Interaction of Nicotine with $\pi$ and $\sigma$ Electron Acceptors

M. M. A. Hamed

Received November 23, 1992; Revised April 22, 1993

Interaction of nicotine with tetracyanoethylene and iodine was investigated spectrophotometrically and found to form strong CT complexes ($n-\pi$ and $n-\sigma^*$, respectively). The donor site involved in CT interaction is the pyrrolidine nitrogen. The nicotine-I$_2$ complex exists as the ionic structure (nicotine) I$^+$ - I$_3^-$. Formation constants of the CT complexes in various solvents were determined from 10 to 25°C and are discussed in terms of the nature of the electron acceptor and solvent polarity. Solid CT complexes were synthesized and were characterized by microchemical analysis and infrared spectra techniques.

KEY WORDS: Molecular complexes, solvent effect, stability, solid CT complexes, nicotine.

1. Introduction

Generally charge-transfer complexes play an important role in biological systems as well as in the analytical field. For example, the formation of CT complexes between alkaloids and $\sigma$ or $\pi$-electron acceptors has been widely used for spectrophotometric determination of these biologically important compounds. However, the literature survey reveals that little attention has been paid to thermodynamic and electronic spectral characteristics of the formed CT complexes of alkaloids. Abu-Eittah et al. investigated the CT complexes of some ephedrines with iodine and they deduced that such CT complexes are of the $n-\sigma^*$ type. Since the literature does not contain any information on the CT complexes of the biologically important nicotine compound, the present article is devoted to the investigation of the CT interactions of this compound with tetracyanoethylene, TCNE (as $\pi$-acceptor) and with
iodine (as σ- acceptor). Synthesis and characterization of the CT complexes were carried out. Moreover electronic spectral characteristics and stability of these CT complexes were examined and discussed in terms of the nature of both the electron acceptor and solvent employed.

2. Experimental

2.1. Materials and Solutions

Nicotine, 3-(1-methyl-2-pyrrolidinyl)pyridine was of A.R. grade (BDH). TCNE (Merck reagent) was recrystallized twice from chlorobenzene. Analytical grade iodine was used and its concentration in solution was checked spectrophotometrically. All solvents used were of spectral grade (BDH). Stock solutions of nicotine or of acceptors were freshly prepared in deoxygenated solvent prior to use. Computation was based on unweighted linear least squares fits.

2.2. Physical Measurements

Electronic spectra were recorded on a CECIL CE 599 Spectrophotometer equipped with a temperature controlled cell holder thermostatted to ±0.5°C. IR spectra of the solid CT complexes carried out using a PERKIN-ELMER 599 B IR spectrophotometer.

2.3. Synthesis of Solid CT Complexes

The nicotine-TCNE solid CT complex was synthesized by mixing the donor (in excess 3.0 mmol) and acceptor (2.5 mmol) solutions, each dissolved in the least amount of CH₂Cl₂. On the other hand, the nicotine-I₂ CT complex was prepared by mixing dichloromethane solution of nicotine (2.2 mmol) with that of I₂ (in excess, 3.2 mmol). In both cases the reaction mixture was left at room temperature for 3 h. The solid CT complexes which separated out were filtered and washed several times with minimum amounts of ethanol and dried. The analytical data of the prepared complexes (C, H, N, I) along with some of their physical properties viz. color and melting point are listed in Table I. The iodine content was estimated spectrophotometrically as triiodide ion.

3. Results and Discussion

3.1. Electronic Characteristic of the CT Complexes

On mixing dichloromethane solution of nicotine with that of TCNE, a yellow-orange color is developed immediately. The absorption spectrum of this solution displays two main absorption bands within the wavelength range 300 to 600 nm (λmax =336, 403, and 421 nm)