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The Electronic Absorption Spectra of UV Irradiated Anilines Adsorbed on Porous Vycor Glass

Tadayoshi SAKATA, Toshihiro OKAI,* Hiroaki SUGIMOTO,** and Hiroshi TSUBOMURA
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

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Synopsis. Cation radicals of aniline and its derivatives were formed on porous Vycor glass plates by UV-irradiation. One of the absorption bands appearing in the visible region is assigned to the transition to the first excited state of the cation radical by comparison with the reported photoelectron spectrum. The charge resonance band of the dimer cation was also observed in the near infrared region in most cases.

The electronic absorption spectra due to the transition to the first electronic excited states of the cation radicals of anilines do not seem to have been observed, although they are expected to exist in the visible or near infrared region both from theoretical calculation[1] and photoelectron spectra (PES)[2–4] of anilines.

The porus Vycor glass (PVG) which adsorbed a large amount of anilines was exposed to ultraviolet (UV) light at 77 K by using a 250 W high pressure mercury lamp and a Toshiba glass filter UV-D25, transparent in the region from 200 to 400 nm.

The electronic absorption spectra obtained after UV-irradiation of aniline (AN), *N*-methylaniline (NMA) *N*,*N*-dimethylaniline (DMA), *N*,*N*-diethylaniline (DEA) *N*,*N*-dimethyl-*p*-toluidine (DMT), and *m*-phenylenediamine (MPD) are shown in Fig. 1. The peak positions of the visible strong bands obtained for the cation radicals of anilines are given in Table 1, together with those reported by others.[5] They agree fairly well with each other, though the absorption shape is rather broader in our case. The reason for this broadening might be attributed to the effect of adsorption or the high concentration of anilines. ESR (electron spin resonance) spectra were observed for the irradiated specimens containing NMA and DMA, which decayed above ~150 K. The electronic absorption spectra also changed remarkably above the same temperature. All these facts suggest that the obtained visible absorption bands are those of the cation radicals of anilines. Besides these bands there appear one or two weak bands at the longer wavelength as seen in Fig. 1.

In order to assign them, we estimated the energies of the first and second excited states of the cation radicals from the results of photoelectron spectroscopy (PES). The results are compared with ours in Table 2, showing that the peak positions of the new bands agree fairly well with those estimated from PES for AN, NMA, and MPD, each having only one new band. Therefore, the first absorption bands of these compounds seem to be attributable to the first excited state of the cation radical.[6]

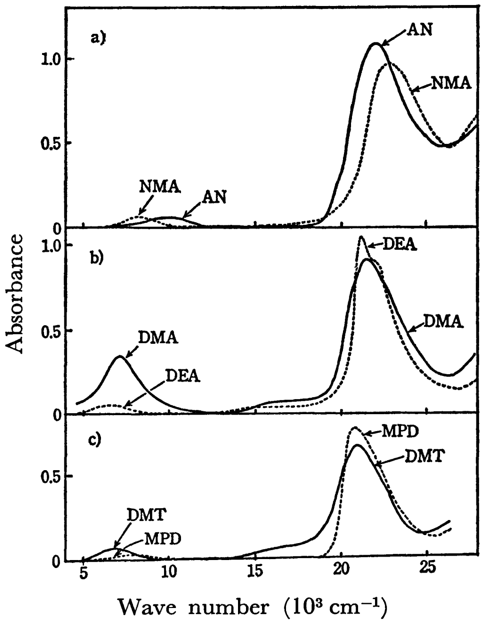

Fig. 1. The absorption spectra of the UV-irradiated anilines.
a) ——: aniline, ----: *N*-methylaniline.
b) ——: *N*,*N*-dimethylaniline, ----: *N*,*N*-diethylaniline.
c) ——: *N*,*N*-dimethyl-*p*-toluidine, ----: *m*-phenylenediamine.

TABLE 1. ABSORPTION MAXIMUM OF THE STRONG BAND IN THE VISIBLE REGION

Anilines	This study	Literature
AN	2.75	2.93[9]
NMA	2.85	2.91[10]
DMA	2.65	2.64[11]
DEA	2.63	2.64[12]
DMT	2.62	2.63[9]
MPD	2.61	2.56[13]

(unit: eV)

TABLE 2. THE ABSORPTION MAXIMA OF THE UV-IRRADIATED ANILINES AND THE FIRST AND SECOND EXCITED STATES OF THE CATION RADICALS ESTIMATED FROM PES

Anilines	This study	PES
AN	1.26, 2.77	1.16, 2.76[2]
NMA	1.04, 2.88	1.30, 2.51[3]
DMA	0.89, ~2.0, 2.65	1.59, 2.43[2]
DEA	0.84, ~1.9, 2.63	1.60, 2.28[3]
DMT	0.83, ~1.9, 2.62	1.59, 2.28[2]
MPD	0.87, 2.61	0.63, 2.54[4]

(unit: eV)

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* Present address: Nippon Paint Co., Ltd., Osaka

** Present address: Central Research Laboratory, Sumitomo Chem. Co., Ltd., Takatsuki, Osaka

There appear two new bands in each of the case of DEA, DMA, and DMT as seen in Fig. 1. The first excited state of the cation radical estimated from PES seems to correspond well to the weak absorption band observed at 500—700 nm in these cases. Then, what is the origin of the near infrared band in these cases ? To clarify this, the change of intensity with temperature from 77 K was followed for the visible band (2.65 eV), the near infrared band, and the ESR absorption of DMA cation. As shown in Fig. 2, all shows similar temperature dependency, indicating that the cation radical of DMA begins to decompose at about 150 K and almost disappears at 270 K[7]. The possibility that these bands are due to solvated electrons can be denied because they do not change by the irradiation in the visible or near infrared region.

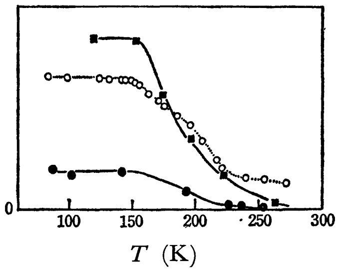

Fig. 2. The temperature dependence of the intensity on the visible band (2.67 eV) (○), the near infrared band (●), and the ESR absorption (■).
As for ESR the ordinate shows the intensity of ESR absorption multiplied by temperature, so that it represents the number of paramagnetic species.

Since in our experiments a large amount of anilines were adsorbed on PVG and only their small part is photoionized, this band can be most reasonably assigned to the charge resonance band of the dimer cation formed between the cation radical and its neutral molecule,[8] not to the charge transfer band of the cation dimers. The weakness of the charge resonance bands can be attributed to the small concentration of the dimer cations.

It is possible in the cases of AN and NMA that similar charge resonance bands exist in the energy region of the first excited band of the cation. Therefore, the observed IR bands for these cases might be a superposition of the cation band and the charge resonance band. This assumption seems fairly reasonable because the charge resonance interaction is thought to be stronger in these cases than in the other three compounds, taking account of the steric hindrance of the methyl group. If one assumes further that the IR bands consist mostly of the charge resonance bands, the excitation energies of these bands are in reasonable sequence as regarded to be the charge resonance bands for all compounds, decreasing in the order, AN, NMA, DMA, DEA, DMT, parallel to the increasing steric hindrance. From the excitation energy of these resonance bands, the intermolecular resonance integrals are estimated to be from 0.4 to 0.5 eV for these dimer cations which seem resonable. For MPD, the corresponding charge resonance band might be located in the longer wavelength region.

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5) Prof. T. Shida of Kyoto University kindly informed us his recent spectral data of the cation radicals of aniline and *N*,*N*-dimethylaniline which are formed in the solid solution by γ radiolysis, according to which the first absorption band of the cation radicals of AN and DMA appears at 900 nm and 650 nm, respectively.

6) The energy and the intensity of the first excited band of AN and MPD cations were calculated by Katsumata and Kimura.[1] Our results agree well with the estimated values.

7) It is due to the unknown chemical products that the intensity of the visible band does not reach to zero.

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