The Photo-Ionization of Molecules in Solutions. II. Electron Transfer from Aromatic Diamine to Pyrene

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(Received March 23, 1966)

We have found that the process of the photo-ionization of *N*, *N*, *N'*, *N'*-tetramethyl-*p*-phenylenediamine (TMPD) in solutions shows interesting differences depending on the nature of the solvent and on the temperature.[1]

The deoxygenated rigid matrix at 77°K composed of 1 part methylcyclohexane and 1 part isopentane (hereafter called MP), which contained 10^{-4} mol./l. TMPD and various concentrations of pyrene (Pyr) (10^{-2}—10^{-4}mol./l.), was illuminated by a Hg lamp at wavelengths between 3000—4000 Å. It showed not only the absorption spectrum of $TMPD^+$, but also that of Pyr^-. The latter is identical with the spectrum obtained by Hoijtink and others by the reduction of Pyr with sodium.[2] The spectrum persists for a long time at 77°K. As there is no sign of complex formation between TMPD and Pyr at either 77°K or 20°C, as may be seen from the absorption spectra, it may reasonably be assumed that they are distributed randomly. Then, we can estimate the mean distances between TMPD and Pyr, which should be proportional to $[Pyr]^{-1/3}$ under conditions where $[Pyr^-] \gg [TMPD^+]$. (Here [ ] means the concentration.) The ratio ω defined by $[Pyr^-]/[TMPD^+]$ can be determined experimentally by the use of the molecular extinction coefficients of both species. The ω values thus obtained are plotted against [Pyr] in curve b, Fig. 1. Here, for instance, $\omega=0.5$ means that one half the electrons ejected from TMPD are trapped in the matrix, while the rest of them reach Pyr. From a simple statistical treatment, we can conclude that, in MP, some of the electrons can travel at least 80 Å away from TMPD. This result may be the first definite proof that the photo-ejected electrons can migrate a considerable distance away from the molecule.

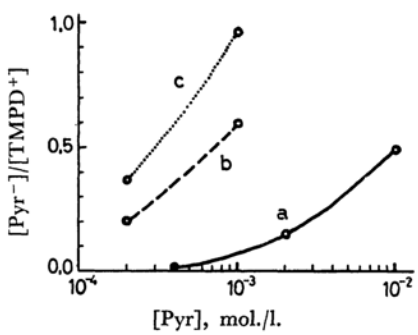

Fig. 1. Formation of ions by ultraviolet excitation of TMPD: a) in EPA matrix, b) in MP matrix, c) the same, illuminated with infrared light. (With prolonged ultraviolet excitation the ratio ω decreases in all three cases.)

By the illumination in the infrared (0.7—5 μ) region, the MP matrix containing $TMPD^+$ and Pyr^- emits light. At the same time, $[TMPD^+]$ slightly decreases and $[Pyr^-]$ largely increases (curve c, Fig. 1). This shows that the electrons trapped in the matrix are excited by the infrared light and migrate randomly in the matrix. The emission is probably due to the fluorescence and phosphorescence of TMPD.[3] By pulling the sample cell in which the ionized species are contained out of the Dewar, a thermoluminescence was observed; when this was measured photographically, it was seen that there is only one band, with a maximum at 476 mμ. We may assume that this emission is due to the transition from the charge transfer state formed by the encounter of $TMPD^+$ and Pyr^- in the half-melting matrix to the ground state.[4]

In degassed EPA matrices at 77°K containing TMPD and Pyr, $TMPD^+$ and Pyr^- are also formed by the ultraviolet excitation. This time, however, the ratio ω is much smaller than that for the MP matrix, showing that more electrons are trapped in the solvent (curve a, Fig. 1). The illumination in the infrared region and down to 6000 Å does not change $[TMPD^+]$ and $[Pyr^-]$, nor does it stimulate the emission. Illumination in the range of the absorption spectrum of Pyr^-, ($\lambda<5000$ Å), lowers the $[Pyr^-]$ value. The color of the solution fades instantaneously as the matrix is warmed, although a small amount of the cation remains for some time. However, no thermoluminescence is observed.

1) H. Tsubomura, N. Yamamoto, K. Kimura, T. Sato, H. Yamada, M. Kato, G. Yamaguchi and Y. Nakato, This Bulletin, **38**, 2021 (1965). The spectrum shown by curve a in Fig. 1 was later concluded to be the T–T' absorption of TMPD. The details for this will be published in a near future.

2) P. Balk, S. deBruijtink and C. J. Hoijtink, *Rec. trav. chim.*, **76**, 907 (1957).

3) Some related phenomena are obtained: K. D. Cadogan and A. C. Albrecht, *J. Chem. Phys.*, **43**, 2550 (1965); J. D. W. Van Voorst and G. J. Hoijtink, ibid., **42**, 3395 (1965).

4) Luminescence from the recombination of organic cations and anions are also reported. E. A. Ckandros, J. W. Longworth and R. E. Visco, *J. Am. Chem. Soc.*, **87**, 3259 (1965).