Photochemistry of Nitrobenzene in Concentrated Sulfuric Acid

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Brand *et al.*[1] investigated the electronic spectra of nitrobenzene and its derivatives in concentrated and fuming sulfuric acid and found new absorption bands which they attributed to the protonated form. They obtained the following results for nitrobenzene: (1) The molar ratio of the ionized species against the neutral molecules is very low in the concentrated acid, while it is very large in the fuming acid (for example, following figures can be obtained from their data: 4.5% of nitrobenzene is ionized in 99.55% H_2SO_4, 46% in 100.05% H_2SO_4 and 99.9% in 101.97% H_2SO_4) and (2) the intensity of the band of the protonated form (at 348 mμ) decreases exponentially with time.[2] These authors assumed that protonation occurred on the nitro group. The theoretical study of the electronic spectrum of nitrobenzene[3] has shown that the 250 mμ band is a charge-transfer (CT) band, with the benzene ring as the electron donor and the nitro group as the electron acceptor. We have studied the behavior of nitrobenzene excited at the region of this CT band in concentrated sulfuric acid (in this medium the CT band is shifted to 290 mμ).

Experimental

Nitrobenzene was recrystallized several times and then distilled over phosphorus pentoxide. Sulfuric acid (98%) of G. R. grade and fuming sulfuric acid (containing 60% SO_3) of E. P. grade were used without further purification. Solutions of nitrobenzene in these acids (*ca.* 10^{-5} mol/*l*) were irradiated with an Ushio high-pressure mercury lamp (250 W) in fused quartz cells. To excite only the CT band, a Toshiba UV-25 or UV-27 filter was used. The electronic spectra were recorded with a Cary recording spectrophotometer model 15.

Results and Discussion

The electronic spectra of nitrobenzene in 98% sulfuric acid before and after the irradiation are shown in Fig. 1. Irradiation produced a new band at 355 mμ (band P). No ESR signal was detected for this solution. On prolonged irradiation the band P at first increased in intensity at the expence of the 290 mμ band of nitrobenzene,

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[1] J. C. D. Brand, *J. Chem. Soc.*, **1950**, 997, 1004; J. C. D. Brand and M. B. Thornley, *ibid.*, **1952**, 1374.

[2] Gillespie *et al.* carried out the conductivity measurements for nitrobenzene and its derivatives dissolved in 100% sulfuric acid and found that the conductivity increases with increasing concentration of the solute. From this result they concluded that the solute is ionized. The values of the basic dissociation constant, $K_b=[BH^+][HSO_4^-]/[B]$ determined from their measurements was in good agreement with those of K_b's obtained from the spectroscopic study of Brand *et al.*[1] The values of K_b's obtained by Gillespie *et al.* by cryoscopic measurements also agree reasonably well with those values: R. J. Gillespie and C. Solomons, *J. Chem. Soc.*, **1957**, 1796.

[3] S. Nagakura, M. Kojima and Y. Maruyama, *J. Mol. Spectroscopy*, **13**, 174 (1964).

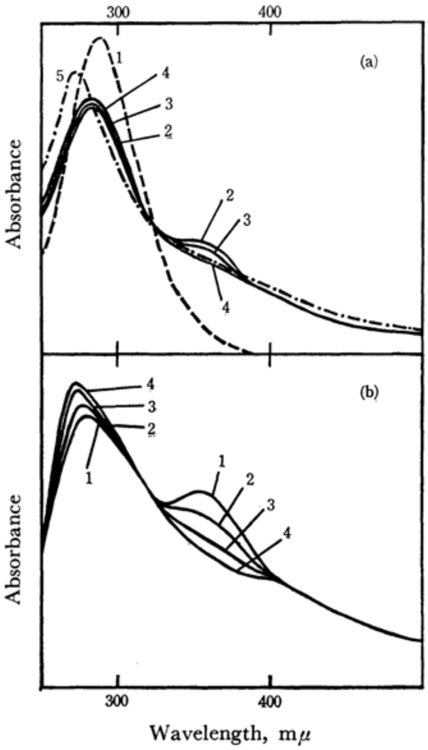

Fig. 1. The absoption spectra of nitrobenzene irradiated in concentrated sulfuric acid (98%).

(a) 1: before irradiation; 2: after irradiation for 10 min; 3: after irradiation for 10 min, kept in the dark for 30 min at room temperature; 4: after irradiation for 10 min, kept in the dark for 2 hr at room temperature; 5: after irradiation for 20 min.

(b) 1: after irradiation for 10 min; 2—4: after irradiation for 10 min, kept in the dark (at 50°C) for 5, 20 and 45 min, respectively.

but after attaining a certain maximum intensity it decreased in intensity with an appearance of a band at 270 mμ (the band X). If the irradiation was ceased when the band P attained its maximum intensity and then the solution was kept in the dark, the band P gradually decreased in intensity. This decay was accompanied by the change in the 270—290 mμ region of the spectrum, as shown in Fig. 1, which seems to occur by the appearance of the band X and by the partial recovery of the 290 mμ band of nitrobenzene. While the former predominates at higher temperature (*e. g.* 50°C), both seem to occur at room temperature. The decay of the band P was found to obey the first order reaction kinetics for 40°C, 50°C and 60°C, the half life being 15, 9, and 5 min, respectively.

Brand1) observed that the 348 mμ band in fuming sulfuric acid decayed with time. According to the present authors' experiment for solution of nitrobenzene in fuming sulfuric acid (containing 30% SO_3), this decay was accompanied by an appearance of a band at 270 mμ. An isosbestic point was found in this spectral change.

Thus, there are many similarities between the behavior of nitrobenzene in 98% sulfuric acid under the CT excitation and that in fuming sulfuric acid in the dark. It is, therefore, tempting to attribute the species giving the band P to the protonated species. This species has, however, a too long lifetime to be assigned to the species protonated in the excited state and give a little difference in the position of the band (355 mμ and 348 mμ). Therefore, no definite conclusion should be drawn at present as to the species giving the band P. The nature of the species giving the 270 mμ band is also left for future study.