Electron Donor-Acceptor Interaction between Piperidine & 7,7,8,8-Tetracyanoquinodimethane

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The reaction between 7,7,8,8-tetracyanoquinodimethane (TCNQ) and piperidine (PD) has been studied spectrophotometrically and by PMR spectroscopy in chloroform. The results indicate the formation of nucleophilic substitution products both 1:1 and 1:2 (TCNQ-PD) via an inner complex as intermediate with the elimination of hydrogen cyanide.

7,7,8,8- Tetracyanoquinodimethane (TCNQ) is a strong π-acceptor with an electron affinity of 1.7 eV on Briegleb's scale¹ and its acceptor strength is comparable to those of tetracyanoethylene² and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone³. The authors, very recently, reported⁴ the interaction between piperidine (PD), a strong n-donor and 1,4-benzoquinone, a weak π-acceptor. TCNQ containing different exocyclic groups may differ much in its reactivity⁵ towards PD and hence, the authors undertook the present study of the molecular interaction between PD and TCNQ in chloroform.

TCNQ (Fluka, purum) was used as such. Piperidine (PD) and methyl substituted PDs viz. 4-methyl, 3-methyl, 2-methyl, N-methyl, 3,5-dimethyl and 2,6-dimethyl PDs (all Fluka samples) were purified as reported earlier⁴. Chloroform (BDH, specpure) was used after further purification⁶. CZ UV-VIS spectord and speckol spectrophotometers were used for recording the spectra and absorbance measurements, respectively, using solvent blank, with matched, stoppered corex cells of 1 cm path. PMR spectra were recorded on a Perkin-Elmer R32 spectrometer, operating at 90 MHz, by locking the chloroform signal at 7.25 δ.

The spectrophotometric investigations were carried out at two different concentrations of PD.

Absorption spectra for the equimolar components—The time dependent absorption spectra for equimolar mixture of TCNQ and PD in chloroform were recorded. Immediately on mixing it a green coloured solution resulted which exhibited λ_max at 741 and 838 nm, characteristic of the TCNQ anion radical⁷. But the green colour was slowly transformed to a blue colour having λ_max at 582 nm. Similar radical formation was noticed with other methyl substituted PDs such as α, β and γ-methyl piperidines, N-methyl piperidine, 2,5-dimethyl piperidine and 2,6-dimethyl piperidine.

In the presence of excess of PD (250-fold to that of TCNQ) the blue colour in solution was transformed to a stable yellow colour, with λ_max 460 nm. Most of the nitrogen bases immediately react with strong organic π-acids to form monosubstituted products which are subsequently transformed to give a final, generally, disubstituted product⁸,⁹.

The absorption maxima, in the present investigation, at 582 (for equimolar solution) and 460 nm (for solutions containing excess PD) may be due to mono- and disubstitution products. The possibility of nucleophilic substitution during the reaction of TCNQ with PDs was indicated by a positive palladium-dimethyl glyoxime-nickel test¹⁰ for HCN shown by the blue and yellow coloured solutions.

Attempts to isolate solid products at any stage of the reaction were unsuccessful. However, PMR spectra of PD and 1:1 and 1:2 mixtures of TCNQ and PD recorded in chloroform at 90 MHz provided clear indication of the interaction between TCNQ and PD. Thus the signal at δ 2.05, due to NH proton of PD (0.05 M in CHCl₃) disappeared in the spectra of 1:1 and 1:2 mixtures (TCNQ-PD). Further the signals due to α-H and β, γ-Hs of PD appearing at δ 2.74 and 1.51 respectively registered a downfield shift and appeared at δ 3.19, 1.74 and δ 3.30, 1.75 in 1:1 and 1:2 mixtures. The intensity ratio of N-H, α-H and β, γ-Hs in PD was 1:4:6 while intensity ratio of α-H and β, γ-Hs in 1:1 and 1:2 mixtures was 2:3.

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