The Formation of Crystal Violet by the Reaction of *N, N*-Dimethylaniline with Aluminum Chloride

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As has been reported in a previous paper,[1] aniline and *N*-methylaniline adsorbed on aluminum chloride show electronic absorption spectra which are different from those of gaseous molecules; in these spectra the bands are brought nearer to those of toluene and ethylbenzene. This finding was interpreted from the LCMO point of view, and it was concluded that there was a rise in the ionization potential of the amino- or *N*-methylamino-group on adsorption.[2] It was also assumed that the lone-pair electrons of the nitrogen atom in these molecules interact with an electron-accepting center on aluminum chloride to form a Lewis acid-base type, i. e., a sigma-type complex.[1,2] In this paper, the reaction of *N, N*-dimethylaniline with aluminum chloride will be studied. No molecular complex such as is found in the cases of aniline and *N*-methylaniline is formed. The formation of crystal violet is observed in its stead.

Experimental

Aluminum chloride was prepared from silver chloride and aluminum foils in vacuo according to Wallace and Willard's procedure.[3] *N, N*-Dimethylaniline of the Tokyo Kasei, G. P. grade, was dried with sodium hydroxide and distilled in vacuo before use. The middle fraction was used for the

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[1] H. Sato, K. Hirota and S. Nagakura, This Bulletin, **38**, 962 (1965).

[2] H. Sato, S. Nagakura and K. Hirota, This Bulletin, **38**, 1730 (1965).

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

experiment. Since the system studied here is very sensitive to moisture, the adsorption and spectrometry procedures were carried out in vacuo. The vacuum system apparatus used in this experiment was the same as that already reported,1) except for one point — a glass tube for the ESR measurement was attached directly to the quartz cell. Aluminum chloride was sublimed by heating it over a free flame via a break-off seal into the cell-system composed of the quartz cell and the ESR tube. Then the vapor of *N, N*-dimethylaniline was introduced by opening the stopcock. The electronic spectrum recorded after the evacuation of this cell system did not show the presence of any adsorbed species, contrary to the cases of aniline and *N*-methylaniline.1) Therefore, a larger amount of *N, N*-dimethylaniline was distilled in vacuo into the cell system. The distilled liquid, initially colorless, gradually became blue. This blue color deepened with time, until finally a deep blue solution was obtained. The electronic and ESR spectra of this solution were then recorded. The electronic spectra were recorded by a Hitachi recording spectrophotometer, model EPS-2.

The electronic spectra of commercial crystal violet $C_{25}H_{30}N_3Cl \cdot 9H_2O$ in *N, N*-dimethylaniline and in methanol were also measured for the purpose of comparison.

Results and Discussion

The electronic spectrum of the blue solution is shown in Fig. 1a. It was stable, even for several months, when kept in vacuo. When the cell system was opened to air, however, a muddy greenish color developed (with another absorption band around 400—430 mμ) and a gel-like precipitate (presumably a hydrolyzed product of aluminum chloride) appeared, and finally the liquid phase turned violet. This violet liquid was also obtained when methanol was added to the greenish mixture. The electronic spectrum of this methanol solution is shown in Fig. 1b. No ESR signal was detected for these solutions. In Fig. 2 the electronic spectra of crystal violet in *N, N*-dimethylaniline and in methanol are presented. The spectrum of an aqueous solution (Merrill and Spencer4)) is reproduced in the figure for the sake of convenience. The spectra shown in Fig. 1a and Fig. 1b seem to be identical to those of crystal violet.

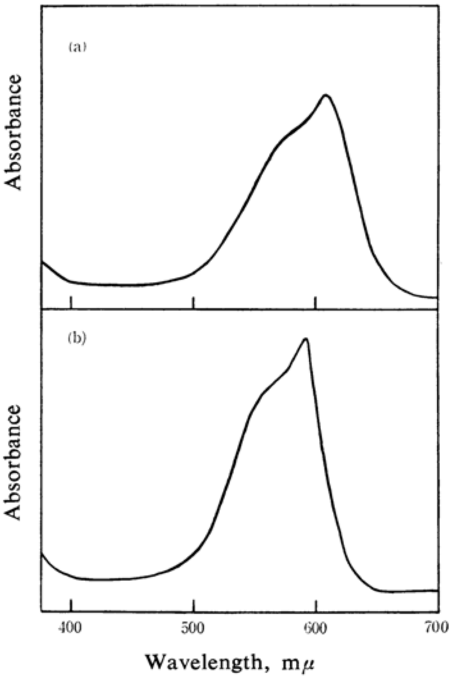

Fig. 1. The electronic spectra of the blue solution obtained by the reaction of *N, N*-dimethylaniline and aluminum chloride (a), and of the violet solution obtained when methanol was added to the reaction mixture (b).

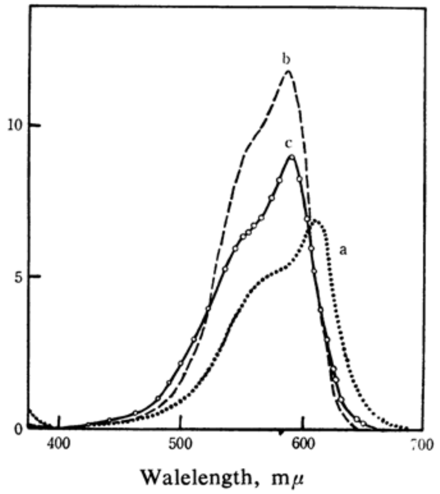

Fig. 2. The electronic spectra of crystal violet.
(a) in *N, N*-dimethylaniline
(1.1×10^{-4} mol./l.)
(b) in methanol (1.1×10^{-5} mol./l.)
(c) in water4) (1.0×10^{-5} mol./l.)
The ordinate shows $10^{-3}\varepsilon$ (ε=molar extinction coefficient) for a and $10^{-4}\varepsilon$ for b and c.

Adams and Rosenstein5) have already shown that a green or a yellow solution is obtained when crystal violet is dissolved in hydrochloric acid (the color depending on the concentration of the acid), and that the color fades in sunlight. According to these authors, such a

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4) R. C. Merrill and R. W. Spencer, ibid., **70**, 3683 (1948).

5) E. Q. Adams and L. Rosenstein, ibid., **36**, 1452 (1914). Analyzing the spectra of crystal violet in hydrochloric acid, these authors proved the presence of three colored species in equilibrium (violet with λ_{max}=590 mμ, green with λ_{max}=630 mμ and yellow with λ_{max} not located). In the present study these findings were reinvestigated and confirmed. The λ_{max} for the yellow species was found to be 430 mμ.

characteristic is common in the chromogens derived from triphenylmethane, and is especially pronounced in the cases of methyl violet and crystal violet. These facts seem to explain what happened when the cell system was opened to air. The moisture reacted with aluminum chloride to give hydrochloric acid and aluminum hydroxide on the surface of the reaction mixture, the acid reacting with crystal violet to give green species. With time this green color was faded by sunlight and/or by the reaction of hydrochloric acid with the remaining *N*, *N*-dimethylaniline. Finally, by the complete reaction with moisture, there developed the violet color which is like the color of crystal violet dissolved in water. These experimental findings seem to prove the presence of crystal violet in the reaction system, though chemical analysis was impossible.

The formation of crystal violet results from the oxidation of *N*, *N*-dimethylaniline by aluminum chloride, though the detailed mechanism of the reaction is not clear. The low ionization potential of *N*, *N*-dimethylaniline will facilitate this reaction. The central carbon atom in the crystal violet may come from the methyl group in the *N*, *N*-dimethylaniline molecule. The formation of crystal violet ions, $C_{25}H_{30}N_3{}^+$, will require one electron per ion to be caught in the gegen-anion or elsewhere. In the present case this electron may rest in the vacant orbital of aluminum chloride. Therefore, the finding that the blue solution gave no ESR signal could be interpreted, among other ways, in terms of the possibility that the electron may be paired in the vacant orbital.

Eastman et al.(6) have observed that *N*, *N*-dimethylaniline and chloranil react to give crystal violet as the final product via the formation of a charge-transfer (CT) complex. Their CT complex has an absorption maximum at 650 mμ. This CT complex has also been found by Briegleb et al.(7) and Mukherjee et al.(8) In the present case also, such a CT complex might be formed during the course of the reaction, though it was not found in the present study.

Summary

The reaction of *N*, *N*-dimethylaniline with aluminum chloride in vacuo has given a deep blue solution. This blue solution turns violet because of moisture or the added methanol. The electronic spectra of these solutions seem to be identical with that of crystal violet. The finding that transient green species appear when the vacuum cell system is opened to air can be interpreted in terms of the color of crystal violet dissolved in hydrochloric acid. From these findings the formation of crystal violet has been concluded.

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6) J. W. Eastman, G. Engelsma and M. Calvin, *J. Am. Chem. Soc.*, **84**, 1339 (1962).

7) G. Briegleb and J. Czekalla, *Z. Electrochem.*, **58**, 249 (1954).

8) D. C. Mukherjee and A. K. Chandra, *J. Phys. Chem.*, **68**, 477 (1964).