The Photo-Ionization of N, N, N', N'-Tetramethyl-p-phenylenediamine in Organic Matrices

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The photolytic formation of Wurster's blue cation from N, N, N', N'-tetramethyl-p-phenylenediamine (TMPD) in an organic rigid matrix is well known after the pioneering research of Lewis and his collaborators.[1] Not much investigation has been made, however, into the behavior of the electron ejected in the matrix, except for the interesting work reported by Dolan and Albrecht.[2]

We have made flash-photolytic experiments of TMPD, using two argon-filled flash lamps, with a total discharge energy of 200—400 joules and the duration of which is less than 4 μsec. In deoxygenated liquid paraffin at room temperature, the flash photolysis of TMPD showed the transient absorption spectrum shown in Fig. 1a. From this result, although there is some difference in spectral position between the curves shown in Fig. 1, it seems certain that Wurster's blue cation is formed in the liquid paraffin solution at room temperature. The transient spectrum decayed exponentially with $\tau_e = 82$ μsec. With deaerated n-heptane solutions, and also with aerated liquid paraffin solutions, no transient spectrum was obtained.

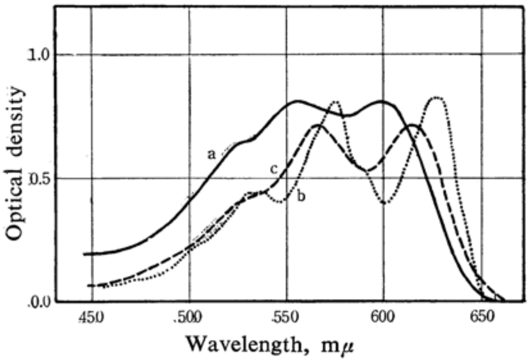

Fig. 1. Absorption spectra of Wurster's blue cation formed

a) by the flash photolysis of TMPD in liquid paraffin at room temperature
b) by the ultraviolet illumination of TMPD in ethanol at 77°K.
c) Absorption spectrum of Wurster's blue perchlorate in ethanol at room temperature.

We have measured the fluorescence and phosphorescence spectra of TMPD at 77°K in ethanol, EPA and MP. These spectra, together with the absorption spectrum, may well be understood as those of the substituted benzenes.[3] In other words, no special band, such as the charge-transfer absorption band or the charge-transfer fluorescence band, appears at all in these solutions. The life-times of the phosphorescence spectrum for ethanol and MP solutions at 77°K have been found to be 1.57 and 2.12 sec. respectively. These life-times are also normal for substituted benzenes. From these results, we can conclude that, on excitation, TMPD goes first into its singlet excited level, and that then some of the molecules return to the ground state, either emitting fluorescence and phosphorescence or radiationlessly, while others are transferred into the ionized state.

The TMPD cation produced by the flash illumination of deoxygenated ethanol solutions has been found to have a surprisingly long life. It returns to the original state after two days, and the experiment can be repeated for several times. In aerated ethanol, only very few cations were formed by a flash with approximately the same energy as that used for deoxygenated solutions, and no transient absorption spectrum was photographed, even if the spectral flash lamp was fired at 10 μsec. after the photolysis flash.[4] We also photo-ionized the deoxygenated ethanol solution by the flash, and then introduced oxygen into the colored solution. The color did not change at all. These results show that oxygen quenches the photo-ionization at the initial stage.

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

[2] E. Dolan and A. C. Albrecht, *J. Chem. Phys.*, **37**, 1149 (1962); **38**, 567 (1963).

[3] K. Kimura and H. Tsubomura, Unpublished results.

[4] The cation in this case stays permanently.