The Electronic Spectra of Aniline and *N*-Methylaniline Adsorbed on Aluminum Chloride. I

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Recently, the electronic spectra of organic molecules adsorbed on solid catalysts, especially on such cracking catalysts as silica gel and silica-alumina, have been investigated by several authors.(1) The adsorbates studied include benzene derivatives, cata-condensed hydrocarbons, and aromatic amines. On silica gel, these molecules are adsorbed physically or interact with the surface hydroxyl group of the catalysts. On silica-alumina, on the other hand, chemically-adsorbed species are also found. The Lewis-acid nature of silica-alumina is now well known. The molecules chemically adsorbed on silica-alumina either give an electron to the catalyst surface, thus forming cation-radicals, or form a sigma-bond with some electron-accepting center on the catalyst surface by sharing an electron-pair. Such cata-condensed hydrocarbons as anthracene and perylene give cation radicals other than the carbonium ions.(2,3) Aromatic amines form sigma complexes because of the Lewis-base nature of these compounds. In their investigation of aniline adsorbed on silica-alumina, Kotov and Terenin attributed the hypsochromic shift of the 2800 Å band of aniline to the interaction of the adsorbed aniline molecule with some electron-accepting center on the catalyst surface.(4) The aim of the present study is to investigate the interaction of the aniline molecule with aluminum chloride, one of the typical Lewis acids, extending the measurement over the vacuum ultraviolet region.*[2]

Experimental

Materials. — Aluminum chloride was prepared from silver chloride and aluminum foils in vacuo according to Wallace and Willard's procedure.(5) Aniline and *N*-methylaniline of Tokyo-Kasei, G.P. grade, were dried with sodium hydroxide and distilled in vacuo before use. The middle fraction was used for the experiment.

Procedure. — Since the system studied here is very sensitive to moisture, all preparations and measurements were carried out in vacuo. The apparatus used in this experiment is shown in Fig. 1. Aluminum chloride was sublimed, via a break-off seal, into a quartz cell by heating it over a free flame.*[3] The vapor of aniline (or *N*-methylaniline) was then introduced into the cell by opening the stopcock. After evacuation, the electronic spectrum was recorded.

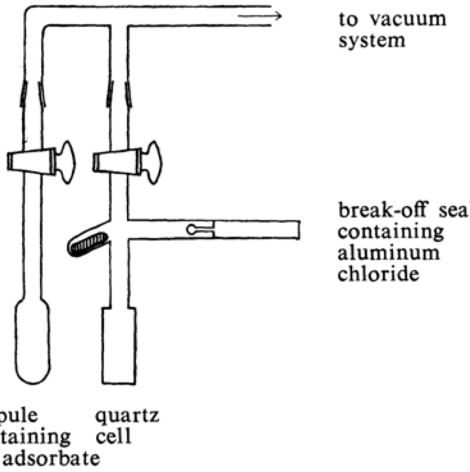

Fig. 1. Apparatus for the absorption study.

The electronic spectra were recorded by a Hitachi recording spectrophotometer model EPS-2 for the 220—340 mμ range; by a Cary recording spectrophotometer model 15 being flushed with dry nitrogen for the 180—300 mμ range, and by a vacuum ultraviolet spectrophotometer constructed in the Institute for Solid State Physics (reported on earlier)(6) for the 150—220 mμ range.

Experimental Results

The observed electronic spectra of adsorbed aniline and *N*-methylaniline are, in Fig. 2,

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1) For a survey of the literature, see H. P. Leftin and M. C. Hobson, Jr., *Advances in Catalysis*, **14**, 115 (1963).

2) W. K. Hall, *Journal of Catalysis*, **1**, 53 (1962).

3) D. M. Brouwer, ibid., **1**, 372 (1962).

4) E. I. Kotov and A. N. Terenin, *Doklady Akad. Nauk S. S. S. R.*, **124**, 865 (1959).

*[2] Kotov and Terenin in Ref. 4 state that, in the case of a molecular complex of aniline with anhydrous aluminum chloride, a similar hypsochromic shift of the 2800 Å band to the spectrum of aniline adsorbed on silica-alumina can be observed, but no further details are given in that article.

5) C. H. Wallace and J. E. Willard, *J. Am. Chem. Soc.*, **72**, 5275 (1950).

*[3] This technique was developed by T. Imanaka; see K. Hirota and T. Imanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 960 (1963).

6) H. Tsubomura, K. Kimura, K. Kaya, J. Tanaka and S. Nagakura, This Bulletin, **37**, 417 (1964).

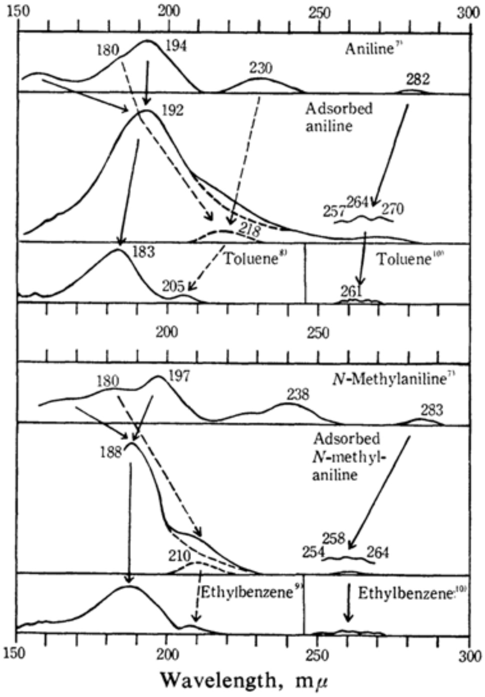

Fig. 2. The electronic spectra of adsorbed aniline and N-methylaniline.
Ordinate: optical density (in arbitary units). The enlarged spectra near 260 mμ are also shown. The spectra of aniline, N-methylaniline (Kimura et al.[7]), toluene (Kimura et al.[8], Am. Petr. Inst.[10]), and ethylbenzene (Hammond et al.[9]) are shown for purposes of comparison. For ethylbenzene, the spectrum around 260 mμ is drawn according to the data of the isooctane solution (Am. Petr. Inst.[10]). The arrows, → and ⇢, indicate the corresponding bands among these spectra. As to the reference spectra, the ordinates indicate qualitatively the strength of the absorption.

compared with those of vapor aniline, vapor N-methylaniline, and vapor alkylbenzenes (cf. Kimura, Tsubomura and Nagakura,[7] Kimura and Nagakura,[8] Hammond, Price, Teegan and Walsh,[9] Am. Petr. Inst.[10]). Because evaporated film was used, no quantitative measurement of the extinction coefficient of the adsorbates could be made. The spectrum of adsorbed aniline consists of a strong band at 192 mμ and a weak band with a vibrational structure around 265 mμ. The former band seems to be accompanied with a band hidden near 218 mμ.

The spectrum of adsorbed N-methylaniline consists of a strong band at 188 mμ, with a shoulder near 210 mμ, and a weak band with a vibrational structure around 260 mμ.

Discussion

The spectrum of aniline has been the subject of many investigations,[7,11-14] and its correlation with the spectra of benzene and alkylbenzenes seems to be well-established. The spectra of adsorbed species can also be interpreted in terms of this correlation (see Fig. 3).

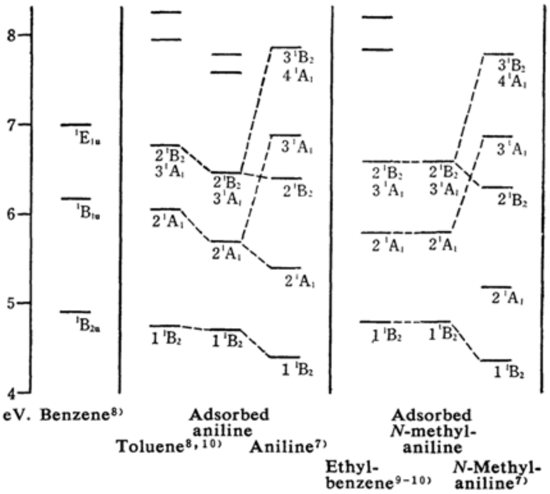

Fig. 3. Correlation diagram of excited states.

The spectrum of adsorbed aniline can be interpreted as follows. The weak band around 265 mμ (with a vibrational structure) is situated just between the 282 mμ band of aniline (broad), and the 261 mμ band of toluene (with a vibrational structure). The strong band at 192 mμ may be correlated with the 194 mμ band of aniline and 183 mμ band of toluene, and the hidden band near 218 mμ, which has something of a charge-transfer character, with the 180 mμ band of aniline and the 205 mμ band of toluene.

The spectrum of adsorbed N-methylaniline is nearly the same as that of ethylbenzene.

Another striking feature of these spectra is the disappearance of the 230 mμ band of aniline and the 238 mμ band of N-methylaniline, i. e., the intramolecular charge-transfer bands of the two.

These characteristics in the spectra of aniline and N-methylaniline can be consistently interpreted in terms of the electron donation from

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7) K. Kimura, H. Tsubomura and S. Nagakura, This Bulletin, **37**, 1336 (1964).

8) K. Kimura and S. Nagakura, *Molecular Physics*, to be published.

9) V. J. Hammond, W. C. Price, J. P. Teegan and A. D. Walsh, *Discussions Faraday Soc.*, **9**, 53 (1950).

10) American Petroleum Institute Research Project No. 44, I (1945).

11) J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 969 (1955).

12) T. E. Peacock, *Molecular Physics*, **3**, 453 (1960).

13) I. Fischer-Hjalmars, *Arkiv för Physik*, **21**, 123 (1961).

14) J. E. Bloor and F. Peradejordi, *Theoret. Chim. Acta* (*Berlin*), **1**, 83 (1962).

the nitrogen atom in the aniline (or *N*-methylaniline) molecule to some electron accepting center on aluminum chloride-evaporated film. This view is supported by the fact that, in the spectrum of adsorbed aniline, the position of the absorption band draws nearer to that of the anilinium ion, which has peaks at 203 mμ and 254 mμ.15) It has been shown by many investigators that, in a sigma complex with Lewis acid, the absorption spectrum is like that of the proton complex, but it generally accompanies some shift.1,16,17) The electron-accepting center is assumed to be the vacant sp^3-orbital of the aluminum atom. This interaction will reduce the electron density on the nitrogen atom, making the intramolecular charge-transfer band vanish and the other part of the spectrum draw nearer to that of alkylbenzenes.

A brief qualitative discussion of the positions of the absorption bands in these spectra will be given here.18) Attention should be paid to the relative location of the intramolecular charge-transfer (CT) configurations and locally excited (LE) configurations in these molecules. In the case of aniline, two CT configurations ($^1A_1$ and $^1B_2$) lie in the region of 5—6 eV., amidst the LE configurations. These lift the degeneracy of the $^1E_{1u}$ state of benzene and cause hypso- and bathochromic shifts of the absorption bands compared with those of benzene, as Fig. 3 shows. In the case of toluene, however, with the CT configurations beyond the LE configurations, the degeneracy of the $^1E_{1u}$ state of benzene is lifted to a much smaller extent and all the absorption bands shift slightly in the red direction. In the case of adsorbed aniline, just the intermediate case can be expected as to the location of CT configurations; i. e., the CT configurations lie higher than in case of aniline, but lower than in the case of toluene. This will make the spectrum nearer to that of toluene, but with a larger red shift of some absorption bands.

The spectra of *N*-methylaniline, adsorbed *N*-methylaniline and ethylbenzene can be discussed in a similar way. In these cases, however, a larger rise in the energy of the CT configurations of adsorbed *N*-methylaniline reduces its spectrum to almost the same as that of ethylbenzene.

Summary

The electronic spectra of aniline and *N*-methylaniline adsorbed on evaporated film of aluminum chloride have been measured (150—300 mμ for the former adsorbate and 185—300 mμ for the latter). In the case of *N*-methylaniline, a spectrum which is nearly the same as that of ethylbenzene has been obtained. In the case of adsorbed aniline, the spectrum shows features intermediate between those of the aniline vapor spectrum and those of the toluene vapor spectrum. These results can be interpreted in terms of the electron donation from the lone-pair electrons on the nitrogen atom of these molecules to some electron-accepting center on aluminum chloride, presumably to the vacant sp^3-orbital of the aluminum atom on the surface, resulting in the weakening of the conjugation between the amino- (or *N*-methylamino-) group and the benzene ring. The positions of the absorption bands are interpreted qualitatively in terms of the relative location of charge-transfer and locally-excited configurations in these molecules.

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15) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, New York (1962), p. 257.

16) C. Reid, *J. Am. Chem. Soc.*, **76**, 3264 (1954).

17) W. I. Aalbersberg, G. J. Hoijtink, E. L. Mackor and W. P. Weijland, *J. Chem. Soc.*, **1959**, 3055.

18) A more detailed discussion will be published later in this Bulletin.

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