Spectrophotometric studies of charge transfer complexes of Piroxicam with 2,3-dichloro-5,6-dicyano-1,4-benzoquinon

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Introduction

Electron donor–acceptor (EDA) or charge transfer complexes (CT) are recently gaining importance as potential high efficiency non-linear optical materials, organic superconductors as well as photocatalysts [1,2]. EDA interaction is also important in the field of drug–receptor binding mechanism, in solar energy storage and in surface chemistry as well as in many biological fields [3,4]. On the other hand, the charge transfer reactions of certain n-acceptors have been successfully utilized in pharmaceutical analysis. For these wide applications, extensive studies on CT complexes of n-acceptors have been performed. The solid complexes were synthesized and studied by chemical analysis (C, H, N), infrared, electronic absorption, H NMR and ESR spectra as well as the magnetic moment and electrical conductivity measurements.

It is well known that when the colorless solutions of different donors are mixed with the yellow solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinon (DDQ) a distinct change in color occurs. The resultant initial color, however, fades with time and is replaced by another color. To the best of our knowledge there is no published report on the complexation of piroxicam (PRXM) with DDQ in acetonitrile (AN) solutions.

Experimentals

The solid CT complex of PRXM with DDQ was prepared by mixing 1 mmol of the donor in acetonitrile with 1 mmol of the acceptor in the same solvent. The mixture was

stirred at room temperature for 2 h, where the solid precipitated after the reduction of the volume of the solvent. The separated complex was filtered off, washed several times, and then dried. The analytical data of the CT complexes (C, H, N content) along with some of the physical properties, IR and 1H NMR spectral were investigated.

Results and Discussion

The electronic spectrum of CT complexes of PRXM as donor with π-acceptor, DDQ, was recorded in AN solvent. The π-electronic spectra were scanned against the same electron acceptor concentration as in the test solution to eliminate the possible overlap that may arise between CT complex band and that of the acceptor. The stoichiometry of the CT complex was determined by applying Job's continuous variation method. The symmetrical curves with maximum at 0.5 mol fraction indicate the formation of 1:1 CT complexes. The association constant (K) values and molar extinction coefficients (‹) of the CT complexes studies have been determined using the rearranged form of the Benesi-Hildebrand equation [5]:

$$[A] + [D] = (‹l[A][D]/d) − 1/K \tag{1}$$

Where, [A] and [D] are the initial molar concentrations of the acceptor and donor, respectively, l the length of the light path in cm and d the optical density. The values of ‹ and K were found 3.6 Lmol^{-1} and 485 Lmol^{-1}cm^{-1},respectively from the gradient and negative intercept of the linear plot of [A] + [D] against [A][D]/d.

Generally, the low K values suggested that the formed complexes are of weak type, i.e., that the ground state wave functions has predominantly a non-bonding structure. The CT complex of PRXM with DDQ is predominantly of n-n* type. This is due to the fact that PRXM is planar compound. Comparison of the infrared spectral bands of the free donor and the acceptor (DDQ) with the corresponding ones appearing in the IR spectra of the CT complex shows the following:

1. The vibration frequency of the C÷N group for DDQ observed at 2240 cm^{-1} is shifted to 2216 cm^{-1} in the IR spectrum of the CT complex.
2. The C=O group stretching vibrations of DDQ appearing at 1674 is shifted to 1626 cm^{-1}.
3. The group of bands connected to C–Cl vibrations which appeared at 802, 722 cm^{-1} (DDQ) exhibit a shift to lower wave number in the corresponding CT complexes: 775, 705 (DDQ)

4. The characteristic bands of the free donor such as ν_{NH} which appeared at 3260 cm^{-1} is observed in the IR spectra of the CT complexes with small shift to higher wave number.

The shift of the IR bands of the acceptor part to lower wave numbers and those of the donor part to higher values reflects a donor to acceptor charge transfer of the n-n* type, DHOMO‹ALUMO transition [6].

The electronic absorption spectra of the solid CT complex formed is characterized by only one CT band within the wavelength range 520–528 nm which can be assigned to the n-n* interaction. The existence of single CT band indicates that the n–n* interaction would have low contribution to the bonding in the CT complexes or even absent. The energy of the n - n* interaction (E_{CT}) is calculated using the following relation [7]:

$$E_{CT} = 1243.667/h_{CT} \, nm \tag{2}$$

where h_{CT} is the wavelength of the CT band of the complex.

The E_{CT} values calculated from Eq. (2) are 2.39 eV.

References

1. F. Vogtle, Supramolecular Chemistry, An Introduction, Wiley, New York, 1991, p. 312;
2. R. Dabestani, K.J. Reszka, M.E. Sigman, J. Photochem. Photobiol. A 117 (1998) 223.
3. K. Takahasi, K. Horino, T. Komura, K. Murata, Bull. Chem. Soc. Jpn 66 (1993) 733.
4. S.M. Andrade, S.M.B. Costa, R. Pansu, J. Colloid. Interf. Sci. 226 (2000) 260.
5. H.A. Benesi, J.H. Hildebrand, J. Am. Chem. Soc. 71 (1949) 2703.
6. R.D. Kross, V.A. Fassel, J. Am. Chem. Soc. 79 (1957) 38.
7. G. Briegleb, Z. Angew. Chem. 72 (1960) 401.