

Reactive Silica

XVII. The Nature of the Reaction Center¹

All of the various experimental data concerning the properties of reactive silica (RS) were reexamined and reevaluated. The assignments of two bands of surface silane species appearing in infrared spectra of RS were found to be wrong and had to be revised. Although none of the assignments of other bands of surface species were affected, this revision, along with certain unsatisfactory features concerning the activation mechanism and RS reactivity, made the model of the RS center untenable. That center was a dual one, incorporating two spatially separated silicons, each of which acted as a reaction site. The reaction site now proposed is also a dual one, as demanded by the various data, but is a single silicon which acts as the dual site. The entire RS center consists of two 6-membered rings, each consisting of three siloxane bridges, joined at and incorporating the dual-site silicon. The latter is in octahedral rather than the usual tetrahedral configuration. The new model is consistent with all experimental observations concerning the formation and reactions of RS. © 1987 Academic Press, Inc.

INTRODUCTION

There is now extensive work (*1*) showing that ordinary silica can be transformed into an extremely active adsorbent, termed "reactive silica" (RS). Its "activity" has been ascribed to the presence of special reaction centers having the properties indicated schematically by **I** of Fig. 1. However, **I** has never been entirely satisfactory. It correctly describes the properties of the center and is a convenient mechanistic device but, as stated in previous papers, implies little about the geometry. Objections to **I** include the following.

(a) The recent intense interest in amorphous hydrogenated silicon, which is photovoltaic and contains various silane groups, has prompted infrared studies which indicate with certainty that the wavenumbers for silane bands fall in the order:



Consequently, the original assignments of the 2300-cm⁻¹ silane band observed with RS to =SiH₂ groups, and the 2226-cm⁻¹ si-

lane band to ≡Si-H groups, as shown in Fig. 1, are wrong (2-10) and must be changed. The RS center **I** is untenable.

(b) There are several reversible chemisorptions similar to reaction A in which simple molecules form structures such as that on the left of Fig. 1 containing both an Si-H and an Si-NH₂ group; i.e., a hydrogen is abstracted from the adsorbate forming a Si-H group on one of the sites and the residue R forming a Si-R group on the other site. These are summarized in Table 1. The Si-H groups formed in this way are structurally identical but absorb at various frequencies and, to account for this, it was necessary to invoke some kind of long-range effect of Si-R group on the Si-H group. This is unsatisfactory.

(c) The location and bonding of the two oxygens associated with the center are uncertain and the Si-O-O-Si linkage as drawn in **I** implies a peroxy bridge. That had never been initially intended; the choice of that schematic representation was an unfortunate one.

(d) The destruction of the center in reaction C without the participation of additional silicons would lead to geminal hydroxyls. The existence of these is unlikely

¹ See Ref. (*1*) for Part XVI.

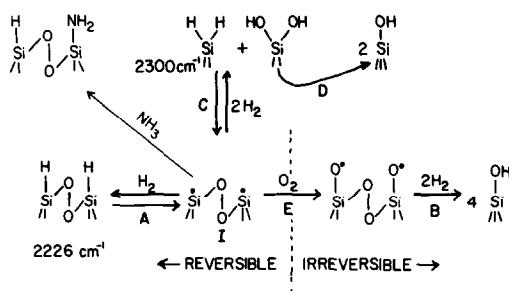


FIG. 1. Formation of RS and some reactions.

at the high temperature at which the reaction is carried out, so that another step D in which $\equiv\text{Si}-\text{OH}$ groups are formed has to be introduced. The mechanism for step D is vague.

(e) The center I contains only two silicons but three are required for reactions C plus D, and four silicons are needed for reaction B, a mechanistically explainable but still unsatisfactory condition.

(f) It is difficult to employ the accepted mechanistic concepts of conventional organic chemistry to "explain" many of the reactions RS undergoes with organic adsorbates. In order to do so it is necessary to devise complex mechanisms incorporating unusual intermediates and steps whose existence at times seems unrealistic. These difficulties became particularly apparent when considering the reactions of RS with relatively stable molecules such as methane, benzene, cyclohexane, and toluene (I). The major difficulty is that whatever

mechanisms are devised have to involve reactions occurring at two spatially separated sites. The mechanisms become easier and more conventional and plausible if a silylene-like site is used in which a single silicon is bifunctional.

(g) The mechanism of the initial decomposition of surface methoxy groups which leads to the formation of RS is plausible, but a final step leading to the formation of SiH_2 groups is vague.

(h) It is not possible to find suitably spaced pairs of silicon atoms on normal silica lattices.

These objections, particularly (a) and (b), suggest the revised mechanism outlined in Figs. 2 and 3.

SiO_2 ACTIVATION AND GENERATION OF THE RS CENTER

In practice, RS is formed when methoxylated silica is heated under vacuum or in H_2 , this leading to the formation of silane and silanol groups, followed by a degassing which removes these newly formed groups. Extensive work dealing with the pyrolysis of a variety of adsorbed organic groups is described elsewhere, as is a mechanism for the disruption of surface methoxy groups (II). The detailed data and discussion lead to the conclusion that the most likely initial step in the methoxy pyrolysis is the unimolecular cleavage of the alkyl-oxygen

TABLE I

Summary: Reaction $\text{RS} + \text{HR} \rightarrow \text{Si-R} + \text{Si-H}$

Adsorbate	Si-R group ^a	Si-H (cm ⁻¹)	Stability ratio of R [36]
Toluene	Si- \emptyset -CH ₃	2208	3.67
Toluene	Si-CH ₂ - \emptyset	2210	3.67
CH ₄	Si-CH ₃	2210	3.61
NH ₃	Si-NH ₂	2246	3.84
Cyclopropane	Si-CH=CH-CH ₃	2250	3.64*
H ₂ O	Si-OH	2266	4.30

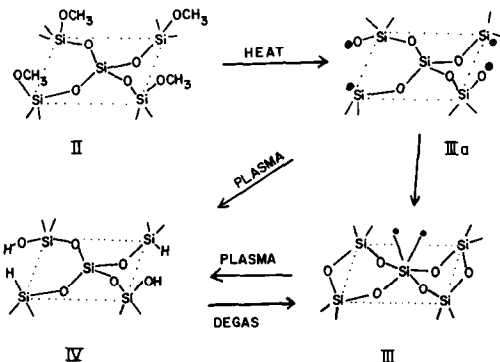
^a $\emptyset = \text{C}_6\text{H}_5$ 

FIG. 2. Formation of RS: Revised mechanism.

bond, yielding a surface siloxy radical, which would weaken the silicon–oxygen linkage of a neighboring methoxy group so that a siloxy–silicon radical pair results. This then leads to the formation of the RS center.

In view of this mechanism of formation, which is retained, it is suggested that the decomposition of two neighboring methoxy groups leads to a siloxy–silicon radical pair, which then coalesces to form a “strained siloxane bridge” much like the strained siloxane bridges which have been invoked to account for some of the properties of dehydroxylated silica (e.g., (12–14)). The decomposition of methoxy groups at a surface region of suitable geometry, such as **II** of Fig. 2, leading to two transient radical pairs, as in **IIIa**, would lead to the formation of two unstable ring systems joined by a suitably located silicon atom. That atom is induced to rehybridize to an sp^2d^3 configuration and together with the two ring sys-

tems forms the RS center **III**. The latter would abstract hydrogen from the supernatant plasma (it must be remembered that RS is formed when the sample is red-hot) resulting from the pyrolysis to form structure **IV**. An alternative path is the reaction of **III** with plasma to form **IV**. In either case, the result is a surface containing silane and silanol groups, i.e., structure **IV**. Degassing then leads to the simultaneous destruction of silane and silanol groups, as is always observed, with the reformation of the RS center **III**. Initial electron spin resonance (esr) measurements had shown that radicals were present on the RS surface, that they were quenched with O_2 , and that they were quenched with H_2 . Subsequently, detailed parallel esr and infrared measurements were carried out, using the same sample for both measurements. The course of reactions A, B, C, E, F, G, K, and J of Fig. 3, as well as the reverse of these, were followed in detail. The earlier observations were

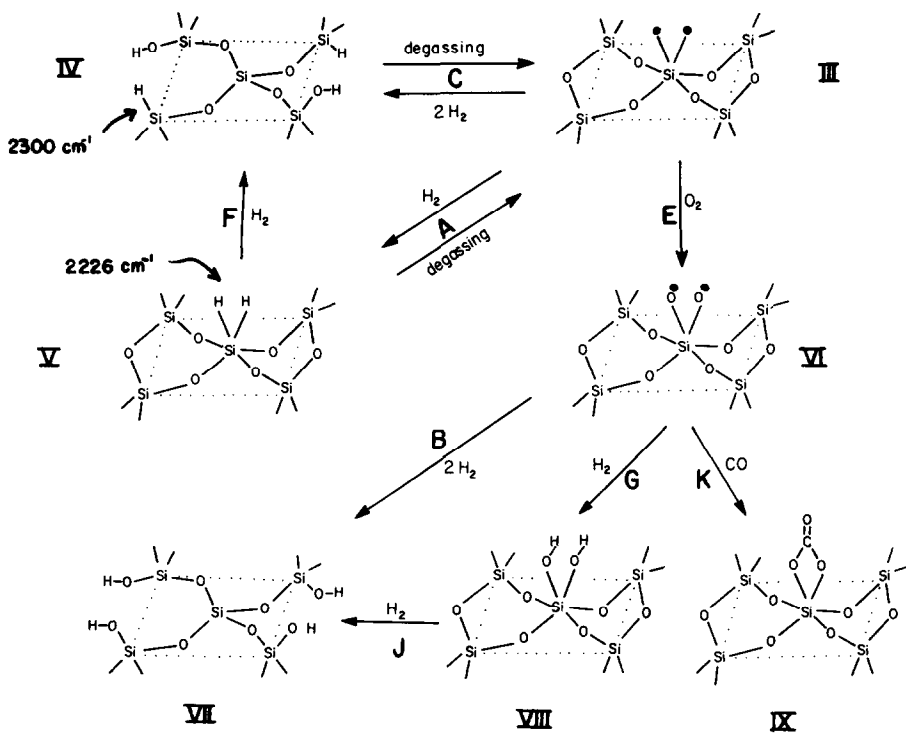


FIG. 3. Formation of RS: Revised mechanism.

qualitatively confirmed, i.e., that surface radicals were generated when RS formed and that the esr signals changed as various reactions were carried out. Unfortunately, a small amount of surface acetylide and other carbonaceous material which is probably similar to "catalytic coke" is formed on the RS during the pyrolysis of methoxy groups and the esr signals from these unknown carbonaceous species were superimposed on signals from other species so that an unequivocal interpretation of the esr spectra could not be made.

The suggested sequence of steps $\text{II} \rightarrow \text{IIIa} \rightarrow \text{III}$ and $\text{II} \rightarrow \text{IIIa} \rightarrow \text{III} \rightarrow \text{IV} \rightarrow \text{III}$ and $\text{II} \rightarrow \text{IIIa} \rightarrow \text{IV} \rightarrow \text{III}$ are in line with the experimental observations. (i) When a methoxylated silica sample is pyrolyzed in dynamic vacuum the resulting sample is not very reactive in terms of participating in reactions such as A, B, or E. The spectrum of the sample shows the presence of some (and, frequently, of many) silanol and 2300-cm^{-1} silane groups. Then, when the sample is degassed at high temperature, the silanol and silane groups disappear, and the sample becomes more reactive. (ii) When a methoxylated sample is pyrolyzed in the presence of H_2 , the resulting sample is completely inactive. The spectrum shows the presence of numerous hydroxyl and silane groups. Degassing causes the simultaneous removal of these groups and the sample becomes increasingly more reactive. RS samples prepared in this fashion are generally more reactive than those pyrolyzed under vacuum. (iii) RS samples prepared under vacuum by a relatively slow pyrolysis at the lower temperatures ($750\text{--}800^\circ\text{C}$) frequently are less reactive than those produced by a relatively rapid pyrolysis at the higher temperatures ($>850^\circ\text{C}$). In either case, if the vacuum is poor, the sample is only partly active and in some cases inactive. The implication is that secondary reactions of **IIIa** and **III** with the plasma generated during the pyrolysis cause the special geometry required for the RS center to be destroyed.

MECHANISM

Reactions A, B, C, and E (reaction D of Fig. 1 is not needed) of Fig. 3 are the same as those of Fig. 1 and correctly express the stoichiometry as required by the quantitative gas adsorption measurements, as do the additional reactions F, G, J, and K. In another reaction, which is not shown in Fig. 3, RS adsorbs O_2 and then NO; the O_2 :NO ratio is 1/2.

The 2300- and 2226-cm^{-1} silane bands are now correctly assigned to the Si-H and SiH_2 groups indicated by the arrows by structures **IV** and **V**, in line with other work (2-10). It is to be noted and stressed that no other bands of any of the numerous surface species found with RS require reassignment.

Variation of the Si-H frequency (objection (b) and Table 1) is now not caused by some hypothetical long-range effect which would have to purvey a perturbation occurring at one silicon along a chain of atoms to a Si-H group located on a second silicon. Rather, the variation can be directly attributed to the disturbance of the Si-H stretching by another atom or group bonded to the *same* silicon, the extent of the disturbances being related to the electronegativity of the second atom or group (6-10). This is a well-defined effect. For example, Smith and Angelotti (9) related the shift of the Si-H stretching band of various silane molecules to the electronegativities of the other substituents present on the silicon, and Lucovsky (2), using Sanderson's electronegativity principle (15, 16), showed the Si-H vibration of silanes as well as in *a*-Si and its *a*- SiO_2O to vary systematically with the electronegativities of the next neighbor atoms. Such Si-H shifts have also been taken up in detail by Zanzucchi (6) and also by Sacher (7, 8), who used Hammet-Taft inductive constants, and the shift of surface-bound Si-H groups by adsorbed species has been considered (17). In the present case (Table 1), the Si-H bands follow the

trend of increasing wavenumber with increasing electronegativity (the "stability ratio" is a measure of the electronegativity of the group; the number marked with an asterisk may need correction).

The previously termed anomalously reactive oxygens (objection (c)) which are demanded by some of the reactions are those of the siloxane bridges at the lateral edges of **III**. These do not take part in reversible reactions such as A, so that the integrity of the center is retained. During the irreversible reactions such as B or J those siloxane bridges are broken, and the center is disrupted. Grouping **III** contains the "proper" number of silicon atoms (objections (d), (e), (f)) and oxygen atoms; the number of atoms is compatible with the number of atoms required for the various reactions, and it is no longer necessary to invoke complicated and vague mechanisms involving siloxane linkages adjacent to the RS center and other hydroxyls in the reactions and in the formation and destruction of the center.

Grouping **III** and its precursor **II** involve what amounts to two joined rings. The number of atoms involved is rather large and their spacing is unusual. This is in line with the small number of such groupings which apparently exist and groupings **III** which can be formed. Quantitative measurements of the adsorption of H_2 and of O_2 by active RS had shown that the number of hydrogen or oxygen atoms adsorbed was approximately $0.16/100 \text{ \AA}^2$ or $0.08/100 \text{ \AA}^2$, respectively. The number of Si—H groups was estimated in another experiment by heating a hydrogenated RS sample in O_2 in order to "burn" the silane; approximately $0.3 O_2$ molecule was used per 100 \AA^2 of surface. If the surface concentration of silicon atoms is taken to be $4.6/\text{ \AA}^2$, as on a [0001] face of β -trydimite, or $4/\text{ \AA}^2$, as on a [100] face of β -cristobalite, the number of centers **III** formed is quite small, i.e., about 2% of the available surface silicon atoms.

The center retains its dual-site nature and contains not two spacially separated sili-

cons each of which acts as dual site, but only one silicon which acts as a dual site. As pointed out, this change does not make it necessary to revise any of the band assignments of the numerous surface structures which have been described. However, it does require changes in the bonding of certain surface species which are held to the RS center by two bonds, i.e., previously depicted with one bond to each of the spacially separated sites of **I**. Such a doubly-held species would now be depicted as having two single bonds with the single, central silicon of **III**; e.g., in structure **I** each of the two sites represents one of the two bonding orbitals of the central silicon of **III** so that the surface species would not be changed substantially.

The bifunctional site also removes objection (f) in that the formation of surface species can involve conventional mechanisms of organic chemistry. Structure **III** is thus useful because it is compatible with the experimental observations and with mechanisms. One point of difficulty might be thought to be that the central silicon is in an octahedral configuration, in contrast to the usual tetrahedral one. However, octahedral silicon may be unusual but is not implausible.

The preponderance of the very voluminous literature dealing with silica and siliceous surfaces considers silicon to take part in surface reactions and to form surface species in its conventional tetrahedral state. Direct analogies are drawn between "surface silicon" and the silicon of the majority of bulk silicon compounds. However, there are a few scattered remarks in the literature about unusual sites using terms such as "valence unsaturation" or "coordinationally unsaturated silicon," and this topic has been briefly taken up by Kiselev and Lygin (13). The earliest mention of silicon in other than fourfold coordination in connection with surfaces appears to be that of Weyl, who suggested that the presence of water on silica may cause the silicon to

expand its coordination (18). Much later Pak (19) observed an intense absorption at 380–200 nm with silica gel but not with aerogel or quartz and ascribed the absorption to an increase in the coordination of surface silicon atoms from the usual 4 to 6, and it has been suggested (20) that penta- or hexa-coordinated silicon sites might account for the extraordinary chemical reactions found with some siliceous surfaces (21–24). For such unusual cases, including structure III, it seems reasonable to draw analogies with the lesser known compounds of silicon.

There exist literally hundreds of compounds in which silicon is penta- or hexa-coordinated (25); the mechanisms of reactions of silicon compounds routinely used five- or sixfold transition states; and the literature dealing with this topic is substantial although, of course, only a fraction of that dealing with “ordinary” silicon. There is consequently ample precedent for structure III.

ACKNOWLEDGMENT

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