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Infrared Study of the Surface Dehydration of 1-(o-Chlorophenyl)ethyl Alcohol on γ-Al_2O_3

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An adsorbed complex of 1-(*o*-chlorophenyl)ethyl alcohol exists on the surface of γ-Al_2O_3 at temperatures near 250°C. Both infrared and mass spectral data suggest that the dehydration of 1-(*o*-chlorophenyl)ethyl alcohol over γ-Al_2O_3 to *o*-chlorostyrene proceeds via this surface intermediate. The spectral features of the surface intermediate indicate that the phenyl ring is highly perturbed, there exists no formal C–O linkage, there is a surface —Cl interaction resulting in weakening of the ring-Cl bond, and there appears to be a residual positive charge on the α-carbon atom. A structure for the surface intermediate is proposed in terms of the spectroscopic interpretations.

Introduction

Although the use of infrared spectroscopy to characterize adsorbed molecules is well documented and extensively reviewed, there is little published infrared data on adsorption of high boiling liquids on catalytic surfaces. The introduction of this type of sample into a cell, in such a way that it can interact with an activated catalytic surface, presents a difficult, but not insurmountable experimental problem. We have recently described a sample-inlet system designed for this type of application (*1*).

As part of our continuing interest in the adsorption of alcohols on metal oxide surfaces, we initiated a study of the surface dehydration of 1-(*o*-chlorophenyl)ethyl alcohol to *o*-chlorostyrene on γ-Al_2O_3. The present study was aimed at characterizing the surface species present during the dehydration reaction. Reported here are the results of this study.

Experimental Methods

The infrared cell and the sample-inlet system used have been described previously (*1*, *2*). The catalyst sample was prepared by slowly spraying a water–acetone slurry of small particle size alumina (Alon C*, surface area 70.5 m^2/g) onto a potassium bromide support plate with an artist's air brush. Uniform high surface area films (coverage about 6 mg/cm^2) can be prepared by this technique (*3*).

After the alumina layer was placed in the cell it was heated to 450°C in 500 Torr of oxygen to remove any organic contaminates and then evacuated to 10^{-5} Torr at 300°C over a period of several hours. The cell was kept evacuated at 10^{-5} Torr prior to the introduction of the 1-(*o*-chlorophenyl)ethyl alcohol.

Both infrared and mass spectral analysis showed that the sample of 1-(*o*-chlorophenyl)ethyl alcohol used in these experiments contained about 1% 1-(*p*-chlorophenyl)ethyl alcohol but no other detectable impurities. The presence of 1-(*p*-chlorophenyl)ethyl alcohol would neither account for the formation of benzofuran (which was detected only in trace quantities) nor alter the interpretation of results.

The sample-inlet system is an extension of the cell and is constructed from stain-

* Godfrey Cabot Inc., Boston, Massachusetts.

less steel tubing. The sample, 1-(*o*-chlorophenyl)ethyl alcohol (bp 190°C), was placed into a small metal container located in the inlet system (which is isolated from the main cell by a welded bellows valve) and cooled with liquid nitrogen while the inlet system was evacuated to $\sim 10^{-5}$ Torr. The sample was allowed to warm up to room temperature and then the entire inlet system was heated to about 200°C. At this point the welded bellows valve between the inlet system and main cell was opened and 1-(*o*-chlorophenyl)ethyl alcohol vapor was flushed into the cell with preheated nitrogen. This gaseous mixture enters the cell via a $\frac{1}{16}$-in. stainless steel nozzle, placed a few millimeters from the powdered alumina film. The nitrogen gas is removed by evacuation. Temperatures of the alumina and the inlet system are controlled independently. The amount of 1-(*o*-chlorophenyl)ethyl alcohol introduced into the

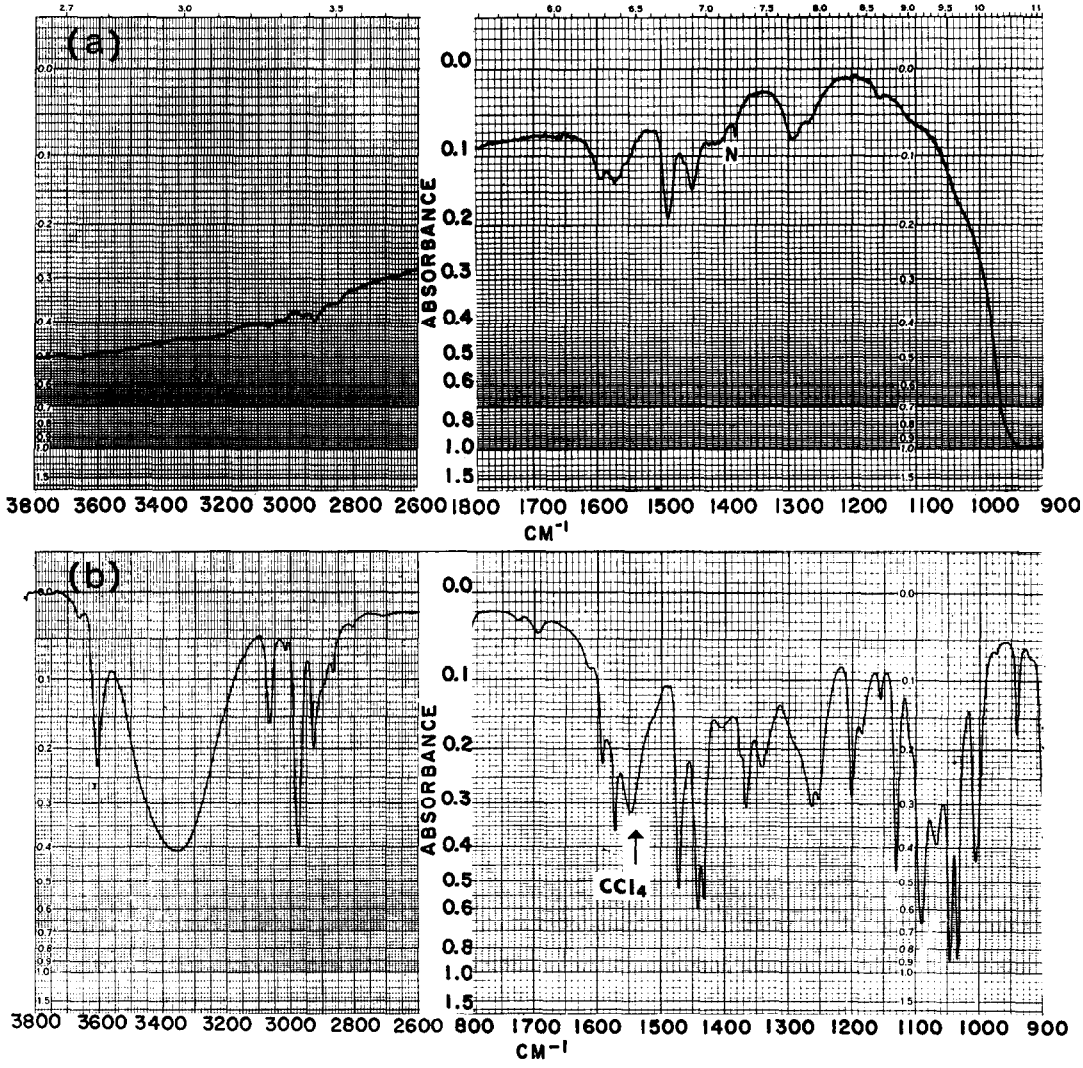


FIG. 1a. Species I: 1-(*o*-chlorophenyl)ethyl alcohol vapor chemisorbed on a γ-Al_2O_3 surface; surface temperature, 280°C. The sample was cooled to 25°C and subjected to prolonged evacuation at 10^{-5} Torr before scanning. The bands designated "N" are due to a KNO_3 impurity in the KBr windows. (b) 1-(*o*-chloropheryl)ethyl alcohol in 10% CCl_4 solution (3800–1333 cm^{-1}) and in 10% CS_2 solution (1333–900 cm^{-1}) using a 0.1-mm KBr cell.

cell is controlled by the flow rate of nitrogen and the temperature of the inlet system.

Adsorption processes were monitored on a Perkin-Elmer model 12 C single beam spectrometer (NaCl optics). When adsorption was observed the cell was cooled, detached from the vacuum system, and the spectrum of the adsorbed species (at room temperature) was obtained with a Beckman IR-9 spectrometer in the region from 900 to 3800 cm^{-1}. Because of the low transmission of the alumina films it was necessary to introduce an attenuator into the reference beam and use a 2× slit program. A mass spectrometer was used to monitor the gaseous materials coming out of the cell during the desorption process.

Results and Discussion

It is well known that phenylmethyl carbinol dehydrates to styrene and water when heated to 250°C over TiO_2 (*4*); all of our adsorption experiments were carried out in this temperature range.

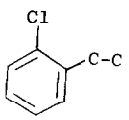
The infrared spectrum (obtained at room temperature) of an alumina film which had been exposed to 1-(*o*-chlorophenyl)ethyl alcohol while at 280°C is shown in Fig. 1a. The spectrum of 1-(*o*-chlorophenyl)ethyl alcohol, obtained in CCl_4/CS_2 solutions is shown in Fig. 1b for comparison. Quite clearly the chemical nature of 1-(*o*-chlorophenyl)ethyl alcohol is different when adsorbed on the alumina surface than in liquid (or solution) form.

The adsorbed material producing the spectrum in Fig. 1a, which we shall call Species I, is not removed by prolonged evacuation at pressures $<10^{-5}$ Torr and temperatures up to 250°C. With evacuation at temperatures above 250°C the Species I spectrum disappears; mass spectral analyses shows the effluent gases to be a mixture of mostly *o*-chlorostyrene and water, with only minor amounts of chlorobenzene, *o*-chloroethylbenzene, styrene, benzene and benzofuran. We interpret these data as indicating that Species I is a chemisorbed surface intermediate in the dehydration reaction. The remainder of this paper discusses the nature of this species.

A possible hypothetical structure for Species I is *o*-chlorostyrene adsorbed on the alumina surface. We can rule this out at once, for the introduction of *o*-chlorostyrene into the cell under the same conditions failed to produce an adsorbed species having the spectrum shown in Fig. 1a, and only a weakly adsorbed species was observed.

When *o*-chloroethyl benzene was introduced into the cell under the same conditions, an adsorbed species resulted whose spectrum was identical to that of Fig. 1a. Furthermore, its desorption products are identical to those produced from 1-(*o*-chlorophenyl)ethyl alcohol. However, neither ethylbenzene nor 1-phenylethanol showed any evidence for strong adsorption. From these experiments we must conclude that the chlorine atom plays a significant role in the surface reaction.

As noted, spectral features of Species I (Fig. 1a) are quite different from those of the liquid alcohol (Fig. 1b). In particular, there are large changes in both band position and relative band intensity for all the vibrational modes associated with the phenyl ring. The ring modes at 1440 and 1475 cm^{-1} in the liquid alcohol shift to 1450 and 1490 cm^{-1} in Species I. Bands in 1000–1150 cm^{-1} region of the liquid alcohol are too weak to be observed in the spectrum of Species I. The ring $\nu_{C=C}$ modes at 1570 and 1596 cm^{-1} show no frequency shift, but are considerably broader and intensified in the Species I spectrum. A strong absorption at 1295 cm^{-1} (shoulder at 1270 cm^{-1}) has appeared in the spectrum. These observations clearly indicate that in Species I the phenyl ring is highly perturbed from its form in 1-(*o*-chlorophenyl)ethyl alcohol. The materials recovered in the desorption process indicate that the adsorbed species must have the skeleton:



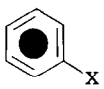
therefore, the perturbations in the spectrum result either from association of the phenyl ring directly with the surface (presumably

through the π-electron system) or very strong association to the surface of the groups joined directly to the phenyl ring, or both.

There is no spectral evidence for the presence of a C–O linkage in Species I: bands in the 1000–1100 cm^{-1} region are expected, and none are observed. The marked difference in adsorption behavior between the chlorinated and nonchlorinated phenylethyl alcohols noted above, and the absence of strong, sharp bands in the 1000–1100 cm^{-1} region characteristic of chlorinated aromatics indicate that the chlorine atom is strongly perturbed, probably because it is highly associated with the surface.

There appears to be a strong perturbation to the α-carbon atom when 1-(*o*-chlorophenyl)ethyl alcohol is adsorbed as Species I. The strong bands at 1295 and 1270 cm^{-1} in the spectrum of Species I are characteristic of a phenyl–X linkage where X is a polar element appearing in the second row of the periodic table (cf. phenols, fluorobenzene, aniline, and ϕ—C(=O)— type compounds). These vibrations are probably mixed modes involving ring deformations and stretching of the phenyl α-carbon atom bond (*5*). Similar bands are observed in spectra of carbonium ions [cf. diphenylethylene carbonium ion (*6*)] where the polar group is a positively charged carbon atom.

We interpret the 1295 and 1270 cm^{-1} bands as vibrational modes of a



group where X is probably a carbon atom which has acquired a residual positive charge as a result of interaction with the surface. This interaction is likely complex.

The γ-Al_2O_3 surface contains at least three different active sites: oxide ions, aluminum ions, and hydroxyl groups (*7*, *8*). A possible explanation for the α-carbon atom–surface interaction in terms of this model for the Al_2O_3 surface is that the alcohol OH group is shared between a surface Al ion and the α-carbon atom. In the case of *o*-chloroethyl benzene, the interaction might involve a surface hydroxyl group and the α-carbon atom. It is also likely that both the phenyl ring and the Cl atom would interact with exposed surface aluminum ions.

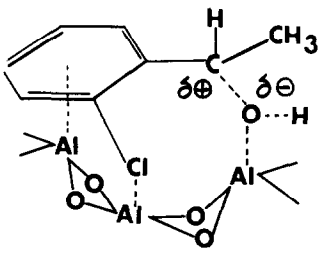


FIG. 2. Proposed structure for the adsorbed state of 1-(*o*-chlorophenyl)ethyl alcohol on γ-Al_2O_3.

We visualize the adsorbed state as the structure shown in Fig. 2, or one of its resonance hybrids. This structure is, of course, highly speculative but is consistent with the observed data. Unfortunately, the spectrum does not tell us where the hydroxyl proton resides. But because of the nature of the products obtained upon desorption (water and *o*-chlorostyrene) it would appear that the proton is an integral part of the surface complex.

CONCLUSIONS

Species I exists on the γ-Al_2O_3 surface below 250°C. Above 250°C, Species I disappears from the surface while *o*-chlorostyrene and water appear in the vapor phase. It is for this reason that we feel Species I is the surface intermediate between 1-(*o*-chlorophenyl)ethyl alcohol and *o*-chlorostyrene. The existence of other surface species at concentrations below our level of detection cannot be ruled out.

Spectroscopic evidence for the structure of Species I includes: (i) frequency shifts and intensity changes of the phenyl ring modes (ring highly perturbed); (ii) lack of bands in the 1000–1100 cm^{-1} region (no formal C–O linkage and weakening of the ring–Cl bond); (iii) benzofuran found as a desorption product (weakening of the ring–Cl bond and oxygen associated in the adsorbed state); (iv) anamolous adsorption behavior of the nonchlorinated analogs of

1-(*o*-chlorophenyl)ethyl alcohol and *o*-chloroethyl benzene (surface–Cl interaction), and (v) new bands which appear at 1270 and 1295 cm^{-1} (interpreted as residual positive charge on the α-carbon atom).

We think that the γ-Al_2O_3 surface is as well defined in these experiments as it is in a normal gas–solid adsorption experiment. Because of our experimental techniques we unfortunately have no way of measuring the extent of surface coverage in this study.

Acknowledgments

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