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Charge-transfer complexes of 4-nitrocatechol with some amino alcohols

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ABSTRACT

Charge-transfer (CT) complexes formed from the reactions of 4-nitropyrocatechol (4-nCat) as an electron acceptor with four amino alcohols: 2-aminoethanol, 1-amino-2-propanol, 4-aminobutanol and N-(2-hydroxyethyl)-1,3-diaminopropane (NHEDAP) as electron donors, have been studied spectrophotometrically in H_2O and H_2O/EtOH at 20, 25, 30, 35 and 40 °C. The calculated values of the oscillator strength and transition moment confirm the formation of CT-complexes. The thermodynamic and spectroscopic parameters were also evaluated for the formation of CT-complexes. The equilibrium constants ranged from 9.00 to 2.20 l mol^{-1} (M^{-1}). These interactions are exothermic and have relatively large standard enthalpy and entropy changes (ΔH values ranged from −15.58 to −3.10 kJ mol^{-1}; ΔS ranged from 26.81 to −3.25 J K^{-1} mol^{-1}). The solid CT-complexes have been synthesized and characterized by IR, NMR, mass spectrometry and thermal analysis. The photometric titration curves and other spectrometric data for the reactions indicated that the data obtained refer to the formation of 1:1 charge-transfer complex of [(4-nCat) (NHEDAP)] and 1:2 charge-transfer complexes of other amino alcohols [(4-nCat) (amino alcohol)$_2$]. The effect of alkali and alkaline earth metals on increasing the equilibrium constant of the CT-complexation was also investigated.

1. Introduction

Electron donor–acceptor (EDA) complexes have gained their importance due to their potential application in many different fields, such as non-linear optical activity [1], assay of different pharmaceuticals [2] and related analysis [3]. In addition, a vast number of organic compounds have been discovered to exhibit significant electrical characteristics [4]. The formation of CT-complexes between π- and n-donors, with σ- and π-acceptors, has been investigated extensively [5,6]. Catechol (1,2-dihydroxybenzene) is a weak diprotic acid, which presents a wide range of biological and environmental applications, such as a chelating agent for metal ions [7]. As stability constants are expected to increase with the addition of an electron withdrawing substituent to the catechol ring [8], the 1,2-dihydroxy-4-nitrobenzene molecule (4-nitrocatechol, hereafter noted 4-nCat) appears to be an effective ligand for the formation of complexes. On the other hand, the nitro substituent leads to a pronounced enhancement of the acidity of the hydroxyl groups [7]. The average pK_a values of the two hydroxyls obtained by potentiometric titrations are 6.7 and 10.8 [9]. These values are much lower than those obtained by potentiometric methods for the catechol molecule (average of 9.2 and 13, respectively) [10,11]. It was shown that such molecules (protonic acids) can form molecular complexes as an electron acceptor with molecules, which have donor sites (especially those with N-donor sites) through hydrogen bonding [4]. Protonic charge-transfer complexes were firstly introduced by Matsunaga and his coworkers [12]. Pauling regarded the hydrogen bond as a special case of charge-transfer interaction [13].

In connection with such studies, we investigated, in this article, the molecular complexes formed during the reaction of N-(2-hydroxyethyl)-1,3-diaminopropane (hereafter noted NHEDAP), 4-aminobutanol, 1-amino-2-propanol and 2-aminoethanol as electron donors with 4-nCat as an electron acceptor. The investigations were designed to explore the nature of the formed complexes and to calculate some spectroscopic and thermodynamic parameters in this regard.

2. Experimental

2.1. Materials and solutions

2-Aminoethanol, 1-amino-2-propanol, 4-aminobutanol, N-(2-hydroxyethyl)-1,3-diaminopropane and 4-nitropyrocatechol were purchased from Merck. Stock solutions of them were freshly prepared and the spectroscopic grade of ethanol (Merck Co.) was used as received. Double distilled water also was used throughout the spectroscopic measurements.

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2.2. Instrumentation and physical measurements

2.2.1. Electronic spectra

The electronic spectra of the donors (2-aminoethanol, 1-amino-2-propanol, 4-aminobutanol and N-(2-hydroxyethyl)-1,3-diaminopropane), acceptor (4-nCat) and resulted CT-complexes in H_2O and mixed H_2O/EtOH were recorded in the region of (190–900 nm) by using a Cary-100 spectrophotometer with quartz cells having a 1.0 cm path in length.

2.2.2. Photometric titration

Photometric titrations were performed at 20, 25, 30, 35 and 40 °C for the reaction of 4-nCat and amino alcohols in H_2O and mixed H_2O/EtOH, by using a Cary-100 spectrophotometer equipped with a PCB-150 water circulator and thermostated multicell holder, as follows.

Freshly prepared solutions of 4-nCat and amino alcohols were mixed just before recording the spectra. An instantaneous color developed on mixing the donor and acceptor solutions indicating the formation of a CT-complex, which was stable for several days. The concentration of 4-nCat was held constant, while that of the amino alcohols was varied for each set of measurements. The precision in reading and recording the spectrum was ±0.01 nm. The temperature was maintained constant to within ±0.1 °C. Sufficient time was allowed for the solutions to attain thermal equilibrium before each spectrum was recorded. As far as possible, all the solutions were protected from direct sunlight.

2.3. Synthesis of the CT-complexes

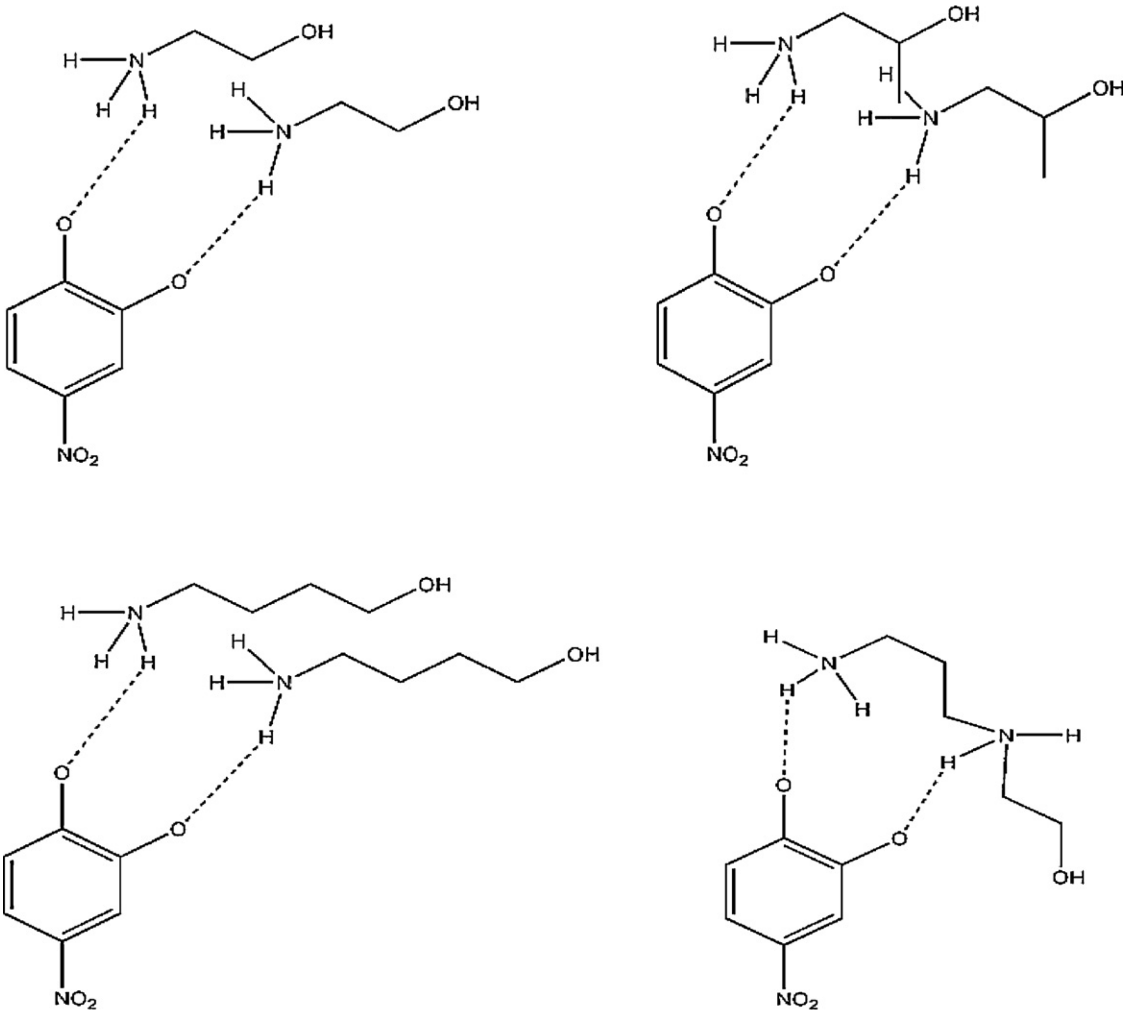
The solid CT-complexes of amino alcohols with 4-nCat were prepared by mixing (1.0 mmol) of the donors and 4-nCat (1.0 mmol) in H_2O (10 ml) with continuous stirring for about 2 h at room temperature. Although the deep red color was developed instantly, the solutions were allowed to evaporate slowly at room temperature, filtered and washed several times. Single crystals of the complexes could not be isolated from any organic solutions, thus, no definite structure could be described. However, the analytical and spectroscopic data enable us to postulate possible structures, as shown in Scheme 1.

2.4. Infrared spectra

IR measurements of donors, acceptor and CT-complexes (0.5 mg of each on the KBr disc) were carried out on a Unicam Matson 1000 FT-IR Spectrophotometer (400–4000 cm^{-1}).

2.5. ^{1}H NMR spectra

^{1}H NMR spectra were obtained on a Bruker 500-DRX Avance Spectrometer. ^{1}H NMR data are expressed in parts per million (ppm), referenced internally to the residual proton impurity in DMSO (dimethyl-sulfoxide, d_6) solvent and the chemical shifts (m, multiple and s, singlet; br, broad) were reported.



Scheme 1. The proposed mode of interactions of [(4-nCat) (2-aminoethanol)$_2$], [(4-nCat) (1-amino-2-propanol)$_2$], [(4-nCat) (4-aminobutanol)$_2$] and [(4-nCat) (NHEDAP)].