The Temperature Dependence of the Absorption Spectra of Wurster's Blue-type Ion Radicals

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Hausser and Murrell1) suggested dimer formation in Wurster's Blue solution and assigned the 12000 cm^{-1} band appearing at the temperature of liquid nitrogen to a charge-transfer absorption. We ourselves have previously studied the absorption spectra of *p*-phenylenediamine bromide (I), *N, N*-dimethyl-*p*-phenylenediamine (Wurster's Red) perchlorate (II), and *N, N, N', N'*-tetramethyl-*p*-phenylenediamine (Wurster's Blue) perchlorate solutions (III).2,3)

The spectra of solutions and solids of I and III are shown in Figs. 1 and 2, respectively. The spectra of II are very similar to those of I except for a slight red shift. The concentration dependence of the intensities of the above three compounds can be interpreted as due to the $2R^+ + X^- \rightleftarrows (R_2X)^+$ equilibrium, assuming that the R and Y bands are to be attributed to the monomer, and R', Y', and C, to the dimer. The heats of dimerization are approximately 8, 10, and 5 kcal./mol. for I, II, and III, respectively. The weak binding in III is probably due to the increased steric repulsion between the methyl groups. The similarity of the solid spectra of I and II to those of the dimer suggests that the radicals exist as dimers in the solids; this is in accordance with ESR studies in this laboratory. The spectra of the solid of III at room temperature resemble those of the monomer, but this does not necessarily mean that the spectra are to be attributed to the monomer, for the main features of the spectra are preserved at low temperatures, where a weak charge-transfer band, C', is observed. Two types of models have been proposed for the low temperature solid of III, i. e., the doublet$\rightleftarrows$singlet1) and singlet$\rightleftarrows$triplet4) models. The concentration of the singlet dimer at the nitrogen temperature estimated from the magnetic susceptibility5) is larger than 85%. The contradiction between the spectroscopic and magnetic data may be eliminated by assuming that the dimers are so loosely bound that the electronic states of the radicals are only slightly perturbed by the dimerization. This "loosely bound" model explains that the low temperature solid spectra are similar to the monomer spectra accompanied by a weak charge-transfer band.6)

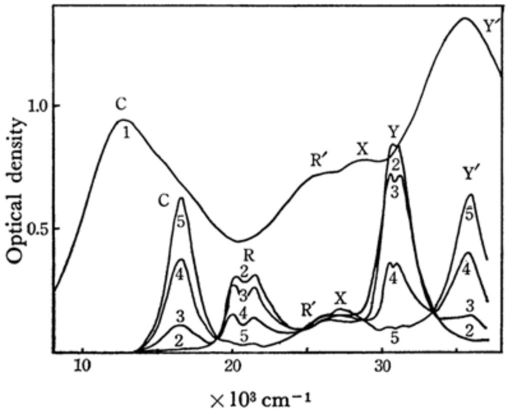

Fig. 1. Spectra of *p*-phenylenediamine radicals. Curve 1: solid (22°C), 2: solution (22°C), 3: solution (−78°C), 4: solution (−99°C), 5; solution (−129°C). Stoichiometric concentration ca. 4×10^{-5} mol./l. Optical path length 1.00 cm. Volume changes of the cell and the solution by cooling were calibrated.

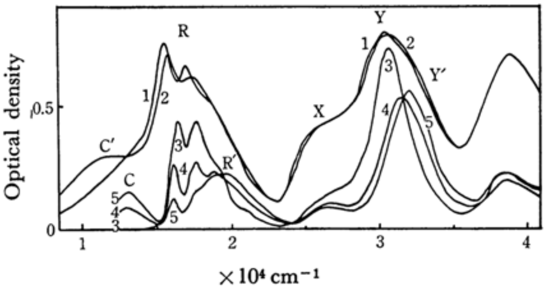

Fig. 2. Spectra of Wurster's Blue. Curve 1: solid (22°C), 2: solid (−196°C), 3: solution (22°C), 4: solution (−149°C), 5: solution (−160°C). Stoichiometric concentration of the solution: 7.58×10^{-5} mol./l. Solvent: ether-alcohol (1 : 2). Optical path length: 0.50 cm. Volume changes of the cell and the solution by cooling were calibrated.

A detailed report will be published later elsewhere.

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1) K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 5000 (1957).

2) A part of this work was presented at the 18 th Annual Meeting of the Chemical Society of Japan, April, 1965.

3) S. Nagakura, J. Tanaka and T. Sakata have also obtained the spectra of Wurster's Blue in alcoholic solution. It was presented at the 18th Annual Meeting of the Chemical Society of Japan, April, 1965.

4) D. D. Thoams, H. Keller and H. M. McConnell, *J. Chem. Phys.* **39**, 2321 (1963).

5) Data of K. Okumura (*J. Phys. Soc. Japan*, **18**, 69 (1963)) was used.

6) Boyd and Phillips recently obtained solution spectra of TCNQ anion radical and analyzed their results by assuming the simple dimerization equilibrium. Their heat of dimerization is of the same order of magnitude with those of II and III (*J. Chem. Phys.*, **43**, 2927 (1965)).