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INTERACTION OF AROMATIC AMINES WITH PYROMELLITIC DIANHYDRIDE

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It is known that condensation of pyromellitic dianhydride with aromatic diamines in a solution of dipolar aprotic solvents (dimethylformamide, dimethylacetamide, dimethyl sulfoxide, etc.) leads to the formation of soluble polyamic acids, from which, by subsequent intramolecular cyclization, high-temperature-resistant aromatic polyimides are obtained (1,2):

$$n\,(\text{pyromellitic dianhydride}) + n\,\mathrm{H_2NRNH_2} \longrightarrow \left[\begin{array}{c}\text{HOOC—aromatic ring—COOH}\\ \text{—NH—OC—aromatic ring—CO—NH—R—}\end{array}\right]_n \xrightarrow{-2n\mathrm{H_2O}}$$

$$\longrightarrow [\text{—N(CO)—aromatic ring—(CO)N—R—}]_n\,.$$

Since pyromellitic dianhydride is an electron acceptor (3), while aromatic diamines are characterized by a low ionization potential (6-7 eV), one may expect, in the course of the reaction, the formation of charge-transfer complexes between the reacting molecules:

$$\text{Anhydride} + \text{Amine} \rightleftarrows (\text{Anhydride}^{-} \ldots \text{Amine}^{+}).$$

This is indicated by the intense coloration that appears upon addition of pyromellitic dianhydride to a solution of the diamine, which, as is known, is a characteristic feature of charge-transfer complexes formed by strong electron acceptors and donors. However, the coloration is unstable, owing to the fact that the transfer of an electron is followed very rapidly by transfer of a proton from the amine to the anhydride group and by formation of an amide bond:

$$[\text{pyromellitic dianhydride}^{\cdot-} \ldots {}^{+}\mathrm{H_2NRNH_2}] \longrightarrow \text{amide-acid derivative}$$

and therefore the intermediate colored products that form cannot be identified with ordinary spectrophotometric instruments.

Fig. 1

Figure 1: Fig. 1

We have studied the ability of pyromellitic dianhydride to form charge-transfer complexes with aromatic diamines in the model system pyromellitic dianhydride —tetramethyl-*p*-phenylenediamine, which makes it possible to investigate only the electron-transfer process.

The study was carried out by spectroscopic methods. Absorption spectra in the visible region were recorded on an SF-4 spectrophotometer, and EPR spectra on an EPR-2 spectrometer. Absorption spectra in the visible region were recorded in quartz cuvettes 8 mm thick. The reagent concentrations were 10^{-2} mol/l. Dimethylformamide was used as solvent. The solutions were prepared in vacuo by condensing definite amounts of solvent into ampoules containing the initial amine and the anhydride separately; the solutions were mixed and the cuvette was filled with the resulting mixture. The solutions for studying the EPR spectra were prepared in an analogous manner. In this case the reagent concentrations were ~ 0.3 mol/l. Pyromellitic dianhydride was obtained by treating pyromellitic acid with acetic anhydride. After isolation it was sublimed in vacuo at 280°. Melting point 286°. Tetramethyl-*n*-phenylenediamine was obtained by decarboxylation of *n*-phenylenediaminetetraacetic acid in vacuo at 180°. The product was then distilled twice in vacuo at 40° and used freshly distilled. Melting point 50–51°.

Fig. 1. Absorption spectrum in the visible region of the system pyromellitic dianhydride—tetramethyl-*n*-phenylenediamine in dimethylformamide. *a*—in vacuo, *b*—in an oxygen atmosphere.

In Fig. 1 (spectrum *a*) is shown the absorption spectrum in the visible region of the system pyromellitic dianhydride—tetramethyl-*n*-phenylenediamine in dimethylformamide (concentration of pyromellitic dianhydride $9.1 \cdot 10^{-2}$ mol/l and of tetramethyl-*n*-phenylenediamine $3.18 \cdot 10^{-2}$ mol/l). As can be seen, absorption is observed at 590 and 650 mµ, characteristic of the cation-radical of tetramethyl-*n*-phenylenediamine (4). In the literature we did not find $\lambda_{\max}$ for the anion-radical of pyromellitic dianhydride; however, Ward showed (5) that on irradiation with UV light of a solution of pyromellitic dianhydride in tetrahydrofuran, anion-radicals of pyromellitic dianhydride are formed. Measurement of the change in optical density of a solution of pyromellitic dianhydride in tetrahydrofuran after irradiation with UV light enabled us to establish that $\lambda_{\max}$ for the anion-radical of pyromellitic dianhydride is ~ 445 mµ. In the spectrum of the system pyromellitic dianhydride—tetramethyl-*n*-phenylenediamine in dimethylformamide (Fig. 1*a*) there is also absorption in this region.

Thus, in a solution of the system pyromellitic dianhydride—tetramethyl-*n*-phenylenediamine in dimethylformamide, amine cation-radicals and anhydride anion-radicals were detected, which indicates the formation of a charge-transfer

Fig. 2. EPR spectrum of the pyromellitic dianhydride—tetramethyl-p-phenylenediamine system in an oxygen atmosphere

Figure 2: Fig. 2. EPR spectrum of the pyromellitic dianhydride—tetramethyl-p-phenylenediamine system in an oxygen atmosphere

complex dissociating into ion-radicals owing to the high dielectric constant of the solvent (dimethylformamide 36.7).

It is known (⁴) that the extinction coefficient of the cation-radical of tetramethyl-*n*-phenylenediamine is 1600 (λ_{max} 575 mμ) and, consequently, the concentration of cation-radicals is:

$$C = \frac{0.538}{1600 \cdot 0.8} = 4.2 \cdot 10^{-5} \text{ mol/l},$$

and the equilibrium constant of the reaction

$$\text{Anhydride} + \text{Amine} \overset{K_p}{\rightleftarrows} (\text{Anhydride}^{-} \ldots \text{Amine}^{+}) \overset{K_p}{\rightleftarrows} \text{Anhydride}^{-} + \text{Amine}^{+} \quad (1)$$

is $6.1 \cdot 10^{-6}$ (assuming that the concentrations of cation- and anion-radicals

are equal). The very small value of the equilibrium constant of this reaction makes measurement of the EPR spectrum impossible.

When oxygen is admitted into a cuvette containing a solution of pyromellitic dianhydride and tetramethyl-*p*-phenylenediamine in dimethylformamide, the color of the solution changes from greenish to violet. At the same time the absorption spectrum of the solution changes (Fig. 1b). As can be seen from the figure, the concentration of amine cation-radicals increases, while that of anhydride anion-radicals decreases. Nitric oxide acts similarly, but to an even greater degree. This is apparently the result of interaction of oxygen or nitric oxide, which are electron acceptors, with anion-radicals of pyromellitic dianhydride, acting as electron donors, since their ionization potential should be close to the electron affinity of pyromellitic dianhydride and, consequently, very low:

Fig. 2. EPR spectrum of the pyromellitic dianhydride—tetramethyl-*p*-phenylenediamine system in an oxygen atmosphere

$$O_2 + \text{Anhydride}^{-} \rightarrow O_2^{-} + \text{Anhydride}.$$

Thus, this reaction should lead to the formation of oxygen anion-radicals O_2^{-} (or, in the case of nitric oxide, the anion NO^{-}), to removal of anhydride anion-radicals from the system and, consequently, to a shift of the equilibrium of reaction (1) toward formation of the amine cation-radicals, which is indeed observed in the absorption spectra. In this case an EPR signal appears (Fig. 2), representing a superposition of two radicals—a singlet, apparently belonging to the O_2^- anion-radical, and the hyperfine structure of the amine cation-radical.

It should be noted that, in the absence of pyromellitic dianhydride, oxidation of tetramethyl-*p*-phenylenediamine by oxygen and nitric oxide does not occur under these conditions.

The effect we observed of oxygen and nitric oxide on the pyromellitic dianhydride—tetramethyl-*p*-phenylenediamine system probably has a general character for charge-transfer complexes dissociated into ion-radicals. Thus, when oxygen is introduced into a solution of the chloranil—tetramethyl-*p*-phenylenediamine system in dimethylformamide, an increase in the concentration of amine cation-radicals and a decrease in the concentration of chloranil anion-radicals are also observed. Thus, oxygen is responsible for the instability of this system, which was noted by Eastman et al. (^{6}). It should also be noted that the action of oxygen is reversible, i.e., upon evacuation of the solution the system returns to its initial state.

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