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Reactive Silica

XII. The Sorption and Polymerization of Several Alkenes[1]

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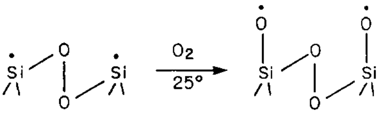
The sorptions of 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, t-1,3-pentadiene, 1,3,5-hexatriene, and 1,4-pentadiene by reactive silica (RS) [Morterra and Low, *Ann. N.Y. Acad. Sci.* **220**, 133 (1973)] were studied by infrared spectroscopic techniques. There were two general reactions. All adsorbates were rapidly taken up to form several chemisorbed species. The conjugated polyenes were then sorbed slowly to form polymers. The results suggest that the special reaction sites on the RS surface acted as initiators for the free-radical-initiated polymerizations.

INTRODUCTION

Reactive silica (RS) is a trivial name applied to high surface area silicas which, after having been subjected to an activation procedure, become remarkably active in chemisorbing a variety of gases (*1–7*). Abundant chemical evidence suggests that the special activity, which leads to the formation of surface structures unlike those found on ordinary silicas, is brought about by the presence of unusual reaction centers, shown schematically as structure I, which can be modified by chemisorbing O_2 at room temperature to give structure II. The schematic structures summarize the properties of the centers, i.e., those of a pair of silicon radicals associated with two anomalously reactive oxygen atoms, but infer little about the geometry besides the requirement that the two silicons be closely spaced.



I
RS center

II
ORS center

It can be argued that the surface-bound radicals should function as initiators of radical-propagated chain reactions and, to test the hypothesis, RS and oxygen-treated RS (ORS) were exposed to ethylene; polyethylene was formed (*6*). It may thus be supposed that "small" molecules containing conjugated double bonds would also be polymerized. In order to test this supposition we examined the sorption of five polyenes, using infrared spectroscopic techniques.

EXPERIMENTAL

Most experimental procedures have been described (*1–6*). RS samples were prepared from Cab-O-Silica (G. Cabot Corp., Cambridge, Massachusetts), methoxylation being carried out with trimethoxymethane (*5, 8*). ORS was prepared by exposing RS to O_2 at 25°C (*3, 4*).

The 1,3-butadiene was research grade (Phillips Petroleum Co., Borgen, Texas); the other adsorbates were 99% pure (Aldrich Chemical Co., Milwaukee, Wisconsin). All adsorbates were subjected to several freeze–pump–thaw cycles.

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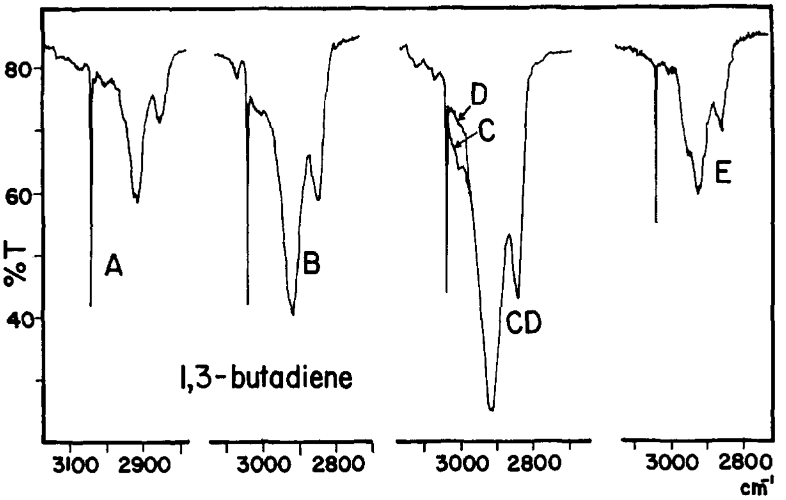


FIG. 1. 1,3-Butadiene sorption: A, after a 10-min exposure to 7 Torr of 1,3-butadiene at 25°C; B, 3-hr exposure; C, 4-day exposure, followed by 0.5-hr degassing at 100, 200, and 300°C; D, after 0.5-hr degassing at 400°C; E, after 0.5-hr degassing at 400°C.

The general experimental scheme involved exposing a freshly prepared sample to adsorbate vapor at room temperature, nominally 25°C, recording infrared spectra after various exposure times, and then degassing the treated adsorbent at successively increasing temperatures, recording spectra as needed. To test the reactivity of silica per se, a sample of ordinary silica which had been degassed for 3 hr at 865°C (thus simulating the degassing step carried out in the preparation of RS) was exposed to 10 Torr of 1,3-butadiene vapor at 25°C. Extremely weak bands near 3002, 2962, 2925, and 2860 cm^{-1} were detected after an exposure period of 3 days. These bands, which do not match the band pattern of gaseous 1,3-butadiene, did not change significantly upon degassing the adsorbent at 100°C for 1 hr and are consequently attributed to surface species more tightly bound than physically adsorbed butadiene; i.e., after a very long exposure time, a very small amount of adsorbed material containing CH_3, CH_2, and $-CH=CH-$ groups (*9–14*) formed. The much more extensive reactions of RS with butadiene, and by inference with the other adsorbents, can thus be attributed to the presence of the special centers on the RS and ORS surfaces.

RESULTS AND DISCUSSION

Exposing a fresh RS sample to 1,3-butadiene at 25°C brought about the rapid formation of bands in the C–H region; some segments of spectra are shown in Fig. 1. The most conspicuous feature of trace A in Fig. 1 (recorded after 10 min) is a relatively intense, narrow band at 3046 cm^{-1} of 5-cm^{-1} half width. There were weak absorptions near 3080 and 3006 cm^{-1}, a fairly strong absorption of two overlapping bands centering near 2927 and 2920 cm^{-1}, and another band at 2848 cm^{-1}.

Upon prolonged exposure, the 2927-2920-cm^{-1} absorptions coalesced to form a band centering at 2920 cm^{-1} (B, Fig. 1); the 2920- and 2848-cm^{-1} bands continued to increase (B and C, Fig. 1), and a broad absorption appeared in the ~2980- ~3030-cm^{-1} range (C and D, Fig. 1). Other absorptions were not affected significantly. Upon degassing, there were no significant changes in the spectra until temperatures above ~400°C were reached, when all bands declined (C, D, and E, Fig. 1).

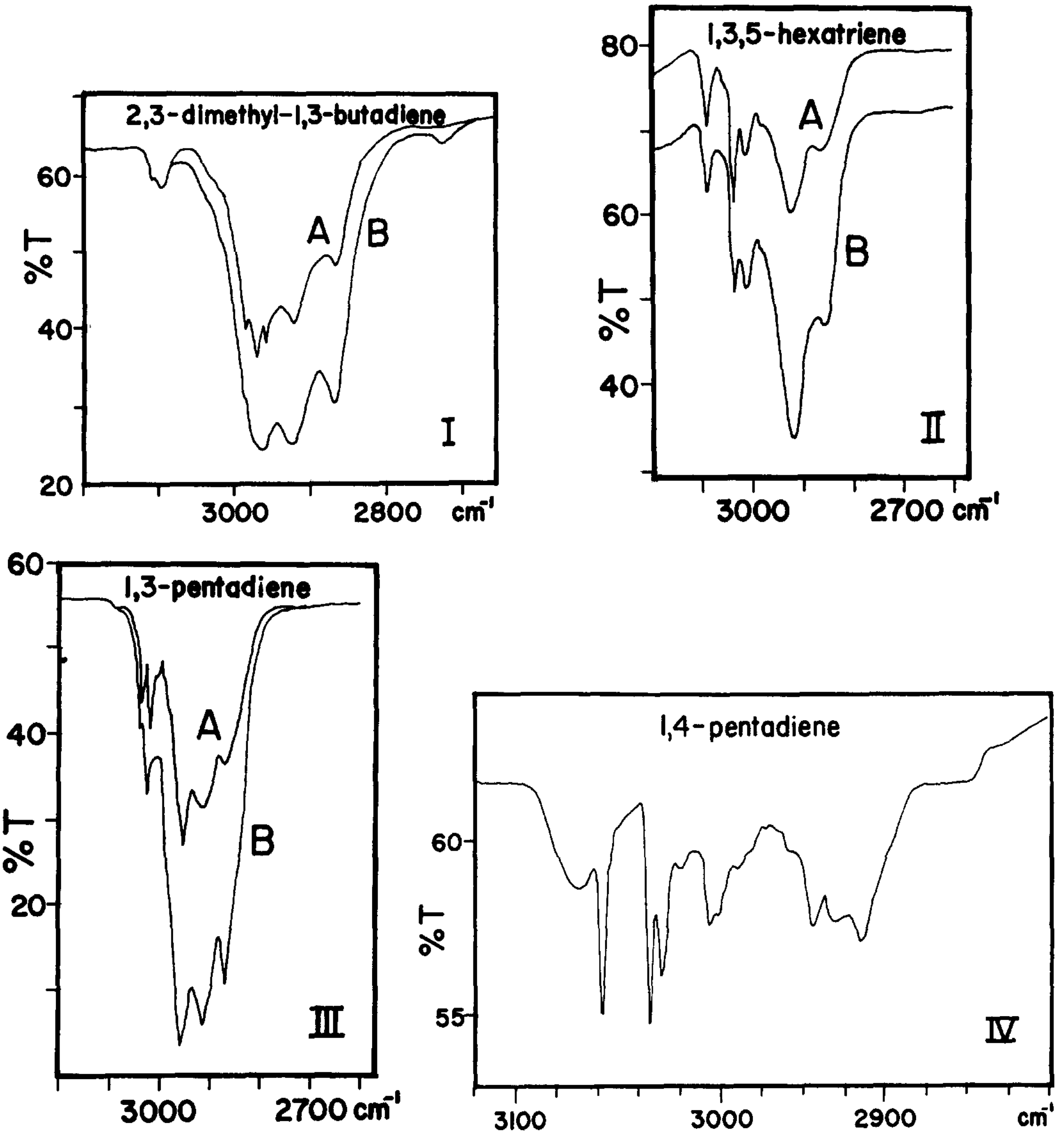


FIG. 2. Polyene sorption. (I) 2,3-Dimethyl-1,3-butadiene sorption: A, ~10 min after exposure of a fresh RS sample to 7 Torr of 2,3-dimethyl-1, 3-butadiene vapor at 25°C; B, after 2-day exposure. The overlapping bands at ~2990, 2970, and 2960 cm^{-1} of trace A became indistinct, forming an absorption centering near 2965 cm^{-1}. (II) 1,3,5-Hexatriene sorption: A, ~10 min after exposure of a fresh RS sample to 4 Torr of 1,3,5-hexatriene vapor at 25°C; B, after exposure for 4 days at 25°C. The ordinate of B is displaced. (III) *trans*-1,3-Pentadiene sorption: A, ~10 min after exposure of a fresh RS sample to 7 Torr of adsorbate vapor at 25°C; B, after exposure for 3 days at 25°C. (IV) 1,4-Pentadiene sorption: The trace is a Scale-expanded segment of a spectrum recorded after exposing a fresh RS sample to 7 Torr of adsorbate vapor at 25°C; there no significant changes in the spectra for exposure times up to 4 days.

The 3750-cm^{-1} ≡Si–OH band remained unaffected during sorption and also during desorption until degassing temperatures of 350–400°C were reached, when the ≡Si–OH band broadened and increased in intensity. There were no changes in the Si–H regions of spectra.

The overall results suggest that there

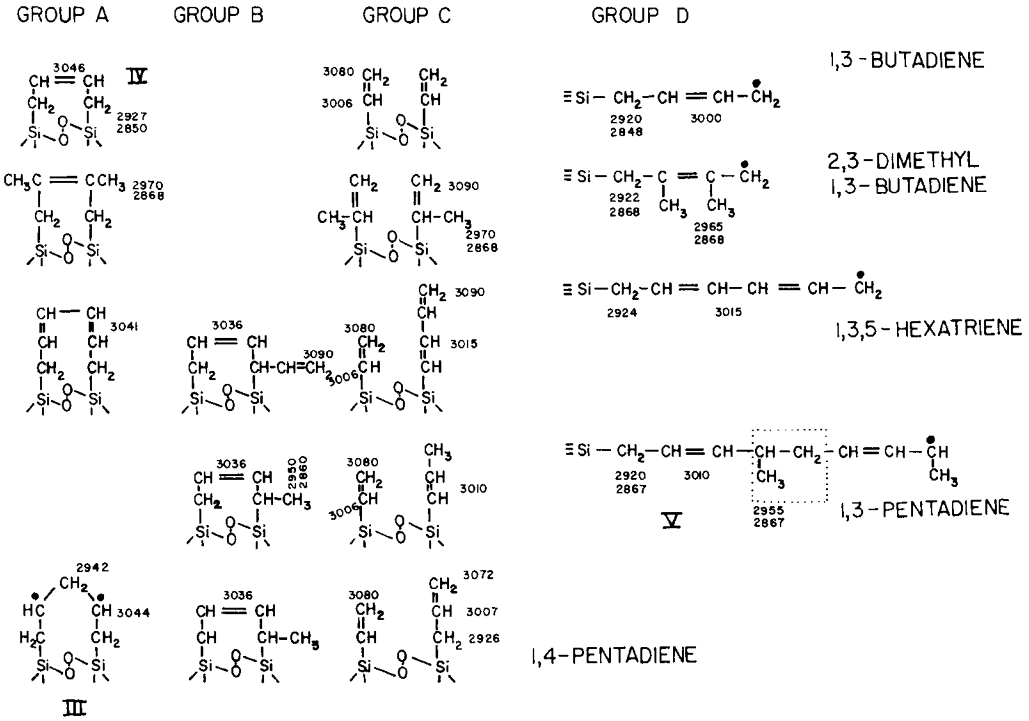


Fig. 3. Surface structures.

were at least two reactions leading to species fairly tightly bound to the surface: a reaction which occurred rapidly and completely upon exposing RS to 1,3-butadiene, leading to the 3080-, 3046-, and 3006-cm^{-1} bands, and a slow reaction leading to the species responsible for the other more intense bands.

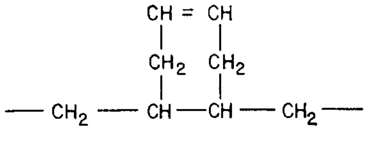
Similar observations were made upon sorbing 2,3-dimethyl-1,3-butadiene, 1,3,5-hexatriene, and t-1,3-pentadiene; i.e., in each case, there was an initial, rapid sorption followed by a second, slow process. With 1,4-pentadiene, however, the slow process was not observed. Some of the results are illustrated by the traces in Fig. 2.

With all adsorbates there were no significant changes in the ≡Si–OH bands when sorption occurred; also, there were no changes in the Si–H region of the spectra.

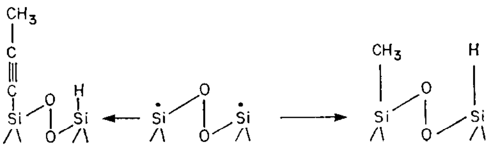
The analysis of the complex results required the examination of the spectra of all adsorbates in terms of appearance of bands, band positions, and changes in them, as well as band intensities and relative band intensities, band assignments being based on group frequencies (*9–14*). The detailed, lengthy analysis is not presented for the sake of brevity, but its results are summarized in Fig. 3 where, also for brevity rather than in a separate tabulation, the band frequencies are written next to the groups thought to be responsible for them.

The structural assignments which have been made are tentative but not unreasonable ones (except possibly for structure III) and serve to amplify the general observation that there was a rapid sorption followed by a slow one, except with 1,4-pentadiene. Structure VI might be "crowded" because of the presence of the methyl groups.

Apparently, the rapid sorption could occur in three ways, each leading to a group of similar surface structures. Judging from relative band intensities, the favored mode of attack was at tne ends of the adsorbate molecules, leading to the cyclic structures of Group A and, to a lesser extent, those of Group B. Bands for $-CH{=}CH-$ and $-R_1R_2C{=}CHR_3-$ modes fall in the 3040- to 3010-cm^{-1} range (*9–14*), thus leading in part to the tentative structures of Group B. The unusual and extreme sharpness of the 3046-cm^{-1} band found with 1,3-butadiene sorption, attributed to structure IV, suggests that the structure is very well defined, the hydrogens not interacting with their environment. It is interesting to note that the spectrum of sorbed 1,3-butadiene recorded after long exposure times, e.g., trace D, Fig. 1, closely matches the spectrum of low molecular weight polybutadiene (*15*) which also shows such a sharp band. The latter might, in analogy, be caused by a structure formed by linking a 1,3-butadiene molecule across a double bond in the polymer chain of polybutadiene.

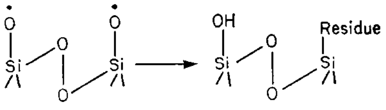


Dissociative chemisorption also occurred, but to a minor extent, to form the structures of Group C. Apparently, an entire vinyl group could be abstracted and bound by one of the sites, the residue being bound by the second site. In contrast, dissociative chemisorption involving only the abstraction of hydrogen and then leading to the formation of a surface silane was not observed; i.e., reactions similar to those found with methane or propyne (*3, 7*), in which $\equiv$Si–H groups were formed, did not occur.



The rapid chemisorptions leading to the formation of the structures of Groups A B, and C involved both sites of the dual center I and thus led to a deactivation of a portion of the available surface. More interesting is the observation of continuing although decelerating growth of C–H bands, which is attributed to the formation of polymers. If the relatively large number of Group A structures indicates that attack was preferential at the ends of the molecules, it follows that attack at only one end is expected and will lead to the structures of Group D. These are shown in Fig. 3 as radical precursors (except that V has two units) which, through the addition of more molecules adsorbing upon them, would lengthen into polymer chains. In general, the band frequencies of the slowly growing species are like those of "normal," not greatly disturbed, methyl and methylene groups. The intensity ratio of the trio of intense bands found with t-1,3-pentadiene (Fig. 2-III, trace B) might be thought to suggest the formation of surface ethyl groups such as those described by Luchesi *et al.* (*16*), but is more readily attributable to the summation of methyl and methylene pairs of structure V (Fig. 3, area enclosed by dotted line).

Only a limited amount of work was carried out with ORS adsorbents. The sorption of 1,3-butadiene and t-1,3-pentadiene gave results similar to those found with RS in that there was an initial fast sorption followed by a slower one leading to polymers identical to those formed on RS, but the bands attributable to the rapidly formed species were also accompanied by growth of the $\equiv$Si–OH band, indicating that hydrogen abstraction reactions of the type



had occurred to a small extent.

In general, then, the various data indicate that RS and ORS became partially deactivated because of strong chemisorptions but retained sufficient activity to cause polymerizations of conjugated polyenes to occur. As in the case of ethylene polymerization (*6*), the reactions occurred at room temperature and at quite low pressures; under more severe conditions the polymerizations might be more extensive. Also, the precursor of RS is simply and fairly cheaply prepared by heating methoxylated silica in vacuum, hydrogen, or inert gas. The product is a free-flowing, generally hydrophobic powder, apparently stable indefinotely at ambient conditions, which is then activated by high-temperature degassing. RS and possibly ORS might thus offer some advantages over other more complex, expensive, and unstable initiators for free-radical polymerizations.

ACKNOWLEDGMENTS

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