JOURNAL OF CATALYSIS 40, 236-248 (1975)

Reactive Silica

VII. Chemisorption and Pyrolysis Procedures in a Flow System[1]

M. J. D. LOW, YORKE E. RHODES
AND PETER D. ORPHANOS

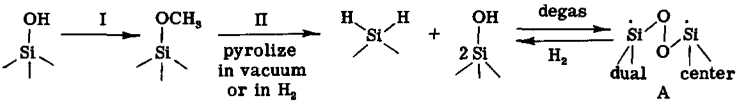
*Department of Chemistry, New York University,
New York, New York 10003*

Received April 22, 1975

The vacuum pyrolysis of surface $\equiv$Si—OCH$_3$ groups leads to the formation of $=$SiH$_2$ and silanol groups which disappear on degassing. The silica then becomes remarkably active. To check if the reaction was unique to $\equiv$Si—OCH$_3$, a variety of reagents were tested using a flow system and monitoring the reactions by infrared spectroscopy. Most alcohols and simple esters became chemisorbed as silyl alkyl ethers. In general, with the exception of benzyl alcohol, a reagent was effective in producing $=$SiH$_2$ if, upon chemisorption, methoxy groups were formed directly or if the adsorbed species itself contained methoxy groups. The results suggest that the initial reaction of a reagent with surface silanols involved a mechanism in which an initial hydrogen bonding led to the formation of a surface-stabilized ion pair which could then readily suffer a direct displacement; the postulated mechanism can account for the observed order of chemisorption. The pyrolysis of alkoxy groups is thought to involve the homolytic cleavage of the O-C bond to generate a siloxy radical which would then react further with desorbed material and/or with neighboring alkoxy groups. With methoxy, the $=$SiH$_2$ and silanols were formed because the siloxy radical was too far from neighboring methoxy groups for interaction to occur. With alkoxy groups other than methoxy, however, the siloxy radical was within bonding distance of the alkoxy, and direct interaction was possible, surface silanols being generated.

INTRODUCTION

High surface area silicas, which generally show little inclination to take part in chemisorption, can be "activated" by a three-step procedure involving methoxylation, pyrolyzing the methoxy layer, and then removing the surface silanes and silanols formed during the pyrolysis,



The adsorbent produced in this fashion, termed reactive silica (RS), is not merely highly "active" in comparison to ordinary silicas, but is capable of chemisorption reactions completely unlike those found with ordinary silicas, and these new reactions and the new surface species found with RS have led to a novel and interesting aspect of the chemistry of silica surfaces (*1–8*).

Extensive work has been carried out and a fair amount of information has been obtained about RS. The three-step preparation has been developed, the initial reac-

---

[1] Part VI: Ref. (*8*).

tion I is reasonably well understood, the stoichiometry of reaction III has been found, and many chemisorption reactions have been studied; these provide compelling evidence that the "activity" of RS is caused by special reaction centers formed in step III. The properties of the center are summarized by the schematic formulation A and are those of a center consisting of a pair of closely spaced silicon radicals, the pair being associated with two anomalously reactive oxygen atoms, although it is stressed that A summarized the properties but implies little about the geometry or structure beyond the requirement that the two silicons be closely spaced. However, nothing concrete is known about the mechanism of step II and the rearrangement which must occur in step III, and it seemed that the preparative method was unique, i.e., that surface methoxy groups were necessary in step II, the pyrolysis of surface species formed from ethanol, *n*-propanol, *i*-propanol, *n*-butanol, acetic acid, and acetyl chloride ineffective in producing RS. We have therefore carried out experiments to search for alternative methods of preparing RS in an attempt to devise such methods and to contribute to the understanding of step II.

EXPERIMENTAL METHODS

If vacuum techniques are employed in preparing RS by steps I, II, and III or in attempting to prepare RS with some reagent other than methanol, the procedures are tedious and time-consuming. As numerous compounds were to be tested, the experiments were simplified by employing a flow system. Also, the tests were further simplified by adopting the criterion that a test was "successful" if the interaction of silica and some reagent led to the formation of surface $=SiH_2$ groups, this being based on the prior observations that if $=SiH_2$ groups were produced, then RS would be formed via reaction III. The time-consuming degassing step and then subjecting the degassed adsorbent to an activity test, e.g., exposing it to H_2 or NH_3, were thus avoided.

The method was basically a simple one: a stream of inert gas was passed over the adsorbent at atmospheric pressure; a reagent was introduced to the gas stream and swept over the silica, causing the surface to be altered, and the changes were monitored by means of infrared spectroscopic measurements. The arrangement used is shown schematically in Fig. 1. A stream of N_2 passed through a Dryerite tube and a liquid N_2-colled trap, D, and was then split. One stream at ~50 ml/min was always passed between the cell windows in order to keep them cool and to prevent contamination. The main gas stream at ~50–100 ml/min was either passed directly to the cell, or, by means of Teflon stopcocks, T, was directed through a bubbler submerged in liquid reagent. Alternatively, the main stream could be diverted by the solenoid valves, S, to flow through the tube of known volume, L, thus introducing the reagent gas within L into the main stream. The effluent from the cell passed through a rotameter, R, and a cooled trap, C. The reagents, usually research-grade materials obtained from various commercial suppliers, were dried with Dryerite; N_2 was bubbled through the liquids to remove dissolved gas. Pyrex, copper, and Teflon-lined tubing was used. The vessel containing reagent and the tubing leading to the cell, as well as the

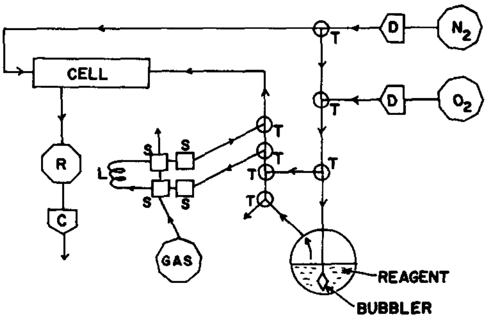


FIG. 1. Flow system.

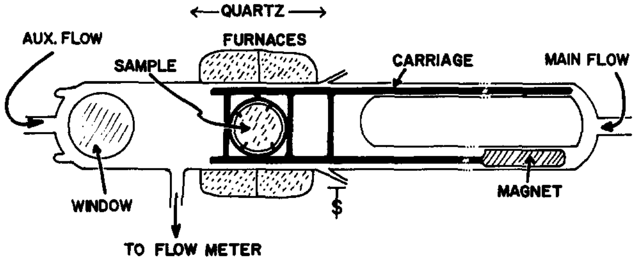


FIG. 2. Infrared cell.

cell itself, were wrapped with heating tape or resistance wire and could be heated. The entire apparatus was mounted on a cart so that the cell could be positioned within the sample section of the spectrometer. Some details of the cell are shown in Fig. 2.

A sample wafer, prepared by compressing ~90 mg of Cab-O-Sil (9) silica into a 1-in. diameter disc at ~10 tons/in.^{2}, was held to a quartz carriage by prongs and Pt wire. A magnet was used to move the carriage so that the sample could be positioned between the NaCl windows for recording spectra or be within the furnace region. Spectra were recorded with a Perkin-Elmer Model 421 spectrophotometer. Wire screens were used in the reference beam to compensate for sample absorption, and ordinate scale expansion was used when appropriate.

Typical operations were as follows. After a sample disc had been installed, a ~50 ml/min N_2 stream was passed between the windows and a ~100 ml/min O_2 stream was passed over the sample at 800°C for 5–10 min in order to burn off the usual carbonaceous impurities found on finely divided silicas and also to dehydroxylate the sample. The O_2 was then replaced by N_2 and, after the system had been flushed for 5–10 min, the furnace temperature was reduced, the sample was moved between the windows, and a "background" spectrum was recorded with the sample at or near room temperature. (Trace A of Fig. 3 is an example of a background spectrum. The 3750 cm^{-1}

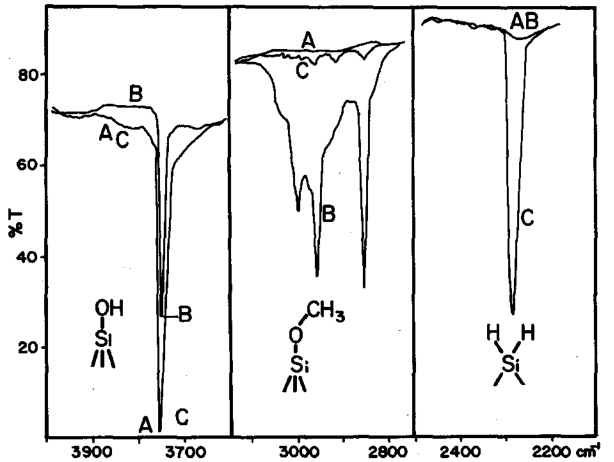


FIG. 3. Methoxylation at low temperature: (A) background spectrum of silica samples after treatment with O_2 and N_2 at 800°C; (B) after exposure to methanol vapor at 400°C for 12 min; (C) after heating in flowing N_2 at 800°C for 5 min.

band of "free" silanols is well defined, and the spectrum is much like the spectrum of a highly degassed silica.) The sample was then returned to the furnace region and kept at an appropriate temperature. The main N_2 stream was passed through the reagent for times ranging from several seconds to many minutes (or through the tube L) so that the sample was exposed to the reagent vapors. The reagent vessel was bypassed, N_2 continued to flow in order to flush the system and, after 5–15 min, the sample was moved out of the furnace region and a spectrum was recorded. The exposure to the reagent-laden N_2 stream, or to pure N_2, was repeated, the exposure times and temperatures being changed as needed.

Three variations of the flow method were examined. In the first, stepwise procedure, the sample was exposed to reagent at successively increasing temperatures (at most, up to 600°C) and/or for increasing exposure times, until surface species had formed to an appreciable extent as judged from the intensities of their absorption bands. The altered sample would then be heated in N_2 at high temperatures in order to pyrolize the surface layer. An example is shown in Fig. 3. In the second procedure the sample would be exposed to reagent at successively increasing temperatures until 800–850°C had been reached. In the third procedure, the sample would be exposed to reagent only at the highest temperatures, e.g., 750 or 800°C; an example of the results is shown in Fig. 4. At the high temperatures the second and third methods are essentially alike in that both chemisorption of reagent and decomposition of adsorbed species occur together; in addition, the reagent may cause the adsorbed species to alter, thermally decomposed reagent may react with the surface, and so on. Although it was possible to produce $=SiH_2$ bands using methanol or methyl esters with the second and third methods, the results were erratic and prompted the exclusive use of the stepwise procedure for the activity tests.

RESULTS

The overall test results are summarized in Table 1. Many details need not be described. However, the following observations are pertinent.

Methanol. Extensive methoxylation occurred when samples were exposed to methanol vapor at relatively low temperatures. An example is shown in Fig. 3:

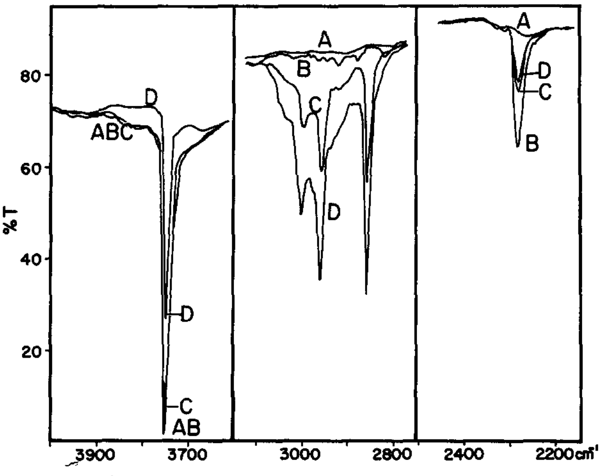


FIG. 4. Simultaneous methoxylation–pyrolysis: (A) background spectrum of silica sample after treatment with O_2 and N_2 at 800°C. (B) after exposure to methanol vapor at 800°C for 2 min; (C) after exposure to methanol vapor at 400°C for 2 min; (D) after exposure to methanol vapor at 400°C for 12 min.

TABLE 1
SUMMARY OF TEST RESULTS

Reactive: The compound was chemisorbed, and pyrolysis of the adsorbed layer led to the formation of $=\mathrm{SiH_2}$ groups

Methanol
Methyl acetate
Methyl propionate
Methyl butyrate
Trimethoxymethane
1,2-Dimethoxyethane
2,2-Dimethoxypropane
2-Methoxyethanol
2(2-Methoxyethoxy)ethanol
α-hydroxytoluene

Unsuccessful: The compound was chemisorbed, but no $=\mathrm{SiH_2}$ groups were formed on pyrolysis

Ethanol
n-Propanol
i-Propanol
n-Butanol
i-Butanol
3-Butene-ol
2,2,2-Trifluoroethanol
Benzyl chloride
Ethyl acetoacetate
Ethyl acetate
Propyl acetate
Butyl acetate
Allyl acetate
Acetic acid
Acetaldehyde
Paraformaldehyde
Acetyl chloride

Unreactive: Chemisorbed species were not detected

Dimethyl ether
Methyl ethyl ketone
Acetone
2,2-Dimethyl-1-propanol
3,3-Dimethyl-1-butanol
Methyl bromide
Cyclopropane
Phenethyl alcohol

the $\equiv\mathrm{Si{-}OH}$ band declined and $\equiv\mathrm{Si{-}OCH_3}$ bands appeared, i.e., reaction I occurred. Then, upon heating in N_2 at high temperature, the $\equiv\mathrm{Si{-}OH}$ band increased, the $\equiv\mathrm{Si{-}OCH_3}$ bands decreased, and an intense $=\mathrm{SiH_2}$ band formed near 2300 $\mathrm{cm^{-1}}$ (C, Fig. 3), i.e., reaction II occurred. The results obtained with the flow system were thus the same, and achieved more easily, than those obtained using vacuum techniques (*1–8*).

Similar results were obtained on exposing silica to methanol at very high temperatures (A, B, Fig. 4), but there were no simple relations between the intensities of the $=\mathrm{SiH_2}$ bands obtained and the severity of the methanol treatments, and the $=\mathrm{SiH_2}$ band intensities were always relatively weak. Tests showed that if a sample which had been treated with methanol at high temperature (B, Fig. 4) was exposed to methanol at a temperature low enough so that additional $=\mathrm{SiH_2}$ groups could not form, the intensity of the $=\mathrm{SiH_2}$ band declined (C, D, Fig. 4), suggesting that the methanol destroyed $=\mathrm{SiH_2}$ groups, in analogy to the destruction of $=\mathrm{SiH_2}$ groups by H_2O or D_2O (*3*).

Esters. All of the simple esters tested (Table 1) reacted with silica above 200°C. The C–H bands of spectra of samples treated with methyl esters were identical to those of methanol-treated with ethyl, propyl, or butyl acetate were like those of samples treated with the corresponding alcohols. The esters were thus cleaved and the alcohol moieties became chemisorbed. The reaction,

$$\mathrm{R{-}OOCR'} + \equiv\mathrm{Si{-}OH} \rightarrow \equiv\mathrm{Si{-}OR} + \mathrm{HOOCR'},$$

is probably a general one. Also, during the course of a series of experiments employing a certain sample of methyl acetate it was noticed that, as the exposure time to methyl acetate was successively increased, the C–H band intensities increased and subsequently decreased to reach an almost constant value. The presence of an acetic acid contaminant was suggested. The effect disappeared when the reagent was heated with methanol and then carefully distilled to remove excess methanol but reappeared when acetic acid was added to the purified methyl acetate, suggesting that the ester chemisorption was reversible, in direct analogy to the cleavage of bulk esters.

If the moiety R is CH_3, then surface $\equiv$Si—OCH_3 groups result, so that the subsequent pyrolysis should be like that found with methanol-treated samples. The results obtained with the methyl esters were, in effect, precisely like those obtained with methanol, e.g., the traces of Fig. 3 could very well be re-labeled and used to illustrate the results obtained with methyl acetate.

Pyrolyses of the surface layers of samples treated with esters other than methyl esters were like the pyrolyses of samples treated with the simple alcohols other than methanol: the bands caused by the surface species declined, the $=SiH_2$ bands were not detected.

Methoxy-containing compounds. The five methoxy-containing reagents listed as Reactive in Table 1 fall into two groups. Trimethoxypropane was readily chemisorbed above 200°C. Spectra illustrating the results obtained with the most "reactive" compound, trimethoxymethane, are shown in Fig. 5. When the silica was exposed to the compound, the $\equiv$Si—OH band declined substantially, and the bands formed in the C–H region match those of $\equiv$Si—OCH_3 groups; pyrolysis then resulted in the formation of $=SiH_2$ groups. The same results were obtained with the other two compounds except that the reactions were not as extensive, some $\equiv$Si—OH groups remaining on the surface. The results suggest that a reaction occurred:

$$\equiv\text{Si—OH} + R(OCH_3)_n \rightarrow \equiv\text{Si—OCH}_3 + R(OH)(OCH_3)_{n-1}.$$

Somewhat different results were obtained with 2-methoxyethanol and 2(2-methoxyethoxy)ethanol. Temperatures near 400°C were needed to chemisorb significant amounts of material and the C–H bands of the chemisorbed species were complex and quite different than absorbed methoxyl. The structure of the surface species is uncertain; probably the alcohol OH group reacted with the silanol, as with other alcohols, to produce a silyl ester. The C–H band patterns changed, and the C–H band intensities declined upon heating the samples in N_2, and at 600°C became like the band pattern of $\equiv$Si—OCH_3 groups. Further heating almost eliminated those bands and only relatively weak $=SiH_2$ bands were formed.

Aromatics. There was extensive reaction when benzyl chloride vapor was passed over silica at 495°C for 1 hr; the

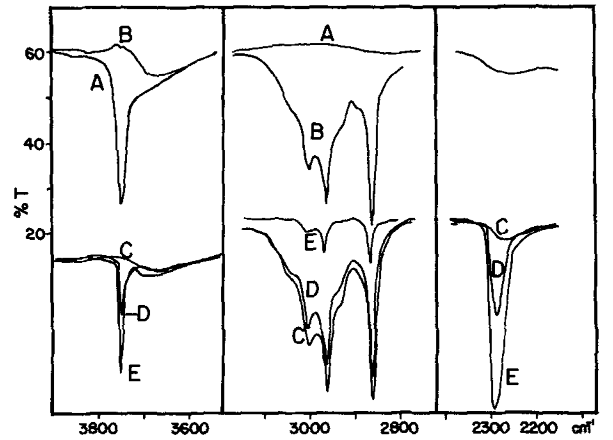


FIG. 5. Silica–trimethoxymethane: (A) background spectrum of silica sample after treatment with O_2 and N_2 at 800°C; (B) after exposure to trimethoxymethane vapor at 270°C for 10 min; (C) after exposure to trimethoxymethane vapor at 380°C for 5 min; subsequent heating in flowing N_2 at 380, 505 and 590°C had no effect. (D) after heating in flowing N_2 at 690°C for 5 min; (E) after heating in flowing N_2 at 800°C for 5 min. The ordinates of spectra C, D and E are displaced.

$\equiv$Si—OH band had almost disappeared and a fairly intense group of bands appeared in the C–H region. Also, the sample became quite dark, showing that carbonization had occurred. When the sample was then heated in N_2 at 598, 680, and 800°C, the C–H bands declined, the $\equiv$Si—OH band was re-formed, and the sample pellet turned progressively darker, indicating that the surface became "coked." The $=SiH_2$ band was not detected.

C–H bands of substantial intensities were formed when phenethyl alcohol vapor was passed over silica for 10 hr at 305°C. However, the $\equiv$Si—OH band declined only slightly, a broad band formed at 3640 cm^{-1} ascribed to the alcohol, and all bands of adsorbed species were removed on heating the sample in N_2 at 495°C for 7 min. It seems probable that most of the reagent had not been chemisorbed under the conditions employed.

A group of relatively weak C–H bands appeared when silica was treated with α-hydroxytoluene (benzyl alcohol) at 310°C, and the sample pellet darkened, i.e., some of the adsorbed species carbonized, so that more severe reaction conditions could not be employed. The C–H bands declined upon heating the sample at 695°C. At 825°C the bands disappeared and a weak SiH_2 band was formed. The results indicate that chemisorption had occurred to a slight extent, the pyrolysis of the adsorbed species then leading to the formation of $=SiH_2$ groups.

DISCUSSION

The choice of reagents was initially based on the guess that heating the methoxylated surface (reaction II) caused the entire methoxy group to desorb, perhaps as a radical, thus tearing an oxygen atom out of the surface; the nonstoichiometric surface region would then rearrange and react with desorbed material. A similar mechanism might be expected with other surface species. Tests employing obvious, simple reagents failed, however, and it seemed that $\equiv$Si—OR groups would not decompose in the "proper" fashion if the R group contained more than one carbon. It was then supposed that the desired result might be achieved if the R group might fragment to yield $\equiv$Si—O—$OH_2\cdot$ or $\equiv$Si—O—CH_n, which might then undergo reaction II. Additional negative results seemed to confirm that only $\equiv$Si—O—CH_3 would pyrolize in the required manner, but also led to the observation that the reagents which became chemisorbed but did not lead to the formation of silane all had β hydrogens, and this generality was partly supported by the observation that silanes could be generated by the pyrolysis of chemisorbed benzyl alcohol. However, in order to derive some reasonable understanding of the results summarized in Table 1 it is necessary to consider the chemisorption and pyrolysis steps in some detail, and it is useful to do so by employing some of the well-known and well-understood concepts of mechanistic organic chemistry (*10*).

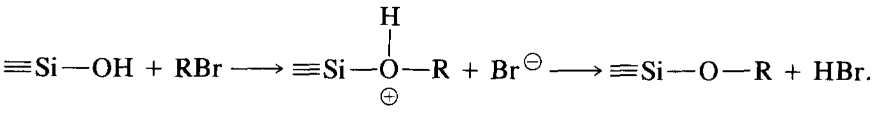
Chemisorption Reactions and Mechanisms

Methanol can react to some extent with siloxane bridges, resulting in the formation of methoxy groups and silanols (*11,12*), and other alcohols probably are able to react in a similar fashion. The silanols generated in this manner would then be subject to further attack by the alcohol. Hockey (*13*) has also pointed out that hydrogen sequestering reagents may attack siloxane bridges. However, the chemisorptions of "reactive" and "unsuccessful" reagents of Table 1 were accompanied by decreases of the silanols. Consequently, the dominant chemisorption mechanism is considered to involve a chemical reaction between the reagent molecule and the surface silanol group.

That cyclopropane was not chemisorbed

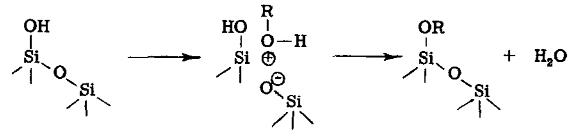
is not surprising; a hydrocarbon would, perhaps, be expected to be inert, although cyclopropane is reactive toward strong acids at low temperatures and is also known to cleave to a diradical at high temperatures (*14*). Acetone and 2-butanone, also not chemisorbed, might form ketal groups with the surface silanols, but these groups are very labile and would be easily removed under the conditions employed. Although almost all the alcohols tested were chemisorbed, the exceptions (neopentyl alcohol and 3,3-dimethyl-1-butanol) are both very bulky and steric hindrance of the methyl groups in each probably prevented the alkylation of the surface; 2-phenylethanol may also fit into this class. Table 1 reveals that all methoxy-containing compounds were chemisorbed, with the exception of methyl ether. The latter is the least reactive, or most chemically inert, of all the methoxyl compounds.

It seems likely that a weak interaction with the silanol is a necessary prior step to chemisorption. In that light it is not surprising that methyl bromide was also not chemisorbed; this compound should be a most reactive methoxylating agent if displacement by ≡Si—OH were the methoxylation mechanism,



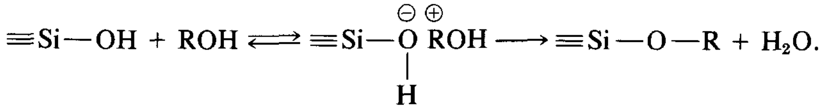
$$\equiv\text{Si—OH} + \text{RBr} \longrightarrow \equiv\text{Si—}\underset{\oplus}{\overset{\overset{\text{H}}{|}}{\text{O}}}\text{—R} + \text{Br}^{\ominus} \longrightarrow \equiv\text{Si—O—R} + \text{HBr}. \qquad \text{IV}$$

On the other hand methyl bromide may dissociate into radicals at the temperatures employed in a completely different reaction than available to the other compounds. The general mechanism may thus involve not displacement by ≡Si—OH on the alkyl carbon of the reacting species as in IV, but addition of alkoxyl oxygen to silicon,



V

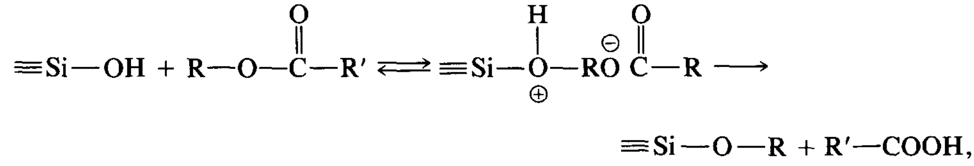
That mechanism, at least for the reactions with alcohols, is more likely than a direct displacement of hydroxyl, which is not favorable. On the other hand, an initial hydrogen bonding process may lead to a surface-stabilized ion pair (the surface playing the role of solvent in stabilizing the ion pairs) which might readily suffer direct replacement:



$$\equiv\text{Si—OH} + \text{ROH} \rightleftharpoons \equiv\text{Si—}\underset{\underset{\text{H}}{|}}{\overset{\ominus}{\text{O}}}\,\overset{\oplus}{\text{ROH}} \longrightarrow \equiv\text{Si—O—R} + \text{H}_2\text{O}. \qquad \text{VI}$$

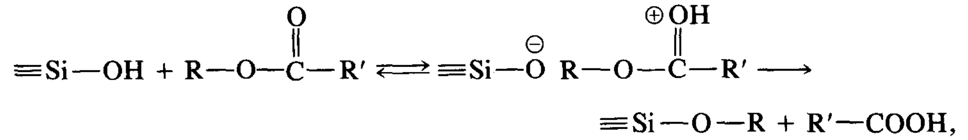
That also seems to account for the differences in reactivity of methyl bromide, benzyl chloride, and the alcohols in general, and is the most likely general mechanism for most of the chemisorptions. Presumably all the alcohols studied were chemisorbed in that manner to form silyl ethers.

For the dissociative chemisorption of the esters, which led to surface alkoxyl formation, either mechanism VII (displacement by hydroxyl on alkyl carbon with loss of a stable carboxylate leaving group) or mechanism VIII (prior hydrogen bonding followed by loss of carboxylic acid leaving group) may apply. Displacement of silanol,



$$\equiv\mathrm{Si{-}OH} + \mathrm{R{-}O{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}R'} \rightleftharpoons \equiv\mathrm{Si{-}}\underset{\oplus}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{O}}}\mathrm{{-}RO}\;\overset{\ominus}{}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}R} \longrightarrow \equiv\mathrm{Si{-}O{-}R} + \mathrm{R'{-}COOH},$$

VII

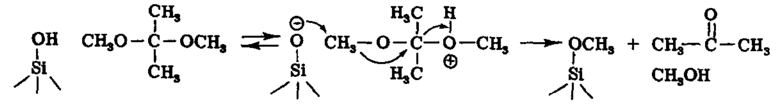


$$\equiv\mathrm{Si{-}OH} + \mathrm{R{-}O{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}R'} \rightleftharpoons \equiv\mathrm{Si{-}}\overset{\ominus}{\mathrm{O}}\;\mathrm{R{-}O{-}}\overset{\overset{\oplus\mathrm{OH}}{\|}}{\mathrm{C}}\mathrm{{-}R'} \longrightarrow \equiv\mathrm{Si{-}O{-}R} + \mathrm{R'{-}COOH},$$

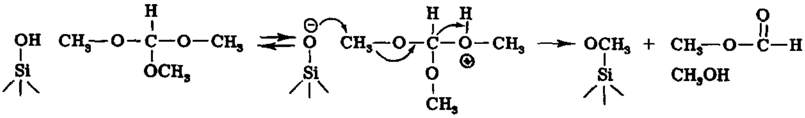
VIII

on the ester (VII or VIII) seems more likely than addition to silicon as in V, considering the steric bulk of the ester and the ease of displacement of the carboxylate groups.

The spectral data for the other alcohols, 2-methoxyethanol and 2-methoxyethyl-2-hydroxyethyl ether, suggest that silyl ethers were formed, as with the other alcohols. Each of the remaining compounds studied contained methoxy groups, but the reactivity increased from 1,2-dimethoxyethane (an ether) to 2,2-dimethoxypropane (a ketal) to trimethoxymethane (trimethylorthoformate), the orthoformate being more reactive than methanol itself. Such reactivity seems unusual, recalling that methyl ether was not reactive although it has been found to form fairly strong bonding to silanols (*15*).

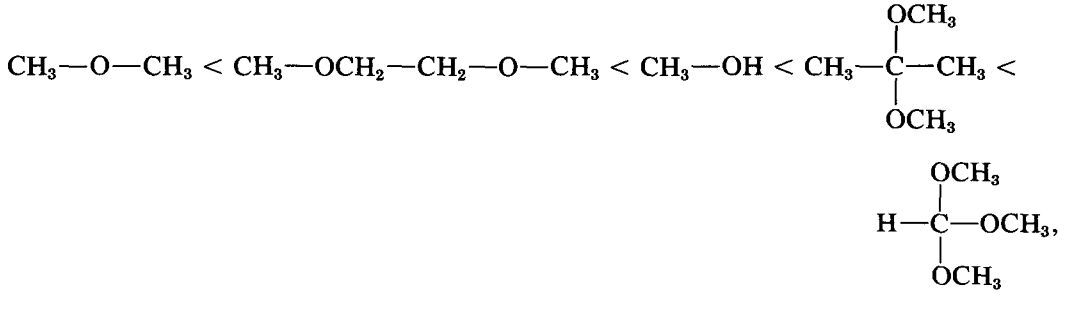


IX



X

Ketal and orthoester are both easily cleaved by mild acid and might be cleaved on the surface silanol to methanol and the corresponding ketone or formate. However, that does not explain why they were more reactive than methanol itself. An alternative explanation would include initial hydrogen bonding resulting in ion pair formation, displacement on the carbon atom of the methoxyl group releasing the neutral leaving group acetone or methanol in IX and methyl formate in X. An order of reactivity as observed can now be understood in terms of the leaving group acidity in a protonated ion pair:



$$\mathrm{CH_3{-}O{-}CH_3} < \mathrm{CH_3{-}OCH_2{-}CH_2{-}O{-}CH_3} < \mathrm{CH_3{-}OH} < \mathrm{CH_3{-}}\underset{\underset{\mathrm{OCH_3}}{|}}{\overset{\overset{\mathrm{OCH_3}}{|}}{\mathrm{C}}}\mathrm{{-}CH_3} < \mathrm{H{-}}\underset{\underset{\mathrm{OCH_3}}{|}}{\overset{\overset{\mathrm{OCH_3}}{|}}{\mathrm{C}}}\mathrm{{-}OCH_3},$$

which parallels also the known reactivity of acid-catalyzed cleavage in solution of ether < alcohol < ketal < orthoester. The mechanisms VI, VIII, IX and X provide a general mechanism for surface alkoxylation consistent with known reactivity patterns.

An alternative mechanism can be proposed which involves surface radical reactions,

$$R\cdot + \equiv\text{Si—OH} \rightarrow \equiv\text{Si—O}\cdot + RH,$$

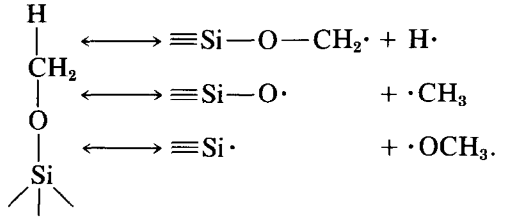
$$\equiv\text{Si—O}\cdot + CH_3\text{—OR} \rightarrow \equiv\text{Si—O—}CH_3 + \cdot OR.$$

It is conceivable that, at the high temperatures employed, radicals might be formed at the surface which would generate a siloxy radical. The latter, however, would then have to undergo a radical displacement reaction on carbon, a type of reaction which has not yet been demonstrated (*17*). This mechanistic type would also not account for the observed pattern of activity of different methoxyl-containing compounds, as is so nicely accommodated by a surface ion pair displacement mechanism.

Silyl Ether Cleavage—Step II

Most of the surface species formed were silyl alkyl ethers, but only a few of them were "reactive" in that their pyrolysis led to silane and silanol formation; and of those few, only those that led to the formation of silyl methyl ether were reactive, with the exception of chemisorbed benzyl alcohol. The pyrolysis of other species led only to the regeneration of silanols. The situation is complex, but it is possible to suggest the probable initial step of the silyl methyl ether decomposition and to provide an explanation for the uniqueness of the surface methoxy group in effecting step II.

Step II can occur with fully methoxylated surfaces and in the absence of reagents (except the desorption products). Apparently, for the pyrolysis reagents other than surface methoxyls are not needed and only high temperature is required. The circumstances strongly suggest that the initial reaction is probably a radical decomposition of the surface methoxy group. Three bonds are available for thermally induced homolytic decomposition:



$$\longleftrightarrow \equiv\text{Si—O—}CH_2\cdot + H\cdot \qquad \text{XI}$$

$$\longleftrightarrow \equiv\text{Si—O}\cdot + \cdot CH_3 \qquad \text{XII}$$

$$\longleftrightarrow \equiv\text{Si}\cdot + \cdot OCH_3. \qquad \text{XIII}$$

From tables of bond dissociation energies (BDE) (*16*), the Si–O bond in silica has a BDE of 114 kcal/mole (reaction XIII), while the C–O bond BDE in methyl ether is only 77 kcal/mole (90 kcal/mole for CH_3OH). These data alone suggest that process XII would be strongly favored over process XIII for such a unimolecular thermal decomposition. No data are available for reaction XI, although the BDE for methane is 104 kcal/mole. Indeed, reactions such as XI are not normally observed in unimolecular decompositions because other bonds are normally much weaker (e.g., C–C alkyl bonds have BDE of 85–88 kcal/mole) and molecules decompose normally by skeletal bond cleavage. Data that are available for hydrogen abstraction by methyl or phenyl radicals or relative oxidizabilities of hydrocarbon (C–H) groups (*17*) indicate an appreciably higher activation energy for the abstraction of hydrogen from an R–O–CH_3 group than for alkanes. This would suggest that the BDE for Si–O–CH_2H is higher than for methane or alkanes in general, providing that the reactions are endothermic and the Hammond postulate obtains (*18*). Thus reaction XII, the homolytic cleavage of the oxygen–alkyl bond, is favored in a unimolecular process over XI, also. A bimolecular process XIV is not considered plausible because the silanol groups of the silica can be exhaustively replaced by methoxy groups and no other adsorbed species are present when the pyrolysis occurs.

$$\equiv\mathrm{Si{-}OCH_3} + \cdot\mathrm{R} \rightarrow \equiv\mathrm{Si{-}OCH_2\cdot} + \mathrm{RH}. \quad \mathrm{XIV}$$

Similarly, bimolecular displacement processes such as XV and XVI on carbon and oxygen atoms are not considered. In addition, it may be inferred that

$$\equiv\mathrm{Si{-}OCH_3} + \cdot\mathrm{R} \rightarrow \equiv\mathrm{Si{-}O\cdot} + \mathrm{RCH_3}, \quad \mathrm{XV}$$

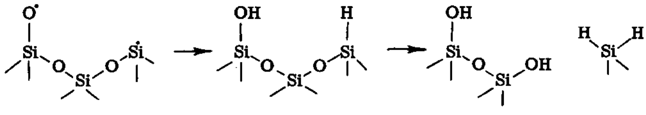
$$\equiv\mathrm{Si{-}OCH_3} + \cdot\mathrm{R} \quad \equiv\mathrm{Si\cdot} + \mathrm{ROCH_3}; \quad \mathrm{XVI}$$

these are less likely than reaction XI; they are commonly not seen (indeed, are rare or without precedent) and the energetic implication is that they would have higher activation energy than XI (*19*).

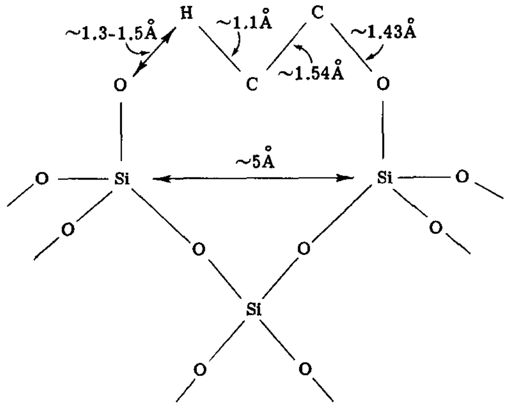
If these assumptions are correct, it would appear that the most probable initial step for reaction II is the unimolecular cleavage of the alkyl–oxygen bond, reaction XII, yielding a surface siloxy radical. Possibly, the formation of a siloxy radical would weaken the silicon–oxygen linkage of a neighboring methoxy group, so that the second step may be the formation of a paired radical, B, which would react with desorbed material to yield species C, which would react further through initial decomposition and hydrogen abstraction from desorbed material to result in species D. The latter would be the precursor of the RS dual center A.

If the best pathway available for methoxy group disruption is the formation of a siloxy radical, the same pathway should be available for the disruption of other silyl alkyl ethers, and may be even easier because of lower activation energies and BDE, so that siloxy radicals should be formed. However, silanes were not formed, i.e., the secondary reactions which occurred with the methyl ether did not occur with other alkyl ethers. Or, put in other words, there were other reactions which could occur with alkyl groups which could not occur with the methyl; methyl had no other pathway available to it and could do nothing else but sequentially decompose and cause the formation of species such as B, C, and D. The probable location of the adsorbed species on the silica surface suggests an answer.

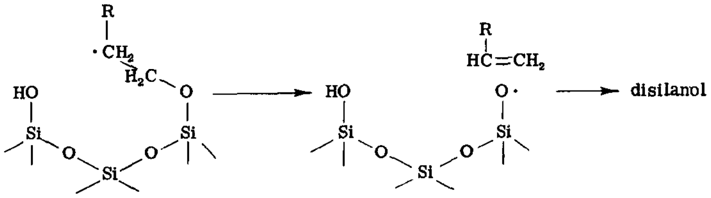
For high index planes (*20*), the silica surface is much like that shown schematically for structure E, i.e., the outermost silicon atoms are about 5 Å apart and there is a silicon atom in a "valley" between them. If a siloxy radical forms at one of the outermost silicons and a methoxy group is bonded to the other, the distance between the methyl hydrogen and the siloxy oxygen is 2.6–2.8 Å; the methyl group is too far away from the radical center to react with it. However, when the methyl group is replaced by an alkoxy group, then β hydrogens or other groups may now lie within bonding distance of the oxy-radical site and hydrogen abstraction may readily occur. If this happens in the high temperature reactions, then the initial siloxy radical site is destroyed, and silanol is regenerated. An alkyl radical would be formed β to an oxygen; fragmentation may occur easily with loss of an alkene, regenerating a new siloxy radical which may abstract hydrogen from desorbed material or



B C D

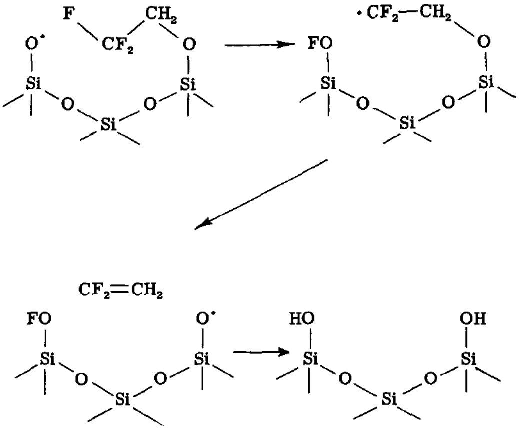


E

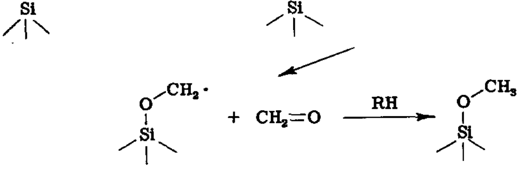


react with still another nearby alkoxylated site until termination occurs. Silanols are thus regenerated.

The reagents 2,4-dimethyl-1-propanol (neopentyl alcohol) and 3,3-dimethyl-1-butanol were chosen as potential substrates to prevent β-hydrogen abstraction because either abstraction would be too hindered and/or could not lead to fragmentation. Other species chosen were those that might have alkyl groups which would preferably cleave to loose benzyl·, allyl·, or $CH_3\cdot$, resulting in $\equiv Si-O-CH_2\cdot$ as an intermediate which would then potentially give rise to silane. None of these groups gave rise to silane, indicating that the fragmentation was competitively easier or that $\equiv Si-O-CH_2\cdot$ was not a reactive intermediate leading to silane, the former reason being the more likely. In the case of trifluoroethanol, however, this would mean that β-F was abstracted, giving a "hypofluorite," which would regenerate silanol.



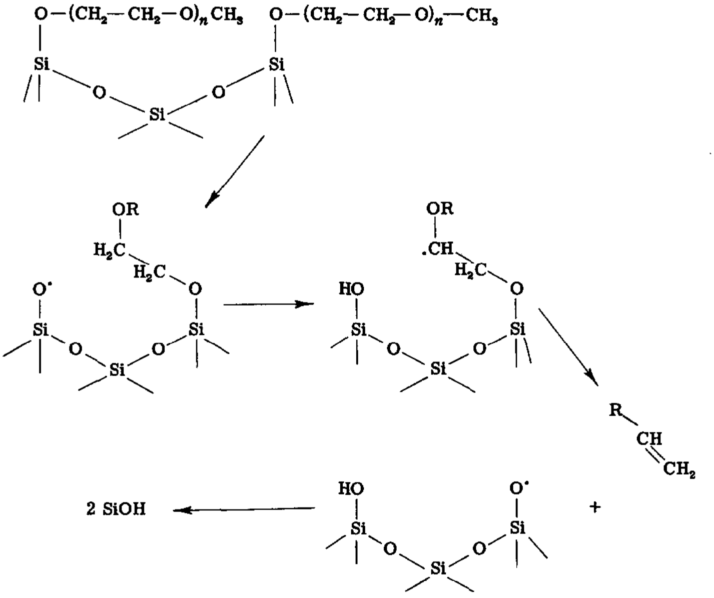
The surface alkylated species obtained from 2-methoxyethanol and CH_3OCH_2-$CH_2-O-CH_2CHC_2H_2-OH$ gave small amounts of silane, indicating either that the surface alkylation was mixed, giving both $\equiv Si-O-CH_3$ as (with other ethers) and $\equiv Si-O-(CH_2-CH_2-O)_n-CH_3$ or that the latter could decompose to give $\equiv Si-O-CH_3$ by a process similar to the initial cleavage of an R—O·CH_3 bond,



and generating ≡Si—OCH_3 eventually from desorbed material reacting with ≡Si—O—CH_2· thus generated.

In any event, decomposition could also regenerate initial silanol as with other alkyl groups, and this is the major observed product.

The formation of silane from benzyl silyl ether is more complicated but can also be explained by a similar mechanism.



ACKNOWLEDGMENT

Support by grant No. 7019-AC5 from the Petroleum Research Fund of the American Chemical Society and grant No. GP-43717 from the National Science Foundation is gratefully acknowledged.

REFERENCES

1. Morterra, C., and Low, M. J. D., *Chem. Commun.* **1968,** 203.
2. Morterra, C., and Low, M. J. D., *J. Phys. Chem.* **73,** 321 (1969).
3. Morterra, C., and Low, M. J. D., *J. Phys. Chem.* **73,** 327 (1969).
4. Morterra, C., and Low, M. J. D., *J. Phys. Chem.* **74,** 1297 (1970).
5. Low, M. J. D., Shimizu, M., and McManus, J. C., *Chem. Commun.* **1971,** 579.
6. Morterra, C., and Low, M. J. D., *J. Catal.* **28,** 265 (1973).
7. Morterra, C., and Low, M. J. D., *Ann. N.Y. Acad. Sci.* **220,** 133 (1973).
8. Low, M. J. D., *J. Catal.* **32,** 103 (1974).
9. G. Cabot Co., Cambridge, Mass.
10. le Noble, W. J., "Highlights of Organic Chemistry." Dekker, New York, 1974; Hirsch, J. A., "Concepts in Theoretical Organic Chemistry." Allyn and Bacon, Boston, 1974.
11. Borello, E., Zecchina, A., and Morterra, C., *J. Phys. Chem.* **71,** 2938 (1967).
12. Low, M. J. D., and Harano, Y., *J. Res. Inst. Catal., Hokkaido Univ.* **16,** 271 (1968).
13. Hockey, J. A., *J. Phys. Chem.* **74,** 2570 (1970).
14. Saunders, M., Vogel, P., Hagen, E. L., and Rosenfeld, J., *Accounts Chem. Res.* **6,** 53 (1973).
15. Little, L. H., "Infrared Spectra of Adsorbed Species." Academic Press, New York, 1966.
16. Walling, C., "Free Radicals in Solution," p. 48. Wiley, New York, 1957.
17. Pryor, W. A., "Free Radicals," pp. 161, 169. McGraw-Hill, New York, 1966.
18. Hammond, G. S., *J. Amer. Chem. Soc.* **77,** 334 (1955).
19. Pryor, W. A., *J. Amer. Chem. Soc.* **77,** 152 (1955).
20. Wells, A. F., "Structural Inorganic Chemistry." Oxford Univ. Press, 1962.