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Spectrophotometric Study of the Charge Transfer Complex of 2,2-Dichloro-5,6-dicyano-1,4-benzoquinone and 1,4,8,11-Tetraazacyclotetradecane in Chloroform Solution

HAMID REZA POURETEDAL*†, ABOLFAZL SEMNANI,
BEHZAD NAZARI and ALIREZA FIROOZ†
Faculty of Science, Malek-ashtar University of Technology, Shahinshahr,
P.O. Box 83145/115, Iran
E-mail: hrpouretedal@yahoo.com

A spectrophotometric study concerning the charge transfer reaction of 1,4,8,11-tetraazacyclotetradecane (CYCLAM) and π-acceptor, 2,2-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) has been performed in chloroform solution at 25°C. The results are indicative of the formation of CYCLAM-DDQ and $CYCLAM^+$-DDQ^- through equilibrium and non-equilibrium steps, respectively. The formation constant of the equilibrium step has been evaluated by the computer fitting of absorbance-mole ratio data as $\log K_f = 5.5 \pm 0.2$. The plotting $\ln (A_t/A_0)$ *vs.* time has obtained the rate constant of non-equilibrium step. The obtained k value is equal to $0.011 \pm 0.001\ \text{min}^{-1}$. Solid complex of CYCLAM-DDQ has been isolated and the IR spectrum of the complex has been compared with the spectra of donor and acceptor.

Key Words: 1,4,8,11-Tetraazacyclotetradecane, 2,2-Dichloro-5,6-dicyano-1,4-benzoquinone, Spectrophotometry, Charge-transfer complex.

INTRODUCTION

2,2-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is the famous π-acceptor and its charge transfer complexes have been a subject of extensive study[1–6]. The investigations were performed with different donors[7–10]. Some of the resulting complexes have been applied for synthetic and analytical purposes[6, 11–15]. Recently, some attention has been paid to the charge transfer complexes of DDQ with crown ethers[16–19]. However, it seems that much more study in this field is needed. We have been currently involved in the study of molecular complexes of crown ethers[20–24].

In this paper, the results of spectrophotometric study of charge transfer complex of DDQ with CYCLAM in chloroform solution have been reported.

EXPERIMENTAL

CYCLAM (Merck Co.) was recrystallized from reagent grade *n*-hexane and dried under vacuum over P_2O_5. Reagent grade DDQ was used without any further purification except for vacuum drying.

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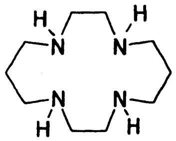
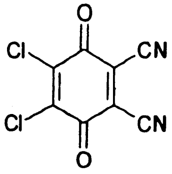
†Faculty of Science, Shahrekord University, P.O. Box 115, I.R., Iran.



CYCLAM



DDQ

UV-Vis spectra were recorded on a Perkin-Elmer Lambada 2 spectrophotometer and absorbance measurements with Philips PU875 spectrophotometer at 25.0 ± 1.0°C. IR spectra were recorded on a Shimadzu spectrometer using KBr pellets.

RESULTS AND DISCUSSION

Absorption spectra of 7.81×10^{-4} M of DDQ in the presence of increasing quantities of CYCLAM are shown in Fig. 1. The spectra were recorded just after making the solutions. As can be seen, addition of CYCLAM results in the appearance of a new band at 470 nm. This can be certainly ascribed to the formation of charge transfer complex. The existence of isobestic point in the spectra means that the complex is formed through an equilibrium reaction[25]. Interestingly, it was observed that the intensity of 470 nm band reduced gradually and simultaneously new band appeared at 425 nm (Fig. 1). Such an observation means that with passing time the first adduct has been converted to another one. As there is no isobestic point in the new spectra, it can be concluded that the final product has been formed through a non-equilibrium reaction. It must be noticed

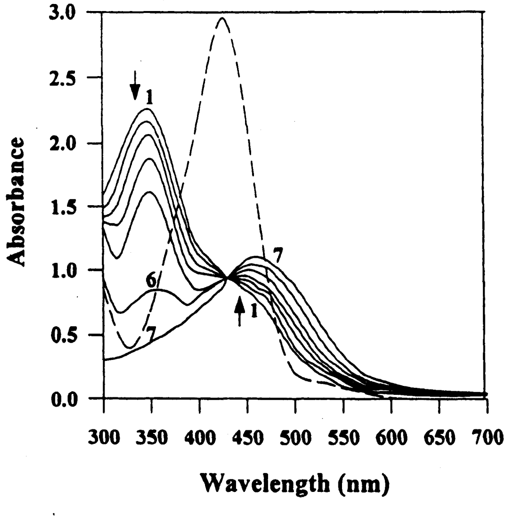


Fig. 1. Absorption spectra of 7.81×10^{-4} M DDQ in the presence of varying concentration of CYCLAM and just after mixing the reagents. The CYCLAM/DDQ mole ratios: 1: 0.17, 2: 0.35, 3: 0.52, 4: 0.69, 5: 0.86, 6: 1.04, 7: 1.35. The dashed curve is the shape of the last spectrum after 24 h

that because of obviousness, the complete spectra are not shown and only a sample spectrum is given in Fig. 1. Keeping in mind that (1) nitrogen has a high donating property[26], (2) DDQ is a powerful π-acceptor[27] and (3) absorbance-mole ratio plot (Fig. 2) confirms a 1 : 1 stoichiometry[28], the equilibrium step can be written as follows:

$$\text{CYCLAM} + \text{DDQ} \rightleftharpoons \text{CYCLAM} - \text{DDQ} \quad (1)$$

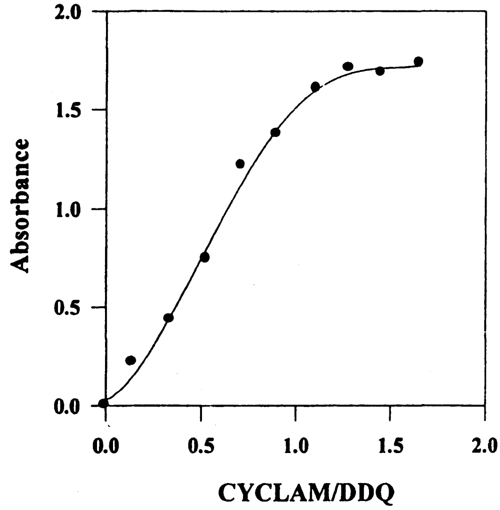


Fig. 2. Plot of absorbance *vs.* CYCLAM/DDQ mole ratio obtained at 470 nm and 25°C

The conversion of DDQ to DDQ^- has been reported frequently[29–32], so the following reaction is suggested for the non-equilibrium step:

$$\text{CYCLAM} - \text{DDQ} \longrightarrow \text{CYCLAM}^+\text{DDQ}^- \quad (2)$$

The above reaction is further supported by monitoring of the absorbance as function of time at 470 nm. It was observed that the kinetic data were in accord with a first order reaction, indicating the conversion of CYCLAM – DDQ to $\text{CYCLAM}^+\text{DDQ}^-$. The corresponding first order kinetic equation can be derived as follows:

$$\text{Rate} = -d[\text{CYCLAM} - \text{DDQ}]/dt = k[\text{CYCLAM} - \text{DDQ}] \quad (3)$$

$$d[\text{CYCLAM} - \text{DDQ}]/[\text{CYCLAM} - \text{DDQ}]_0 = -kdt \quad (4)$$

$$\ln([\text{CYCLAM} - \text{DDQ}]_t/[\text{CYCLAM} - \text{DDQ}]_0) = -kt \quad (5)$$

$$[\text{CYCLAM} - \text{DDQ}]_t = A_t/\varepsilon b \quad (6)$$

$$\ln([\text{CYCLAM} - \text{DDQ}]_t/[\text{CYCLAM} - \text{DDQ}]_0) = \ln(A_t/A_0) = -kt \quad (7)$$

According to equation (7) by plotting $\ln(A_t/A_0)$ *vs.* t at 470 nm, will result in a straight line with a slope equal to the rate constant. The corresponding plot is shown in Fig. 3. The determined k value by this method was $0.011 \pm 0.001\ \text{min}^{-1}$.

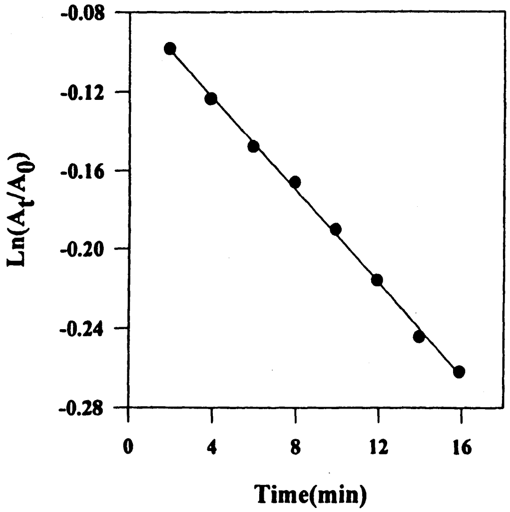


Fig. 3. Plot of Ln (A_t/A_0) *vs.* time at 470 nm for CYCLAM-DDQ system

For the evaluation of the formation constant of the molecular complex [eqn. (1)] from the absorbance-mole ratio data (Fig. 2), a non-linear least squares curve fitting program KINFIT was used[33]. The program is based on the iterative adjustment of the calculated values of absorbance to the observed values by using either the Wentworth matrix technique[34] or the Powell procedure[35]. Adjustable parameters are K_f and ε, where ε is the molar absorptivity of charge transfer complex.

The observed absorbance of a solution at the λ_{max} of complex is given by eqn. (6). The mass balance equation can be written as:

$$C_D = [D] + [DA] \qquad (8)$$

$$C_A = [A] + [DA] \qquad (9)$$

The formation constant of the complex is equal to:

$$K_f = [DA]/[A][D] \qquad (10)$$

Substitution of eqns. (4) and (5) into eqns. (6) and rearrangement yields:

$$K_f[DA]^2 - (K_fC_D + K_fC_A + 1)\,[DA] + K_fC_AC_D = 0 \qquad (11)$$

The free complex concentration [DA] was evaluated from eqn. (11) by means of a Newton-Raphson procedure. Once the value of [DA] had been obtained, the concentrations of all other species involved were evaluated from the corresponding mass balance equations. By using the estimated value of K_f at the current iteration step of the program, refinement of the parameters is continued until the sum of squares and the standard deviation of the data are minimized. The output of KINFIT program comprises the refined parameters, the sum of squares and standard deviation to the data. The determined log K_f and ε values by this method are 5.5 ± 0.2 and 1350 ± 25, respectively.

IR spectra of DDQ, the resulting complex and CYCLAM are shown in Figs. 4 and 5, respectively. As can be seen, the complexation caused shift of CN and CO peaks to lower and higher frequencies respectively. This means a higher charge density on carbonyl and lower charge density on the cyano group[36]. Also considerable shift of C—N stretching bond to lower frequencies indicates the direct involvement of nitrogen atom in complexation.

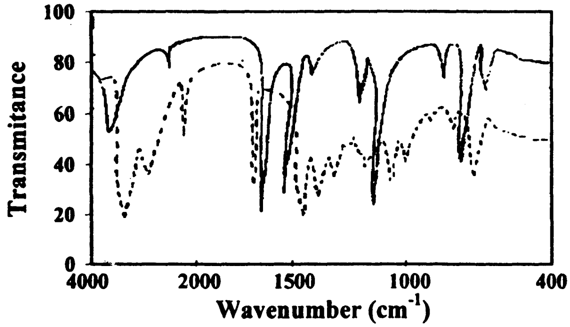


Fig. 4. IR spectra of DDQ (solid line) and DDQ-CYCLAM complex (dashed line)

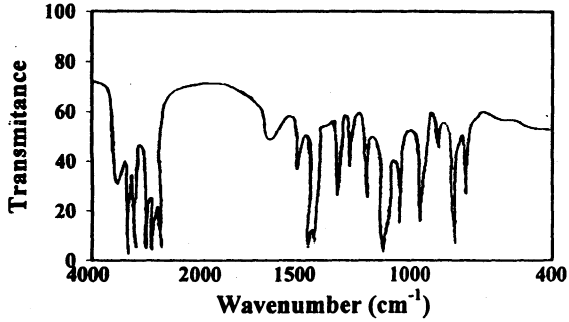


Fig. 5. IR spectra of CYCLAM

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