bands of Group III; (b) increasing the propene pressure to 500 Torr caused only a slight growth of the bands; (c) heating to 200°C at pressures of 500 Torr caused only slight increase in the bands; (d) bands of other groups of Fig. 3 were not observed. The results obtained with propene indicate that the main reaction was the formation of the species giving the Group III bands with cyclopropane. The amount of other species, if formed, was too small to

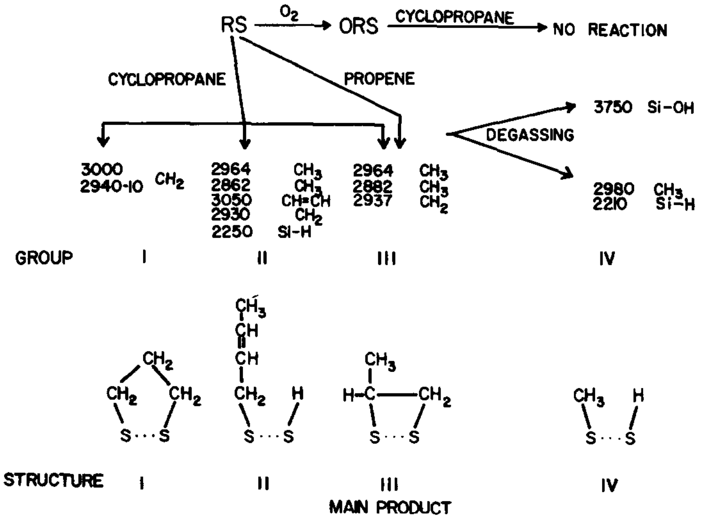


FIG. 3. Summary of cyclopropane and propene sorption.

be detected. Also, the extent to which the propene sorption occurred, judging from band intensities, was relatively small and the reaction was slow in comparison to that of cyclopropane.

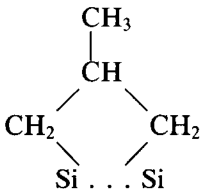
The results suggest that cyclopropane chemisorption lead to at least three surface species, a fourth one forming on degassing (Group IV). Band assignments to definite structures is made difficult because of the band overlapping and also because information about deformation modes is not available partly because the bands were very weak and the absorbent opaque. The following assignments are tentatively advanced, based on (a) group frequency relations (*10–12*); (b) the band groupings themselves, i.e., Groups I–IV, which together with (a) suggest the possibilities of certain structures and the unlikelyhood of others, e.g., a pair of bands near 3095–3075 and 3040–3010 cm^{-1} was never observed, so that structures incorporating terminal $=CH_2$ groups need not be considered; and (c) the type of structures likely to be formed on the RS center. Extensive prior work to show that the RS center has the properties of a dual site although its exact geometry is not known (*1*). Presently the dual site of the center is represented schematically by S . . . S.

The related bands of Group I are a little high in frequency to be the symmetric and asymmetric C—H stretchings of $—CH_2—$, but not too high for $—CH_2—$ groups of ring compounds (*12–14*). Structure I is suggested, formed by one cyclopropane molecule reacting with the dual RS center.

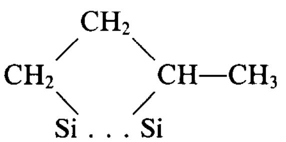
The bands of Group III, the main product, which was formed also with propene, suggest that the chemisorbed species contained only CH_3 and CH_2 groups. A complex structure of this nature might be formed from the adsorption of several C_3H_6 molecules on one RS center with rearrangements and stripping one or more adsorbate molecules of all hydrogen. The simpler structure *III* suggests itself, formed from one C_3H_6 reacting with the RS dual site; the tertiary C—H stretching band would be extremely weak (*10–12*) and not be observed. Such a structure might be formed directly by the addition of the RS center across the propene double bond. With cyclopropane, however, a rearrangement is implied.

The modes of formation and frequencies indicate that the 2250- and 2210-cm^{-1} bands were caused by surface silanes (*1*). The 2210-cm^{-1} band is associated with another structure absorbing at 2980 cm^{-1} (Group IV). Such a pair of bands was formed by the dissociative chemisorption of CH_4 on RS (*1*) and was assigned to a grouping like structure **IV** shown at the bottom of Fig. 3. In analogy, the Group IV bands are assigned to structure **IV**, i.e., there was a decomposition of surface structures at the higher temperatures leading to the formation of **IV**, along with the formation of silanols.

The 2250-cm^{-1} band attributed to an Si—H group is associated with the several C—H absorptions of Group II, thus suggesting the structure **II**, in analogy to structure **IV**. It should be recalled that the four C—H absorptions are related. However, the simplest structure which is consistent with the C—H frequencies observed would contain four carbons, as shown in structure **II**, and not three carbons, as would be expected from the direct reaction of one cyclopropane molecule with the RS center. More than one adsorbate molecule would thus be needed to form a structure such as **II**. This requirement in turn suggests that the Group III bands, in addition to the simplest structure **III**, may also imply the existence of structures **IIIa** and **IIIb**,



IIIa



IIIb

which would absorb at the same frequencies.

Benzene

Several absorptions appeared in the C—H region, and also a weak band near 1480 cm^{-1}, when RS was exposed to benzene at 25°C (A and B, Fig. 4). There were no changes in the Si—H region, but there was a pronounced increase in the Si—OH band. There were no significant changes of the spectrum with increased times of exposure of sample to benzene, or upon increasing the temperature to 200°C. At higher temperatures, however, e.g., 300°C, the Si—OH band increased and a weak band appeared at 2225 cm^{-1} (C, Fig. 4). Degassing in the 25–100°C range caused the bands in the C—H region and the 1480-cm^{-1} band to disappear.

The fairly prominent bands centered near 3090 and 3040 cm^{-1} and the weaker band near 1480 cm^{-1} fall within a few wavenumbers of the bands of gaseous benzene, and are attributed to physically adsorbed benzene. The other, weaker bands in the C—H region near 2960, 2927, and 2985 cm^{-1}, which were not found in the spectrum of benzene, are obviously attributable to the CH_3 and CH_2 groups (*10–12*) of an otherwise unidentified paraffinic species weakly bound to the surface. The results obtained at low temperature thus show that, in addition to physical adsorption, there was another reaction which led to the formation of a paraffinic species, i.e., some of the sorbed benzene became hydrogenated, the source of the hydrogen being other benzene molecules. The relatively large increases of the Si—OH band (A and B, Fig. 4) which accompanied the low-temperature sorption also requires a source of oxygen. The siloxane bridges of ordinary silica cannot be involved in the silanol generation because benzene does not disrupt silica (*13*), but the disruption of the RS center could make some Si—O linkages available. It is thus suggested that benzene was partially stripped of hydrogen, the hydrogen moving to adjacent partially stripped benzene (thus hydrogenating the latter); the stripped or partially stripped benzene, acting much like a carbene, would attack the silicon and oxygen atoms of the center and disrupt it, leading to the formation of silanols and a surface "carbide," in analogy to the carbide formation occurring when acetylene or ethylene was chemisorbed by supported metals (*14, 15*). Some of the RS centers would thus loose their structural integrity and the sample would be partially deactivated. As the silanol band increased in intensity at higher temperatures, e.g., C in Fig. 4, such a deactivation continued as the temperature was raised. Also, another reaction became important.

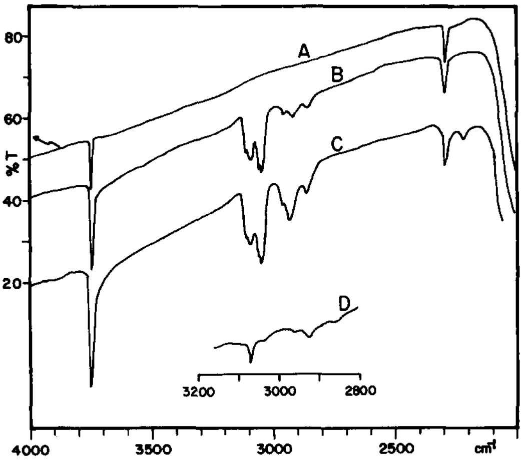
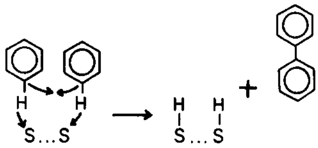


FIG. 4. Benzene sorption. (A) Background spectrum of fresh RS sample, (B) after exposure to 8 Torr of benzene at 25°C for 75 min, (C) after exposure to 10 Torr of benzene at 300°C for 1 h, (D) segment of spectrum recorded after exposing an RS sample to 10 Torr benzene at 610°C for 1 h followed by degassing at 25°C for 10 min.

The 2225-cm^{-1} band formed upon heating in the 300–400°C range (C, Fig. 4) is plausibly attributed to a surface silane, structure V, below, identical to that formed upon chemisorption of H_2 by RS (*1*). The spectra showed no bands in the region 3100–3000 cm^{-1} (after weakly adsorbed material has been removed) which might be attributed to an aromatic C—H stretching, so that no detectable amounts of species such as Si—Ø were formed (Ø is C_6H_5). The source of the hydrogen needed for the formation of the silane species would be the benzene adsorbate. It is known that the reaction, 2 Ø—H → H_2 + Ø—Ø, begins in the gas phase at 500°C (*7*, *16*). In analogy, it is suggested that a similar reaction occurred with RS but at lower temperatures, the hydrogen forming structure **V** rather than H_2, a plausible mechanism being



V

Toluene

As in the case of benzene, exposing an RS sample to toluene led to an increase of the Si—OH band (A and B, Fig. 5), absorptions near 3065, 3035, 2930, and 2878 cm^{-1} in the C—H region, and a weak band near 1496 cm^{-1}. Also, a band was formed at ~2208–2210 cm^{-1}. Degassing at 25°C caused the absorption in the C—H region to decrease (B and C, Fig. 5), residual weak bands remaining near 3070, 3036, 2960, 2930, and 2878 cm^{-1} with ill-defined absorptions near 3090–2909 and 1560 cm^{-1}. Scale-expanded segments of spectra recorded after various degassing are shown in Fig. 5.

The 3065-, 3035-, and 1496-cm^{-1} bands, which were readily diminished by pumping at low temperature, are close to the bands of toluene, and are attributed to physically adsorbed toluene. The 2930- and 2878-cm^{-1} bands probably were also caused mainly by physically adsorbed toluene; it is not certain if, as in the case of benzene sorption, some paraffinic material was formed. However, the realtively large increase of the Si—OH band shows that the general aspects of the low-temperature sorptions of benzene and toluene were similar, i.e., in addition to physical adsorption, there was a reaction of the adsorbate with the RS centers, leading to silanol group formation and partial deactivation of the adsorbent. With toluene, however, some tightly bonded species were formed which, as the sequence of spectra segments DEH shows, remained on the surface until 650°C was reached.

Heating the sample in toluene vapor caused the silanol band and the 2210-cm^{-1} band to increase, and there were increases in intensities and relative intensities of the bands in the C—H region (C and D, Fig. 5). Degassing at successively increasing temperatures led to a continued increase in the Si—OH band, decreases in the C—H bands and changes in their relative intensities. These various changes, including the reversal of the ratios of the intensities of the 3070- and 3036-cm^{-1} bands, e.g., D vs H (Fig. 5), indicates that more than one tightly bound species was present, the bands being grouped: 3070, 2909, 2878 cm^{-1}, and 3036, 2960, and 2878 cm^{-1}.

The absorption at 2208–2210 cm^{-1}, as in the case of benzene, is attributed to an Si—H stretching. However, expanded segments showed the band to be asymmetri-

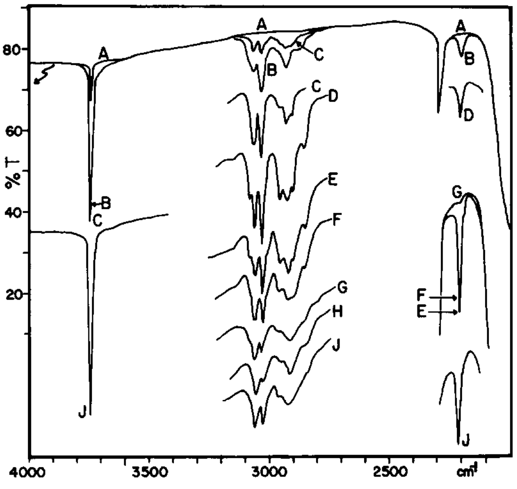


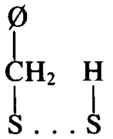
FIG. 5. Toluene sorption. After the background spectrum A of the fresh sample had been recorded, the sample was exposed to 10 Torr of toluene for 1 h at 25 or 200°C (B) and then degassed at 120°C for 20 min and 150°C for 20 min (C). The sample was then reexposed to 8 Torr of toluene for 1 h at 300°C and degassed at 200°C for 30 min (D). The sample was then degassed for 30 min at 300°C (E), 350, 460, and 550° (F), 600° (G), and 650° (H). The sample was then reexposed to 15 Torr of toluene for 30 min at 350°C and degassed for 15 min at 350°C (J). Segments of spectra C–J in the C—H region and of spectra E, F, G, and J in the Si—H region are ordinate scale-expanded.

cal, e.g., E in Fig. 5, indicating that 2208- to 2210-cm^{-1} band was composed of two overlapping absorptions, i.e., there were two Si—H species. Also, there were two distinct aromatic C—H bands *(12–14)* at 3070 and 3036 cm^{-1}. The intensity ratio of these bands changed when the sample was reexposed to toluene (J, Fig. 5), the increase of the 3036-cm^{-1} band being accompanied by an increase in the 2210-cm^{-1} band. The assignment of the 3700-cm^{-1} band to the C—H stretch of a monosubstituted benzene structure *(12–14)* is supported by an observation made with benzene sorption: when R—S was heated in benzene vapor above 400°C, an aromatic C—H band at 3070 cm^{-1} was formed (a segment of a spectrum is shown as the insert trace D in Fig. 4) and is attributable to a Si—Ø structure, i.e., a monosubstitutional benzene. (The high-temperature reaction of benzene with RS has only been partly studied; it is more complex in that benzene also reacts with the 2300-cm^{-1} silane and will not be discussed.)

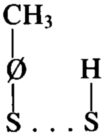
Taken together, the results suggest the following band groupings and assignments:

Group VI		Group VII	
	monosubst.		disubst.
3070	arom. C—H	3036	arom. C—H
2909	CH_2	2960	CH_3
2878	CH_2	2878	CH_3
2210	Si—H	2208	Si—H

which in turn leads to the following structures:


$\begin{array}{ll} Ø & \\ | & \\ CH_2 & H \\ | & | \\ S \ldots & S \end{array}$

VI


$\begin{array}{ll} CH_3 & \\ | & \\ Ø & H \\ | & | \\ S \ldots & S \end{array}$

VII


$\begin{array}{ll} R & R \\ | & | \\ S \ldots & S \end{array}$

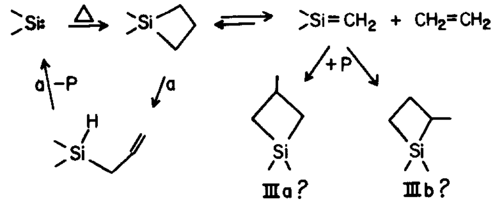
VIII

Structures **V** apparently did not form. Also, it is not known if structures such as **VIII** formed (R is —Ø—CH_3 *or* —CH_2—Ø).

SUMMARY AND CONCLUSIONS

As the various data show, RS is able to cause the disruption of relatively stable molecules, in a manner reminiscent of the action of paired sites on a metal surface. The RS dual center is thus quite "reactive." In general, the reactions follow the pattern observed with other hydrocarbon adsorbates *(17–20)* in that there are several general reactions with complex adsorbates: (A) "end-on" chemisorption, where each end of the adsorbate molecule becomes bound to one of the sites as in structure I, similar structures being formed with alkenes *(18)*; (B) end-on chemisorption with rearrangement of the adsorbate as with the postulated structure III and also with some similar structures formed with alkenes *(18)*; (C) hydrogen abstraction with subsequent formation of an Si—H group and the adsorbed hydrocarbon residue as in the case of toluene of CH_4 *(1)*; (D) "self-hydrogenation," in which the surface structures formed contain more hydrogen than the adsorbate molecule, as with structure II or structures formed with ethylene *(17)* or some alkynes *(19, 20)*; (E) self-hydrogenation with rearrangements, as with structure II and with alkynes *(19, 20)*; (F) free radical-type polymerizations *(17, 18)*. The various surface structures which have been postulated are reasonable ones consistent with the infrared data, and it is possible to provide plausible mechanistic "explanations" for reactions such as A or C, e.g., Mechanism 1. However, difficulties arise in deducing plausible mechanisms for reactions such as B, D, or E in that it is hard to employ the usual and accepted mechanistic concepts of conventional organic chemistry to "explain" such reactions; it is necessary to devise complex mechanism incorporating unusual intermediates and steps whose existence at times seems unrealistic.

The major difficulty is that the unsatisfactorily complex mechanisms must incorporate steps involving two spatially separated silicons which are taken to be the reaction sites. It is interesting and pertinent to note, however, that the mechanistical complexity is greatly alleviated when two *spatially coherent* sites are considered, i.e., if a single silicon were to act as dual reaction site, as in the case of silylene, >Si:, e.g., (*21–28*). For example, the construction of a conventional mechanism leading to the formation of the postulated structures IIIa and IIIb is greatly facilitated through the reaction of a silylene-like structure >Si: in Mechanism 2



Δ = cyclopropane P=propene

in which propene formed through the reaction **a** readily leads to the formation of the complex surface structures **IIIa** and **IIIb**. The formation of surface species containing four carbons from an adsorbate containing only three carbons thus becomes acceptable, e.g., structure **II**. Similarly, other plausible mechanisms involving a silylene-like structure can be written for the reactions of other adsorbates with the RS surface. The >Si: structure is thus a convenient mechanistic device. The actual RS center must be more complicated than the latter, because of its association with additional silicon and oxygen atoms (*1*).

ACKNOWLEDGMENT

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