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Electronic Absorption Spectra of Unstable Species Formed by the Ultraviolet Irradiation of *N*,*N*-Dimethylaniline at 77°K

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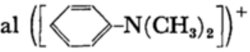
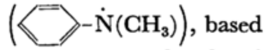
Electronic absorption spectra of unstable species formed by the ultraviolet irradiation of *N*,*N*-dimethylaniline (DMA) were studied in various rigid matrices at 77°K. It was concluded that there are two unstable species which exhibit similar absorption spectra in the visible and the near ultraviolet regions. These species were identified with the cation radical  and the neutral radical , based on various experimental results concerning solvent effect, electron attachment, stimulated emission by the infrared light, *etc*. The molar extinction coefficient of the cation at 470 mμ was found to be about 1200 (*l*/cm·mol).

Studies on the primary photochemical processes of aromatic compounds have been made by use of electronic absorption spectroscopy and ESR technique.[1–9] It has been concluded that there are mainly two different types of processes.[10] One is photoionization and the other is photodissociation. Photoionization occurs predominantly for compounds having relatively low ionization potentials such as *p*-phenylenediamine and its methyl-derivatives.[11,12] On the other hand, photodissociation occurs prevalently for compounds having relatively high ionization potentials such as toluene and *p*-hydroquinone derivatives.[6,13]

Ultraviolet irradiation of *N*,*N*-dimethylaniline (DMA) in EPA (a mixture of ether, isopentane and ethanol) rigid matrix was investigated previously by Lewis *et al.*[3] and by Porter and co-workers.[4–6] They reported two absorption maxima at 3166 and 4590 Å, which they assigned to the *N*-methylanilino radical and the DMA$^+$ cation, respectively. Porter and his collaborators made flash-photolytic experiments on DMA in liquid paraffin solution at room temperature, and obtained absorption bands at 3140 and 4000 Å which were assigned tentatively to the *N*-methylanilino radical.[8]

Recently we have studied the triplet-triplet absorption spectrum of DMA using the flash technique at room temperature.[14] The studies reported here were made to identify the carriers of the absorption bands arising from the ultraviolet irradiation of DMA in the low temperature matrix.

Experimental

Materials. Commercial G. R. grade DMA and *N*-methylaniline (NMA) were purified by distillation from zinc powder under reduced pressure, and kept in a deoxygenated condition. Solvents used as transparent organic matrices were ethanol, MP (1 part methylcyclohexane, 1 part isopentane) and liquid paraffin. Ethanol was purified by fractional distillation. Ether and isopentane were dried with sodium for a day and purified by distillation. Methylcyclohexane and liquid paraffin were purified by passing through a 100 cm column of activated silica gel. About 10^{-3} molar solutions were used in most experiments. All samples examined were deaerated by the freeze-pump-thaw technique.

Apparatus. Absorption spectra were measured with

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1) G. N. Lewis and D. Lipkin, *J. Am. Chem. Soc.*, **64**, 2801 (1942).

2) G. N. Lewis and J. Bigeleisen, *ibid.*, **65**, 520 (1943).

3) G. N. Lewis and J. Bigeleisen, *ibid.*, **65**, 2419, 2424 (1943).

4) I. Norman and G. Porter, *Proc. Roy. Soc.*, **A230**, 339 (1955).

5) G. Porter and F. J. Wright, *Trans. Faraday Soc.*, **51**, 1469 (1955).

6) G. Porter and E. Strachan, *ibid.*, **54**, 2027 (1958).

7) E. J. Land, G. Porter and E. Strachan, *ibid.*, **57**, 1885 (1961).

8) E. J. Land and G. Porter, *ibid.*, **59**, 2027 (1963).

9) N. M. Atherton, E. J. Land and G. Porter, *ibid.*, **59**, 818 (1963).

10) H. Tsubomura, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **89**, 1 (1968).

11) H. Tsubomura, K. Kimura, H. Yamada and M. Kato, *Tetrahedron Letters*, **47**, 4217 (1965).

12) N. Yamamoto, Y. Nakato and H. Tsubomura, This Bulletin, **40**, 451 (1967).

13) K. Kimura, K. Yoshinaga and H. Tsubomura, *J. Phys. Chem.*, **71**, 4485 (1967).

14) K. Kimura, S. Arimitsu, N. Yamamoto and H. Tsubomura, This Bulletin, **41**, 1274 (1968).

a Cary Spectrophotometer, Model 15. The solution in a cylindrical quartz cell 1.3 cm in diameter was immersed in liquid nitrogen contained in a quartz dewar. Photolysis was carried out with a 250-W Ushio high pressure mercury lamp through a Toshiba UV-D25 filter transparent in the wavelength from 250 to 400 mμ. A 500-W Xe-lamp was used as an infrared light source together with a Toshiba IR-D1A filter transparent in the infrared region. Emission spectra and emission decay were measured with an Aminco-Bowman Spectrofluorimeter or a Nalumi RM-23 spectrometer.

Results

Absorption Spectra of Irradiated DMA. When DMA was illuminated in the ultraviolet region at the temperature of liquid nitrogen, the matrix colored yellow. It showed sharp bands in the near ultraviolet region and relatively broad absorption bands in the visible region as shown in Fig. 1. These absorption bands disappeared when the matrix was warmed and did not reappear by refreezing at 77°K. Figure 1 shows the absorption spectra obtained for DMA irradiated in ethanol, MP and liquid paraffin at 77°K.

In the case of non-polar matrices such as MP, illumination of the irradiated DMA in the infrared region diminished the C_1 ($\sim$470 mμ) and C_2 ($\sim$334 mμ) bands as shown by curves 3) and 3′) in Fig. 1 and at the same time the sample emitted blue light.

When a mixture of DMA and diphenyl in a rigid MP matrix was illuminated in the ultraviolet region, a spectrum shown in Fig. 2 was obtained. The absorption band near 400 mμ is identical with that of diphenyl anion.[15,16] When the UV-irradiated sample was treated with infrared light, it was found that the absorption band of the diphenyl anion decreased in intensity slightly, together with C_1 and C_2 bands.

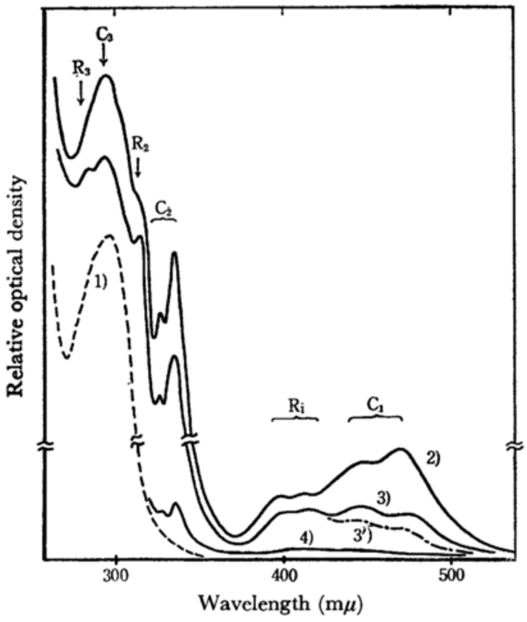

Fig. 1. Electronic absortion spectra of DMA irradiated in various matrices at 77°K. 1: before irradiation; 2, 3, 4: after irradiation in ethanol, MP and liquid paraffin, respectively; 3′: same as 3, after photobleaching by infrared light.

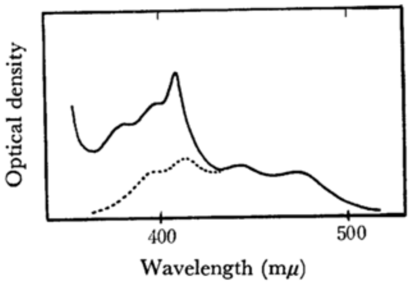

Fig. 2. Electronic absorption spectrum of a mixture of DMA and diphenyl in MP solution irradiated by UV-light at 77°K.

Emission Spectra of Irradiated DMA. A

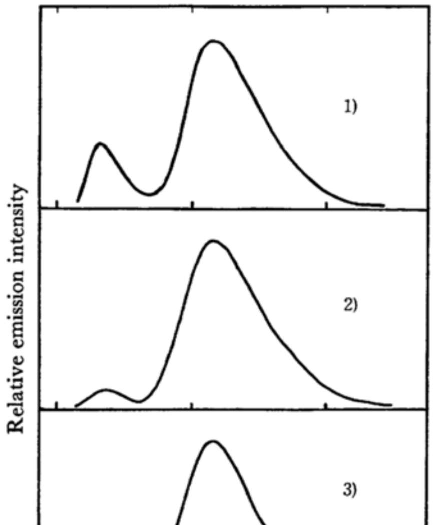

Fig. 3. Luminescence spectra of DMA in MP matrix irradiated in the ultraviolet region.
1, normal fluorescence and phosphorescence spectrum of DMA excited at 300 mμ at 77°K; 2, thermoluminescence; 3, delayed luminescence at 77°K after irradiation.

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15) P. Balk, G. J. Hoijink and J. W. H. Schreurs, *Rec. Trav. Chim.*, **76**, 815 (1957).

16) M. R. Ronayne, J. P. Guariro and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 4230 (1962).

weak emission was observed from DMA irradiated in the non-polar MP matrix even after irradiation was terminated. The emission was stimulated either by illuminating the irradiated matrix in the infrared region or by warming. These luminescence spectra are given in Fig. 3, together with the ordinary emission spectrum of DMA excited by ultraviolet light at 77°K. From Fig. 3, it may be seen that these luminescence spectra are fluorescence and phosphorescence of DMA. The decay of the delayed luminescence at 410 mμ was found to fit in approximately with the first order kinetics with a half-life, $\tau_e=23$ min.

Absorption Spectra of Irradiated NMA. For the purpose of identifying the absorption bands obtained in the case of DMA, we studied the ultraviolet irradiation of *N*-methylaniline (NMA) by a similar procedure. Figure 4 shows the absorption spectra obtained in the case of NMA irradiated in ethanol and MP matrices at 77°K. New absorption bands in the visible and the near ultraviolet regions faded out by warming the matrices. In the case of non-polar matrices such as MP, illumination of the irradiated NMA in the infrared region diminished C_1' ($\sim$450 mμ) band and the spectrum changed from 3) to 3′) as shown in Fig. 4. At the same time, the sample emitted light. Thermoluminescence and delayed luminescence are observed also in the case of the irradiated NMA.

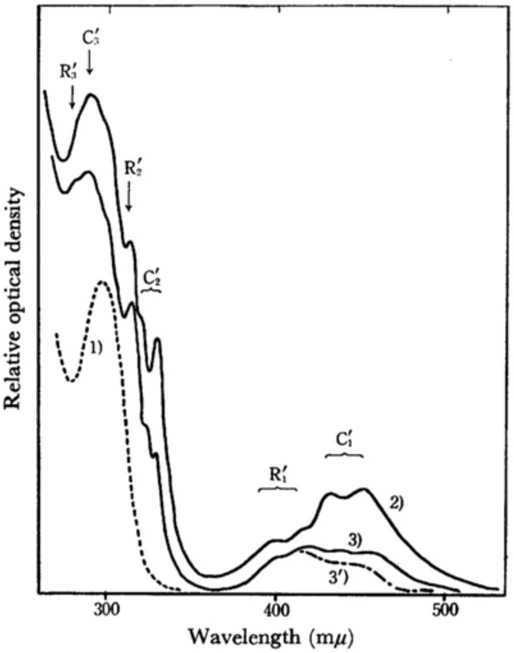

Fig. 4. Electronic absorption spectra of NMA irradiated in various matrices at 77°K.
1: before irradiation; 2,3: after irradiation in ethanol and MP matrices; 3′: same as 3, after photobleaching by infrared light.

Discussion

From inspection of the spectra 2) and 3) in Fig. 1, it may be seen that the absorption spectrum changed with solvents; namely band C_1 is as strong as band R_1 in the non-polar solvents, but much stronger in the polar ones. This shows that there are at least two different species showing absorption in the wavelength region 400—500 mμ. Band C_2 is also stronger in polar medium than in non-polar ones and the ratio of the intensity of the C_2 band to that of the C_1 band is nearly constant. Considering the fact that photoionization occurs more easily in polar solvents than in non-polar ones as observed in the case of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD),[10] absorption bands C_1 and C_2 may be ascribed to the DMA$^+$ cation.

When the DMA irradiated in MP matrix was illuminated in the infrared region, bands C_1 and C_2 decreased in intensity, while the intensity of band R_1 remained the same. This result is quite reasonable, because the action of the infrared light is supposed to excite the electrons trapped in the matrix, to make them mobile till some of them recombine with their parent molecular cations. The diphenyl anion formed in the MP matrix also provides a conclusive proof for the formation of the DMA$^+$ cation. The luminescence stimulated by the infrared light, together with the thermoluminescence, of the irradiated DMA is much stronger in the phosphorescence component compared with the emission of the same sample excited by ultraviolet light. A similar phenomenon is observed for the luminescence of photoionized TMPD.[17,18]

As a results of the experimental analaysis mentioned above, it may be concluded that the absorption bands C_1 and C_2 are assigned to the DMA$^+$ cation.

Similarly, from the experimental results on the absorption and emission spectra of the UV-irradiated NMA, the absorption bands C_1' and C_2' shown in Fig. 4 may be assigned to the NMA$^+$ cation.

It is a little bit more difficult to provide enough evidence for establishing the assignment of the bands which we call R_1 and R_2 for the species formed from DMA and R_1' and R_2' for the species formed from NMA. From the extensive work done by Porter and his group, it has been concluded that fission of the β-bond in the side chain is the main consequence of the photolysis of aromatic compounds. It has also been empirically noticed that a hydrogen atom in the substituent is more easily

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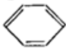
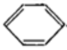
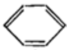
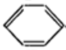
17) E. Dolan and A. C. Albrecht, *J. Chem. Phys.*, **38**, 567 (1963); N. Yamamoto, Y. Nakato and H. Tsubomura, This Bulletin, **39**, 2603 (1966).

18) W. M. McClain and A. C. Albrecht, *J. Chem. Phys.*, **43**, 465 (1965).

photodissociated than a methyl group. Thus, photolysis of $-CH(CH_3)_2$ and $-C(CH_3)_3$ both yield $-\dot{C}(CH_3)_2$.[19] By applying these results to our case, we see that the most probable species formed from the irradiated DMA, except DMA$^+$ cation, must be $-\dot{N}(CH_3)$, and the radical expected from the irradiated NMA must also be $-\dot{N}(CH_3)$.

Bands R_1 and R_1' were not affected by illumination in the infrared light after ultraviolet irradiation at 77°K and their intensities are mostly indifferent to the change of the solvents. It can be seen from our results that bands R_1 and R_2 for DMA is in good agreement with bands R_1' and R_2' for NMA. Thus, it seems quite probable that the species relevant to these bands is *N*-methylanilino radical $-\dot{N}(CH_3)$.

It is also difficult to assign bands C_3 and R_3 shown in Fig. 1. Band C_3 is observed both in ethanol and MP, but band R_3 is observed only in MP. Therefore, we may tentatively assign bands C_3 and R_3 to the DMA$^+$ cation and *N*-methylanilino radical, respectively. As a result of a similar reasoning, the absorption bands C_3' and R_3' shown in Fig. 4 may be assigned to the NMA$^+$ cation and *N*-methylanilino radical, respectively.

N-methylanilino radical and DMA$^+$ cation are π-isoelectronic species and hence they should have very similar electronic spectra. Similarities in the electronic spectra between radicals and cations have been demonstrated in our previous work on *p*-disubstituted aromatics.[12] Therefore, with respect to this view, our conclusion that the C_1, C_2, C_3 bands are for the cation and the R_1, R_2, R_3 bands are for the radical is more reasonable than the assignment of previous authors.

We have found that the weak delayed luminescence emitted from the UV-illuminated DMA shows exponential decay at 77°K. If electrons trapped in the matrix were to migrate in the medium and combine with any of the positive ions distributed at random, the decay of the emission would be of the second order. On the other hand, if the electron returns mostly to its parent positive ion, the decay curve of the emission would be of the first order, in agreement with the experimental results mentioned above.

We also tried to estimate the molar extinction coefficient of DMA$^+$ cation. In the case where a dilute ethanol solution of DMA was irradiated at 77°K, it was observed that only the absorption bands assigned to the DMA$^+$ cation appeared noticeably at the initial stage of irradiation, and the ratio of radical to cation gradually increased as the irradiation was continued. It was also observed that, for a short time of irradiation, the decrease of DMA absorption at 300 mμ was nearly propotional to the increase of DMA$^+$ absorption at 470 mμ. If radical formation is neglected for this short UV-irradiation time, the molar extinction coefficient of DMA$^+$ cation at 470 mμ is found to be about 1200 (l/cm·mol).

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[19] G. Porter and E. Strachan, *Trans. Faraday Soc.*, **54**, 1595 (1958).