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# Dehydrobromination of Bromoalkanes over Cabosil and Alkali-Ion-Exchanged Cabosils

## II. An Infrared Spectroscopic Study

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Infrared spectra of Cs- and Li-ion-exchanged cabosils have been measured after various treatments such as evacuation at 25–400°C and exposure to $D_2O$ or 2-bromobutane, to elucidate the mechanism of anti elimination. Hydroxyl stretching bands of cabosil became weaker by the alkali-ion-exchange. With Cs-ion-exchanged cabosil having a basic character, a broad band at about 2800 $cm^{-1}$ appeared after evacuation at 150–300°C. This broad band, which was reversibly formed by addition and removal of water and showed deuterium isotope shift, was assigned to the hydroxyl groups hydrogen-bonded to basic sites. In accordance with the rapid deactivation in the reaction over Cs-ion-exchanged cabosils, the broad band irreversibly disappeared and a new broad hydroxyl band developed on exposure to 2-bromobutane above 100°C.

## INTRODUCTION

In the preceding paper (*1*), we reported the stereochemical study of the dehydrobromination of 2-bromobutane over cabosil and alkali-ion-exchanged cabosils. Syn elimination by a carbonium-ion-type mechanism seemed probable over weakly acidic cabosil and Li-ion-exchanged cabosils (Li-cabosils). On the other hand, the reaction proceeded mainly via anti mode probably by a concerted mechanism over Cs-cabosils which exhibited a basic character. As discussed before (*1*), geometric constraints induced by the fixed surface sites lead to difficulties in conceiving of an anti elimination which takes place by a concerted mechanism. We proposed a possible model for the transition state of anti elimination, which does not require a particular surface structure (*1*). This model in some respects resembles those proposed by Kibby *et al.* (*2*) and by Knözinger *et al.* (*3*).

In order to gain further insight into the mechanism of anti elimination, we attempted an infrared spectroscopic study of Cs-cabosil. Cs-cabosil may represent the basic solids as far as dehydrobromination is concerned, since the results obtained with cabosils were essentially the same as those obtained with other silica gels (*1, 4*), and other basic solids like CaO and $K_3PO_4$ (*5*) also showed an anti preference similar to that of Cs-cabosil. Surface hydroxyl groups of silica have been studied by infrared spectroscopy and other methods as for the changes on heat treatment and on interaction with various compounds (*6–9*). Interactions of haloalkanes with surface cation and hydroxyl groups have also been studied in the case of metal-ion-exchanged zeolites (*10*).

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It is expected that the present study will provide information concerning the following questions: Where on the surface do the proton and bromide ion released from 2-bromobutane go? How do the basic sites interact with the reactant and products? Are there any differences between syn-preferring silica and anti-preferring silica in the behavior of surface hydroxyl groups on evacuation or on exposure to the reactant? Does water exist on the surface and play any significant role during the reactions?

## EXPERIMENTAL

Cabosil and alkali-ion-exchanged cabosils used in the infrared spectroscopic study were those described in the preceding paper (*1*). Alkali content and surface area of these samples as well as the results of reaction of 2-bromobutane are also given in the same paper [Table 1 in Ref. (*1*)]. Cs(10)-cabosil (exchanged in a solution of Cs salts of pH 10) was studied most, since it showed a high ratio of anti elimination and was well studied in the previous work (*1*). H- and Li(10)-cabosils were also studied for comparison purposes.

The infrared cell used was the same as that described in Ref. (*11*). The cell was connected through a liquid nitrogen trap to a conventional vacuum manifold equipped with a rotary pump. A Pyrex sample holder mounted with a cabosil wafer (50–100 mg) was suspended inside the cell by a Pt wire. The sample was raised to the level of an electric furnace for heat treatment in vacuum or in the vapor of $H_2O$, $D_2O$, or 2-bromobutane, or the sample was moved down into the optical path for the infrared measurement at room temperature. $D_2O$ treatment of the sample was carried out as follows. $D_2O$ vapor at about 7 Torr was directed onto the sample at 200°C for 30 min, and then the sample was evacuated for 1–2 min at the same temperature. This cycle was repeated four times.

2-Bromobutane was a guaranteed grade reagent of Tokyo Kasei Kogyo Co., Ltd., and $D_2O$ was from E. Merck.

## RESULTS

### *Changes in Hydroxyl Bands on Evacuation*

Behavior of surface silanol groups and adsorbed water on evacuation was investi-

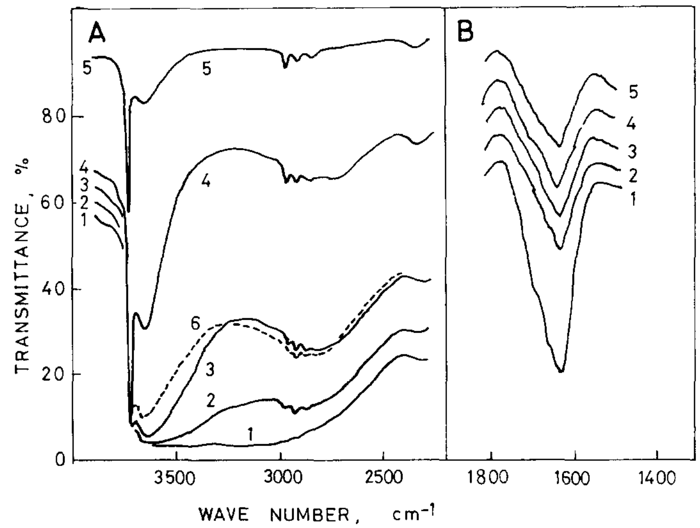


FIG. 1. Infrared spectra of Cs(10)-cabosil evacuated at several temperatures. 1, Before evacuation; 2, evacuated for 1 hr at 25°C; 3, at 150°C; 4, at 300°C; 5 at 400°C; 6, water vapor was added after spectrum (5) was recorded and then evacuated at 150°C.

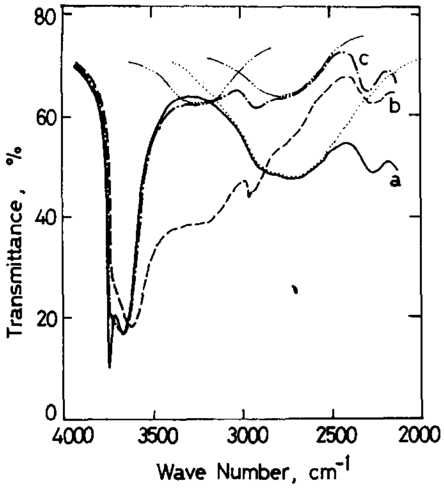


FIG. 2. Changes in the infrared spectra of Cs(10)-cabosil on exposure to 2-bromobutane. a, Evacuated for 30 min at 250°C; b, exposed to about 10 Torr of 2-bromobutane for 20 min at 150°C and then evacuated at 25°C, after spectrum (a) was recorded; c, evacuated for 30 min at 250°C after (b).

gated for Cs(10)-, Li(10)- and H-cabosils. Stretching region of hydroxyl group of H-cabosil showed the presence of free and hydrogen-bonded silanol groups, as well as adsorbed water, the intensity of which decreased with the increasing evacuation temperature. These results were similar to those reported in the literature (*6*, *7*). The OH bands of alkali-ion-exchanged cabosils, which were weaker owing to the decrease in the number of surface silanol groups and in the surface area, behaved similarly on evacuation. Spectra of Cs(10)-cabosil are shown in Fig. 1. The marked difference found in the spectra is that a very broad band at 3200–2500 cm$^{-1}$ having a peak at about 2800 cm$^{-1}$, which was not observed with H- and Li-cabosils, appeared upon evacuation of Cs(10)-cabosil at 150–300°C. This band almost disappeared on evacuation at 400°C, but was restored after the addition of water vapor and subsequent evacuation at 150–300°C (Fig. 1, spectrum 6). The small absorptions at 3000–2800 cm$^{-1}$ are due to the contamination, probably from grease. The contamination was much less in the experiments presented in Figs. 2 and 3.

Bands in the region near 1630 cm$^{-1}$, where the bending mode of water appears, remained unchanged on evacuation at high temperatures, after initial rapid decrease brought about by evacuation at room temperature. No change in this band was observed, after $D_2O$ treatment and subsequent evacuation.

### *Interaction of Cabosils with 2-Bromobutane*

Figure 2 shows the changes in the infrared spectra caused by the exposure of Cs(10)-cabosil evacuated at 200°C to the vapor of 2-bromobutane. Initial spectrum (a) exhibited the broad band at 2800 cm$^{-1}$ in addition to the free and hydrogen-bonded silanol bands. After exposure to 2-bromobutane at 150°C and subsequent evacuation at room temperature, the broad band apparently decreased and a new broad band developed at about 3200 cm$^{-1}$ (spectrum b). Bands assigned to the stretching vibration of $CH_3$ and $CH_2$ of adsorbed 2-bromobutane appeared at 3000–2800 cm$^{-1}$. The spectrum recorded after evacuation at 250°C (spectrum c) seems to contain two broad bands at 3200 and 2800 cm$^{-1}$, in addition to the ordinary silanol bands. It is to be noted that the broad band at 2800 cm$^{-1}$ which is characteristic of Cs-cabosil decreased sharply on exposure to 2-bromobutane and that major portion of the band was not restored even after vacuation at 250°C, although the band at ordinary hydrogen-bonded OH region almost returned to the initial state (compare spectra a and c in Fig. 2). In the case of H-cabosil, no significant change was obserded in the OH stretching region after it was exposed to 2-bromobutane and subsequently evacuated at room temperature.

Similar sets of experiments were carried out with $D_2O$-treated Cs(10)-cabosil. The results are shown in Fig. 3. On $D_2O$ treatment, most of the OH bands shifted to the corresponding OD region. In the presence of 2-bromobutane in the gas phase (strong bands at 3000–2800 $cm^{-1}$ in spectra 3 and 4), the hydrogen-bonded hydroxyl bands (OH as well as OD) became stronger. These bands at the hydrogen-bonded OH region decreased in intensity on evacuation at room temperature (spectrum 5). However, it must be noted that the intensities in the lower-frequency parts of the OH and OD bands, which are at 3600—3000 and at 2600–2200 $cm^{-1}$, respectively, decreased only slightly. These bands almost, but not completely, returned to those in the initial spectrum 2 on evacuation at 200°C. Change in 2300- to 1900-$cm^{-1}$ region caused by $D_2O$ treatment indicates that the broad band at 2800 $cm^{-1}$ shifted to the corresponding OD region (deuterium isotope shift), although the band shape was not clear because of the presence of a broad band due to the lattice vibration. This band also disappeared after exposure to 2-bromobutane.

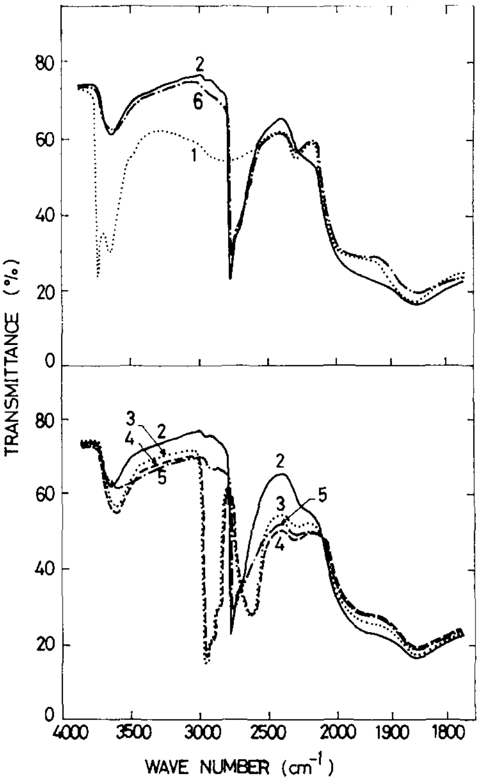
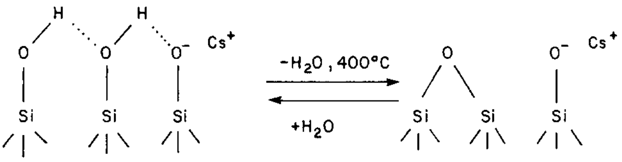


FIG. 3. Infrared spectra of $D_2O$-treated Cs(10)-cabosil and the change on exposure to 2-boromobutane. 1, Evacuated for 30 min at 200°C; 2, $D_2O$-treated at 200°C (see Experimental section); 3 and 4, 15 min in 2-bromobutane of about 10 Torr at 25 and 110°C, respectively; 5, evacuated for 30 min at 25°C; 6, evacuated for 30 min at 200°C. These treatments were performed on the same sample wafer in the order of the number.

## DISCUSSION

*Bands in the 1630-$cm^{-1}$ region.* The band intensities of the 1630-$cm^{-1}$ region for H-, Li-, and Cs-cabosils were very close to each other when normalized to unit weight of the catalyst (not to the unit surface area), and little changed on evacuation at high temperatures. Therefore, this band after evacuation is not due to the adsorbed water but due to the overtone or combination band of lattice vibration of silica (*12*) (cabosil cannot contain structural water in the bulk, in view of the method of preparation).

*A broad band having a peak at about 2800 $cm^{-1}$.* This band appeared only with Cs-cabosil, changed reversibly with the addition and the removal of water (Fig. 1), and shifted to the OD region with $D_2O$ treatment (Fig. 3). Therefore, this must be assigned to some sort of OH stretching band, which has some connection with basic sites of Cs-cabosil. It has been reported that silanol bands shift to lower frequencies by the formation of a hydrogen bond with a surface oxide ion or an adsorbate. The shift is very large when the silanol group interacts with strong bases like ammonia (shift is about 700 $cm^{-1}$) and pyridine (about 900 $cm^{-1}$) (*7*, *8*) or with acrylonitrile (850 $cm^{-1}$) (*10*). If one takes these facts into account, this band, which shows a shift of about 900 $cm^{-1}$ from the free silanol band, may be assigned to the surface silanol groups which are hydrogen-bonded to basic sites. Therefore, the disappearance of the broad band after exposure to 2-bromobutane was probably caused by the neutralization of basic sites by acidic hydrogen bromide produced by the reaction of 2-bromobutane. Adsorbed water may not be considered as the origin of this band, in view of the behavior of the 1630-cm$^{-1}$ band (Fig. 1) and the findings reported in the literature (*13*), although the possibility cannot be excluded. The process accompanying the reversible appearance of the broad band on addition and removal of water may be represented by Eq. (1).



(1)

*Interaction of Cs-cabosil with 2-bromobutane.* It is seen from the comparison of spectra 1 and 2 in Fig. 3 that free or nearly free silanol groups exchange hydrogen with $D_2O$ more readily than the hydrogen-bonded silanol groups do. In spite of this higher rate of exchange of free silanol groups, the free silanol band (OH) was not restored in the subsequent treatments given in Fig. 3, although free OD band was mostly restored in spectrum 6. This result indicates that surface migration of $H^+$ and $D^+$ was not rapid and hydrogen–deuterium mixing on the surface did not significantly take place during the set of treatments given in Fig. 3. Therefore, it may be assumed that the spectra of OH region reflects the change in newly formed SiOH if it did exist, in addition to the change in the surface SiOH which remained unexchanged during $D_2O$ treatments. On the other hand, the change in the OD region shows the perturbation of surface silanol groups caused by 2-bromobutane, butene, or hydrogen bromide.

With this in mind, the examination of the spectra in Figs. 2 and 3 leads to the following statements. Intensities of OH and OD regions increased after the exposure to 2-bromobutane. The extinction coefficient of the hydroxyl stretching band is known to increase when shifted to a lower frequency by forming a hydrogen bond (*7*). Therefore, at least a part of the band increase in the lower-frequency part of OD region (2600–2200 cm$^{-1}$) must be gained by the consumption of free OD band (the higher-frequency part of OD band). However, in contrast to the OD region, there was no decrease in intensity of the higher-frequency part of the OH band (3800–3600 cm$^{-1}$), so that a considerable portion of the band enhancement in the OH region is due to the new hydroxyl groups formed by the reaction of surface oxide ions with 2-bromobutane or hydrogen bromide. In addition to this new hydroxyls, the band in this region (3600–3000 cm$^{-1}$) may contain two other silanols. One is the silanol groups which are hydrogen-bonded to hydrogen bromide and/or 2-bromobutane. The other is the silanol groups hydrogen-bonded to basic sites which became less basic by the reaction with 2-bromobutane or hydrogen bromide. If the linear relationship between the heat of adsorption of a molecule and the band shift of silanol group caused by the adsorption (*8*) is taken into account, the band of hydroxyl groups which are hydrogen-bonded to less basic sites would be expected to appear in the frequency region higher than 2800 cm$^{-1}$. The neutralization process seems to cause the marked decreases of the broad bands at 2800 and 2000 cm$^{-1}$ (Figs. 2 and 3).

*Reaction mechanism.* The dehydrobromination of 2-bromobutane over Cs-cabosil may be described as follows. Surface silanol groups interact with 2-bromobutane, as seen by the increase in the hydrogen-bonded silanol band. A proton and a bromide ion formed from 2-bromobutane react with basic sites as discussed above. The proton forms a new hydroxyl group, neutralizing the basic oxide ion associated with Cs ion. A bromide ion may be coordinated with the Cs ion, as in the case of metal-ion-exchanged zeolites (*10*). At a high reaction temperature, most of the newly formed hydroxyls are removed by desorption probably as $H_2O$ and/or HBr, as seen from the fact that OH bands mostly returned to the initial state on evacuation at 200–250°C. However, the spectrum was not completely restored, and the broad band at 2800 $cm^{-1}$ mostly disappeared in the case of Cs-cabosil, although the spectrum of H-cabosil was almost restored only by the evacuation at room temperature. This fact is in good agreement with the results reported before on the reaction of 2-bromobutane; i.e., deactivation from pulse to pulse caused by hydrogen bromide produced was very large and only a very low stationary activity was obtained for Cs-exchanged silica, in contrast to the result with silicas (*1*, *4*).

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