Reactions of Silica Surfaces with Boron Halides

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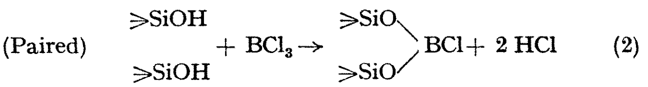
Summary The assumption that the hydrogen sequestering agents BCl_3 and BF_3 react solely with surface hydroxy-groups on silica is incorrect since these compounds will also strongly chemisorb on totally dehydroxylated silica.

THERE have been many recent investigations of the reactions of such hydrogen sequestering agents as the chloromethylsilanes,[1-3] BCl_3,[3-5] BF_3,[6] $TiCl_4$,[3] and $AlMe_3$[5,7] with hydroxy-groups present on oxide surfaces. Particular attention has been paid to these reactions on silica, and by investigation with conventional analytical techniques, sometimes combined with i.r. spectroscopy, attempts have been made to determine the number and degree of pairing of surface silanol groups.[1-4]

The assumption that has usually been made is that these reagents will only react with surface hydroxy-groups. Thus, when BCl_3 reacts with single or paired silanols reactions (1) and (2) have been envisaged.[3]

$$\text{(Single)} \qquad \geqslant\text{SiOH} + BCl_3 \rightarrow \geqslant\text{SiOBCl}_2 + HCl \qquad (1)$$



$$\text{(Paired)} \qquad \begin{array}{l}\geqslant\text{SiOH}\\ \geqslant\text{SiOH}\end{array} + BCl_3 \rightarrow \begin{array}{l}\geqslant\text{SiO}\\ \geqslant\text{SiO}\end{array}\!\!\Big\rangle BCl + 2\,HCl \qquad (2)$$

Under this assumption, measurement of the volume of HCl evolved to BCl_3 consumed, or a measurement of the residual chlorine after reaction, will be directly related to the concentration of surface silanols, and perhaps to the number of single or paired silanols.[3]

Kunawicz, Jones, and Hockey[7] have recently suggested that on silicas which have been dehydrated at high temperatures reaction may also occur on surface siloxane bridges which are formed during the thermal dehydration treatment. We present here evidence which shows that under extreme conditions of dehydration, reactions of BF_3 and of BCl_3 will occur exclusively on reactive siloxane bridge sites.

On the left hand side of Figure (A) is shown the i.r. spectrum in the OH stretching region of a silica sample (Cab-O-Sil, H-5) which has been dehydrated in vacuum at *ca.* 900 °C. This shows the well known sharp silanol band[1-4] at 3749 cm^{-1} indicative of the presence of only single non-interacting SiOH groups. At the right of Figure (A) is shown part of the spectrum obtained in the BO and BF stretching region after admitting 0·5 mmHg of $^{10}BF_3$ to the reaction cell and allowing this to react for *ca.* 30 s prior to evacuation for 5 min. No further changes occur after evacuation for several hours. An additional band is observed at 710 cm^{-1} and this three band spectrum (1500, 1448, and 710 cm^{-1}) has been attributed to a surface $SiOBF_2$ species.[8,9] Under these reaction conditions only *ca.* 3—5% decrease in the SiOH intensity occurs and the intensity of the bands in the 1400 cm^{-1} region is *ca.* 1/5 of that which can be achieved if larger pressures (10 mmHg) are allowed to react for longer periods of time (*ca.* 10 min) until the surface is saturated.

If the silica had been preheated at *ca.* 1200 °C so that virtually all of the SiOH species are removed from the surface, then under similar conditions the same three band spectrum is obtained, Figure (B). Clearly the adsorption of BF_3 on silica does not require the presence of surface hydroxy-groups.

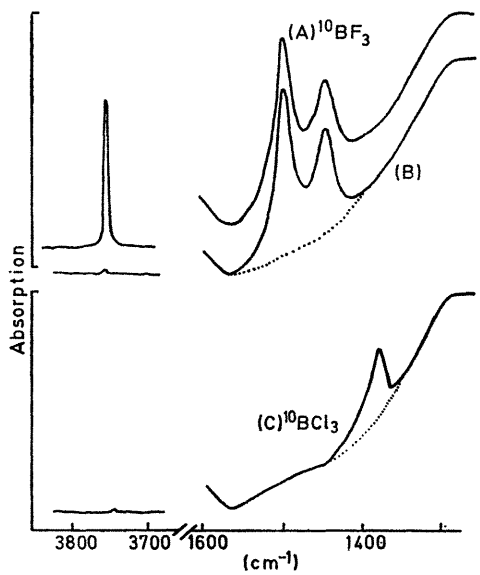


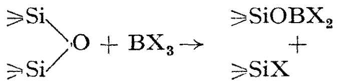
FIGURE. (A) *I.r. spectrum of* $^{10}BF_3$ *chemisorbed on silica at room temperature. The silica had been previously heated at* ca. 900 °C *in vacuum.*

(B) *I.r. spectrum of* $^{10}BF_3$ *chemisorbed on silica which had been previously heated to* ca. 1200 °C *in vacuum. The dotted line indicates the background spectrum before adsorption.*

(C) *I.r. spectrum of* $^{10}BCl_3$ *chemisorbed on silica at room temperature. The silica had been previously heated to* ca. 1200 °C *in vacuum before adsorption.*

The i.r. spectrum of $^{10}BCl_3$ chemisorbed under similar conditions on a totally dehydrated silica is shown in Figure (C). A sharp band is observed at 1385 cm^{-1} in the BO stretching region, and another band near 930 cm^{-1} is observed (not shown) in the BCl stretching region. Again no spectral changes occur on continued evacuation in the absence of trace amounts of water vapour. However, if water vapour is added (or desorbed from the cell walls on to the sample) these two bands gradually disappear accompanied by the growth of several new bands between 1470—1430 cm^{-1}, and of a BOH stretching band near 3700 cm^{-1}. The initial set of bands has been assigned to the corresponding $SiOBCl_2$ species[9] and the spectral changes that occur when water is present have been attributed to a variety of partially hydrolysed products resulting from the initial species.

More complex spectra are observed when both reactions are carried out on silicas that have been dehydrated at lower temperatures (300—800 °C) and these spectra change with time on continuing evacuation. Again, these reactions are due to continuing hydrolysis of the initial species by adsorbed water or surface hydroxy-groups, and the spectral complexity arises from the presence of a variety of partially hydrolysed products. But in all cases the spectral features discussed above are the prominent ones after the initial evacuation of the reactant and these features change only slightly with time when few hydroxy-groups are present initially. Therefore, both BF_3 and BCl_3 are capable of chemisorbing on totally dehydroxylated silica, and we believe that the reaction takes place on reactive siloxane bridge sites as shown in reaction (3).



$$(\geqslant Si)_2O + BX_3 \rightarrow \geqslant SiOBX_2 + \geqslant SiX \qquad (3)$$

Evidence for the presence of these reactive siloxane sites will be published shortly, as will details of these and the accompanying reactions of the boron halides on silica. Although we cannot observe the SiF or SiCl stretching vibration because these spectral regions are obscured by the strong background absorption of silica, when a similar reaction is carried out with B_2H_6 as adsorbent on a totally dehydroxylated silica, a strong spectrum of a chemisorbed BH containing species is observed, along with that of a surface SiH containing species.[10]

We agree with Kunawicz *et al.*[7] that caution must be exercised in utilizing the reactions of hydrogen sequestering agents with silica if the basic assumption in the analysis of the date is that reaction occurs solely with surface hydroxy-groups. However, the reactions discussed above only occur on silica which has been preheated at these rather high temperatures, and this in no way contradicts the findings of Hockey *et al.*[5,11] that at least for BCl_3, the room temperature reaction with silicas which have been preheated at somewhat lower tempartures occurs almost exclusively with surface silanol groups.

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