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Infrared Study of Adsorbed State of Aniline on Alumina and HCl-treated Alumina

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Infrared spectra of adsorbed aniline on alumina showed bands at 1605, 1575, 1495 and 1470 cm^{-1} in the region of ring stretching vibration. Among these wave numbers, 1605 and 1575 cm^{-1} were attributed to the benzene ring stretching (ν_{16a}) and NH_2 deformation, respectively. The intensity of both bands was decreased in comparison with the band of 1495 cm^{-1} (ν_{13a}) as the adsorption temperature increased. These results could be understood if both benzene ring and amino group had some interaction with the catalyst surface followed by the decrease of resonance effect of the molecule. In the spectra of adsorbed aniline on HCl-treated alumina, the intensity of ν_{13a} decreased more than on pure alumina. It was also found that HCl-treated alumina had exclusively Lewis acidity which was revealed in ir measurement. From these results, the adsorbed state of aniline has been discussed.

INTRODUCTION

It is known that diphenylamine is produced from aniline eliminating ammonia on alumina catalyst at higher temperature (*1*). On the other hand, it was found that the HCl-treated alumina was a good catalyst for this reaction (*2*) and a kinetic study was carried out on the same catalyst (*3*).

To study the mechanism of this reaction, it is valuable to obtain some information on the adsorption state of aniline on alumina and HCl-treated alumina by infrared spectroscopy. Spectroscopic studies of adsorbed aniline on the catalyst surface have been carried out by Terenin *et al.* (*4*) (on SiO_2, Al_2O_3 and SiO_2–Al_2O_3) and Hirota *et al.* (*5*) (on $AlCl_3$) by uv spectroscopy. However, infrared studies by other than Russian workers (*6*) are very few.

On the other hand, infrared spectra of ring stretching vibrations on aromatic compounds has been investigated with respect to the substituent effect (*7*). Recently, the linear relationship between the substituent constant of resonance effect, σ_R^0, and the intensity of the 1500 cm^{-1} and 1600 cm^{-1} bands in monosubstituted benzene has been observed by Katritzky *et al.* (*8*). This fact means that the ring stretching vibration is influenced by the electronic properties of substituents. Aniline has a strong electron donating substituent, the amino group. If aniline forms an adduct such as aniline hydrochloride or aniline boron trifluoride, the electron donating power of the substituent should be decreased. In such a case, if Katritzky's rule is applicable, the infrared spectra of the ring stretching vibration of aniline complexes should be different from aniline in the same way as a substituent which is less electron donating. Similarly, it is expected that the infrared spectra of the ring stretching vibration of aniline chemisorbed on alumina would be affected by special electronic effects if amino groups have some interaction with surface Lewis acid sites.

The present experiments were undertaken to investigate the adsorbed state of aniline on alumina and HCl-treated alumina and to discuss the relationship between electronic effect produced by chemisorption and the relative intensity in the region of ring stretching vibration.

Experimental

1. *Materials.* Alumina used in this work was the fluffy powder "Aluminumoxyd C" of Degussa (West Germany), having a purity of more than 97%, particle diameter 5–30 mμ, surface area 80 m^2/g, and sp.gr. 3.4 g/cc. X-Ray structure of this alumina is designated γ-type by Degussa. Reagent grade aniline was distilled with zinc powder just before the measurements. Special grade diphenylamine (DPA) was recrystallized and aniline hydrochloride was used without further purification. *N*-deuteroaniline was produced by the exchange reaction of aniline with heavy water and products were subjected to distillation *in vacuo.* The deuterium content of these products was about 70% by infrared spectra measurement. Aniline boron trifluoride was prepared by slow addition of aniline to cooled boron trifluoride etherate (*9*). The results of elemental analysis of this compound were as follows; Found (%): N, 6.5; C, 41.4; H, 5.8; Calc. (%): N, 8.1; C, 44.8; H, 4.4.

2. *Procedure.* Alumina was pressed into a disc under 200 kg/cm^2 of pressure. The thickness of a disc was 30 mg/cm^2. After calcination at 500°C for 1 hr, the disc was fixed for ir measurements in a cell which resembled the *in situ* cell used by Amberg *et al.* (*10*) and then evacuated at 500°C for 3 hr. After this pretreatment, aniline vapor was adsorbed on the disc at the given temperature and evacuated at the same temperature. Infrared spectra were recorded at room temperature by a Hitachi type EPI-2 prism spectrophotometer. Infrared spectra of both aniline hydrochloride and aniline boron trifluoride were obtained by the KBr pellet method. HCl treatment of the alumina surface was carried out repeatedly in the cell by exposing the disc to 6 mmHg of HCl for 30 min at room temperature and then evacuating at 470°C for 1 hr.

Results and Discussion

1. *Infrared spectra of aniline adsorbed on alumina at 150°C.* After the pretreatment mentioned above, a known volume of aniline vapor was admitted into the cell at 150°C. The vapor pressure of aniline at room temperature was so small that the amount of adsorption could not be evaluated from equilibrated pressure. Therefore, the admitted amounts were roughly estimated from the volume filled with aniline vapor at room temperature and the times of admittance.

The infrared spectrum obtained at 150°C is shown in Fig. 1a and background is also shown in Fig. 1e. The assignment of the

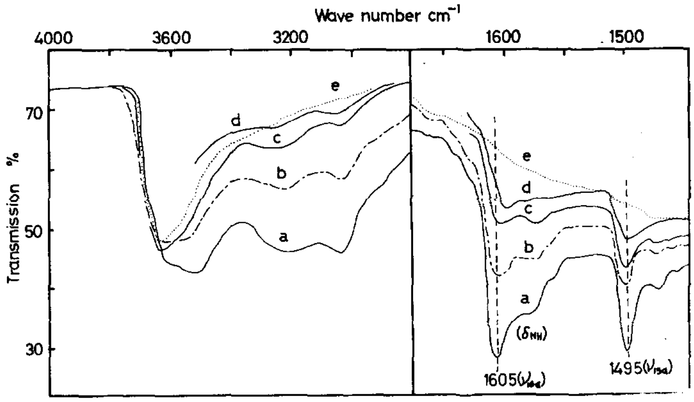


FIG. 1. Infrared spectra of aniline adsorbed on alumina: a. after adsorption of 0.1 ml(STP) of aniline at 150°C for 30 min and evacuation at 150°C for 10 min; b. after exposure to 0.8 mm Hg of aniline at 250°C for 30 min and evacuation at 250°C for 30 min; c. after exposure to 0.8 mm Hg of aniline at 350°C for 30 min and evacuation at 350°C for 30 min; d. after exposure to 0.8 mm Hg of aniline at 450°C for 30 min and evacuation at 450°C for 30 min; e. alumina, after evacuation at 500°C.

spectra was made by comparison with that of liquid aniline, which was explained by Bellamy (*11*). It is known that the NH stretching vibration of aniline is split into the asymmetric vibration at 3481 cm^{-1} and the symmetric vibration at 3395 cm^{-1}. Adsorbed aniline in Fig. 1a showed a broad band at 3240 cm^{-1} due to hydrogen-bonded NH stretching. It cannot be decided in this experiment whether the observed band is single or not.

It is somewhat difficult to identify the four bands observed at 1605, 1575, 1494, and 1470 cm^{-1} in the region of benzene ring stretching vibration. Liquid aniline gives four bands due to NH_2 deformation at 1630 cm^{-1} and ring stretching vibrations ν_{16a}, ν_{13a}, and ν_{13b} at 1605, 1510, and 1465 cm^{-1}, respectively. The bands observed at 1495 and 1470 cm^{-1} in Fig. 1a can be attributed to the ring stretching vibrations ν_{13a} and ν_{13b}. In order to assign the other two bands, the spectra of *N*-deuteroaniline adsorbed on alumina were obtained and the band intensity at 1575 cm^{-1} was observed to be weaker than that of aniline. Therefore, the band at 1575 cm^{-1} is attributed to NH_2 deformation. The fact that the bands due to NH_2 deformation and stretching are observed at considerably lower frequency than those in liquid aniline indicates that amino groups have some interaction with the catalyst surface, such as adsorption onto Lewis acid or hydrogen bonding to surface oxides. It seemed that adsorption of the amino group was not dissociative at 150°C because the bands of NH_2 deformation still remained in the spectra of the adsorbed state. It is also shown in Fig. 1 that the band of the isolated OH groups on alumina (3680 cm^{-1}) shifted to lower frequency (3580 cm^{-1}) and became more broad by aniline adsorption. The similar shift was observed when benzene was adsorbed on the alumina. This could be an indication of the participation of π-bonds in the specific interaction with the OH groups on the alumina surface. It may be the similar interaction as observed in aromatic compounds adsorbed on silica (*12*).

In respect to CN stretching, liquid aniline shows the sharp and intense band at 1280 cm^{-1}, but adsorbed aniline shows a weak and broad band at 1300 cm^{-1} even at large amounts of adsorption.

2. *Spectra of aniline adsorbed on alumina at higher temperatures.* Adsorption of aniline at 250°C and above was carried out as follows. An alumina disc was exposed to 0.8 mmHg of aniline vapor for 30 min. The spectra at 250, 350, and 450°C are illustrated in Fig. 1b, c, and d, respectively. It was observed that the spectra in 1600–1500 cm^{-1} region changed slightly with increasing adsorption temperature. The ν_{16a} band shifts to lower frequency with adsorption temperature and at last to 1590 cm^{-1} at 450°C, while the ν_{13a} band does not shift. Moreover, the intensity of the bands at 1605 and 1575 cm^{-1} decreased compared with 1495 cm^{-1} band with increased adsorption temperature. This behavior is shown in Fig. 2. The decrease in intensity of the NH_2 deformation band suggests some electronic effect resulted from the interaction with the surface.

3. *The spectra of aniline hydrochloride and aniline boron trifluoride.* To interpret the decrease of the ν_{16a} band in Fig. 2, the spectra of both aniline hydrochloride and aniline boron trifluoride were obtained. These are shown in Fig. 3a for the HCl complex and 3b for the BF_3 complex. In both complexes, the intensity of ν_{16a} is very weak compared with ν_{13a}. The spectra of this region are markedly different from that of liquid aniline. Since the extinction coefficient of these bands of complexes was

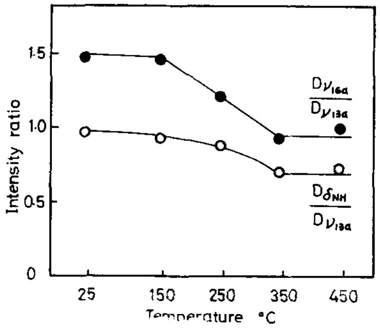


FIG. 2. Relative intensity of 1500–1600 cm^{-1} bands against adsorption temperature. -●-, $D\nu_{16a}/D\nu_{13a}$; -○- $D\delta_{NH}/D\nu_{13a}$.

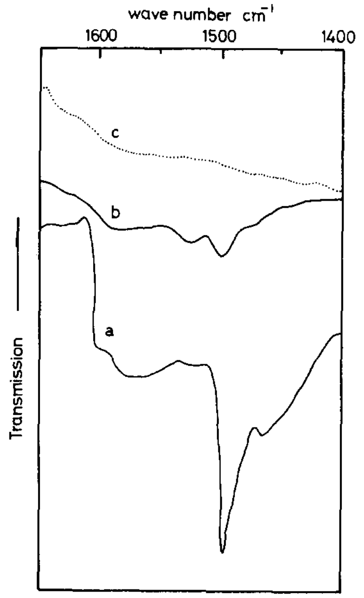
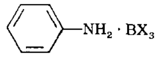
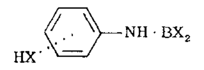


FIG. 3. Infrared spectra of aniline complexes: a. aniline hydrochloride; b. aniline boron trifluoride.

not determined in this experiment, this result cannot be directly compared with Katritzky's rule. However, it may be supposed that the ring stretching bands of aniline were influenced by the decrease of resonance effect caused by complex formation of aniline with HCl or BF$_3$, if the structure of these complexes is a simple acid adduct on amino group. Gerrard and Mooney investigated the structure of complexes of primary aromatic amines with boron trihalides (*9*). They proposed that the structure was not of a simple Lewis acid adduct (I), but of the hydrohalides of arylamine boron dihalides (II).



(I)



(II)

If so, the interpretation of the spectra of the BF$_3$ complex would be more complicated. Although further studies are required to reveal the structure, the decrease of intensity of ν_{16a} in Fig. 2 could be attributed to some kind of complex formation of aniline.

4. *The interaction of adsorbed aniline with HCl.* The infrared spectra of the interaction of HCl with aniline on alumina were recorded. At first, aniline was adsorbed on alumina which preadsorbed HCl sufficiently at 150°C. All spectra were recorded at room temperature. Fig. 4b shows alumina on which HCl was adsorbed. A broad band due to hydrogen-bonded OH groups is observed. It is known that when HCl is adsorbed on alumina, it dissociates to form hydrogen-bonded OH

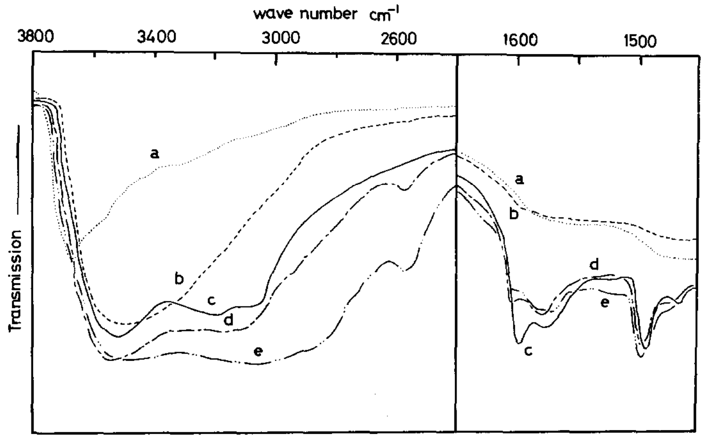


FIG. 4. Interaction of adsorbed aniline with HCl: a. alumina, after evacuation at 500°C; b. after exposure to 30 mm Hg of HCl at 150°C for 30 min and evacuation at 150°C for 10 min; c. after b), contact with aniline at 150°C. d. after c), exposed to 30 mm Hg of HCl at 150°C for 30 min and evacuated at 150°C for 10 min. e. after d), exposed to 30 mm Hg of HCl at room temperature for 15 min and evacuated for 10 min.

groups on alumina (*13*). Fig. 4c shows the adsorbed aniline on such a surface. The intensity of the OH band due to adsorbed HCl was scarcely reduced. If hydrogen-bonded OH groups were Brönsted acids, they should interact with adsorbed aniline and NH_2 groups should be converted to NH_3^+ groups. However, in fact, new bands of NH stretching or deformation due to NH_3^+ groups cannot be observed. This means that OH groups from adsorbed HCl which interact with adsorbed aniline are very few. When further HCl is admitted to the adsorbed aniline, the band intensity of 2300–2800 cm^{-1} region increased and a new band appeared at 2550 cm^{-1}, as shown in Fig. 4d and e. According to Brissette and Sandorfy (*14*), the infrared spectra of aniline hydrochloride showed an NH stretching band at 2810 cm^{-1} and combination bands involving fundamentals of NH_3^+ deformation at 2570 cm^{-1}. Therefore, the spectra obtained in this experiment indicate that the additional HCl in the gas phase interacts with adsorbed aniline to form a hydrogen chloride complex on the alumina surface.

On the other hand, it is illustrated in the spectra of the 1600–1500 cm^{-1} region that this complex formation has a large effect on the ring stretching vibration bands; that is, the intensity of ν_{16a} decreases but that of ν_{19a} remains constant during the addition of HCl; the decrease of intensity means a decrease in the extinction coefficient.

From these results, it seems that new bond formation on the NH_2 group in aniline greatly affects the intensity of ν_{16a}; that is, when the free electron pair of the amino group in aniline is consumed for new bond formation and the extent of the conjugation between the amino group and the benzene ring decreases, the intensity of ν_{16a} decreases. A qualitatively similar effect was observed in a series of monosubstituted benzenes in solution by Katritzky *et al.* (*8*). Accordingly, the decrease of the band at ν_{16a} in Fig. 2 can be interpreted by the interaction of surface Lewis acid sites with the free electron pair of aniline and at higher temperatures aniline more strongly adsorbed on Lewis acid sites would remain on the surface.

5. *Adsorbed aniline on HCl-treated alumina.* It is known that HCl treatment of alumina promotes the catalytic activity for the formation of DPA. From the infrared studies of the reaction of HCl with alumina surface by Peri (*13*), it is concluded that the HCl treatment produces stronger dual acid–base sites than on alumina. In the present work, the effect of HCl treatment on the ring stretching vibration of adsorbed aniline was investigated. Before the adsorption experiment of aniline, the acid properties of the HCl-treated alumina surface were studied by the pyridine adsorption method used by Parry (*15*) and Basila *et al.* (*16*). The result is shown in Fig. 5. The three bands at 1450, 1490, and 1630 cm^{-1} are ascribed to coordinated pyridine. No bands due to the pyridinium ion are observed. Therefore, within the sensitivity of the ir experiments, the surface of HCl-treated alumina has only Lewis acid sites. From this fact, it is presumed that if the Brönsted acidity is present on the halogenating alumina as described by Chapman and Hair (*17*), it is not strong enough to retain a pyridine at the low pressure, because the present data was obtained after evacuation.

The spectra of adsorbed aniline are illustrated in Fig. 6. The intensity ratio of the band of ν_{16a} to that of ν_{19a} was lower than on pure alumina. Taking into account the

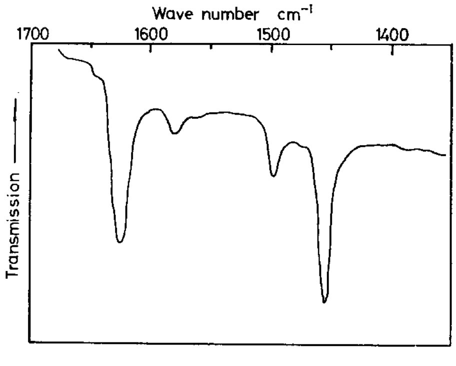


FIG. 5. Infrared spectra of adsorbed pyridine on $HCl\text{-}Al_2O_3$. Pyridine was adsorbed at 150°C.

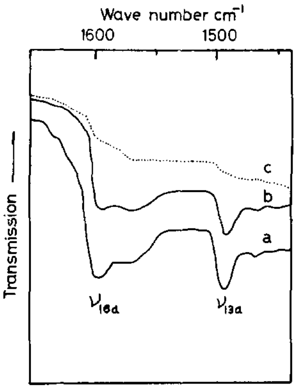


Fig. 6. Infrared spectra of adsorbed aniline on HCl-treated alumina: a. after exposure to 0.8 mm Hg aniline at 250°C for 30 min and evacuation at 250°C for 30 min; b. after exposure to 0.8 mm Hg aniline at 450°C for 30 min and evacuation at 450°C for 30 min; c. HCl-treated alumina.

conclusion mentioned in the last section, this fact could be interpreted in terms of the enhancement of Lewis acidity by HCl treatment.

6. *Spectra of DPA adsorbed on alumina at 470°C.* In Fig. 1, the spectrum of the ring stretching vibration of the adsorbed species at 450°C was somewhat different from other spectra obtained at lower temperatures. Since alumina is also known to be a catalyst for DPA synthesis from aniline, DPA formation is possible at 450°C in this work. Therefore, the spectrum of DPA adsorbed at 470°C was obtained to be compared with Fig. 1. The adsorption procedure was as follows: Very small pieces of DPA crystal to be evaporated were dropped into the cell kept at 470°C from the inlet equipped on the cell. After 10 min, the cell was evacuated for 30 min at the same temperature. The spectra obtained are shown in Fig. 7. Both bands of NH stretching and CH stretching were almost similar to the adsorbed aniline. The band of ν_{16a} was observed at 1590 cm^{-1} which was 15 cm^{-1} lower than in adsorbed aniline. Therefore, the spectrum in Fig. 1 obtained at 450°C is supposed to involve that of DPA formed. An intense band at 1310 cm^{-1} due to CN stretching of adsorbed DPA was observed. In the adsorbed aniline, the CN stretching band was very weak. These facts suggest that the double bond property of the CN bond of DPA was not influenced by adsorption; that is, the conjugation between two benzene rings in DPA could be almost retained in the adsorbed state. This means that the interaction of the free electron pair of nitrogen in the imino group with surface Lewis acid sites is weaker than that of the adsorbed aniline. This interpretation is supported by the fact that aniline is more basic than DPA.

Nevertheless, the result that the adsorption term of DPA is involved in the rate equation for DPA synthesis from aniline (*3*) could be caused by a factor

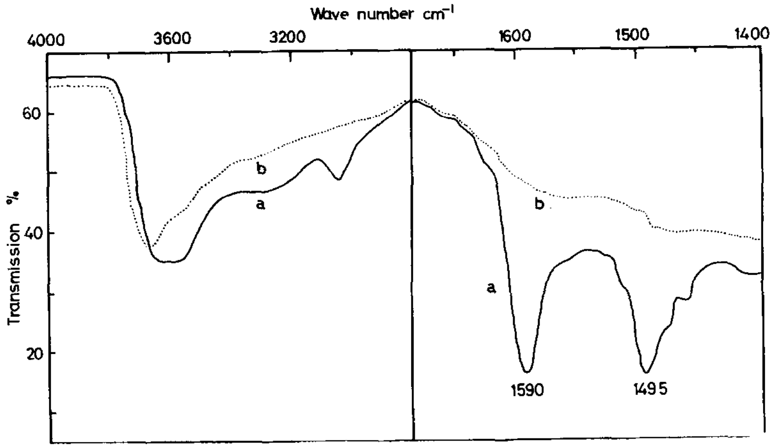


Fig. 7. Infrared spectra of adsorbed DPA on alumina: a. after exposure to DPA at 470°C for 10 min and evacuation at 470°C for 30 min; b. alumina, after evacuation at 500°C.

other than basicity, such as higher boiling point of DPA and others.

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