Charge transfer complexes of o-toluidine and p-toluidine with p-benzoquinone

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ABSTRACT

The charge transfer complexes of o-toluidine and p-toluidine as donors with p-benzoquinone as acceptor have been studied in methanol at room temperature. The complexes have been isolated and investigated using elemental analysis, electronic (UV – Vis) and Infrared spectrophotometry. The chemical analysis data of the resulted complexes, indicated the formation of 1:1 charge transfer complexes. The equilibrium constant, the extinction coefficient and the free energy of the complexes were calculated. The donor (o-toluidine) site involved in CT interaction was the two nitrogen atoms of the amino group but p-toluidine, it has one nitrogen atom forms hydrogen bonding. The electrical conductivity for the solid CT complexes was measured.

Keywords: charge transfer complexes; p-benzoquinone; equilibrium constant; free energy; IR and UV-Vis spectra.

INTRODUCTION

Charge transfer complexation phenomena was introduced first by Mulliken. The term charge transfer gives a certain type of complex resulting from interactions of donor and acceptor with the formation of weak bond (1). Charge-transfer interactions within a molecular complex formed from an electron donor (D) and electron acceptor (A) as a resonance with a transfer of charge from D to A to form a radical cation and anion, respectively: D + A ↔ D⁺, A⁻ (2) and discussed widely by Foster (3). Charge transfer complexes were successfully applied to many interesting studies (4).

p-Benzquinone is the parent molecule of a class of compounds which play a relevant role in biological systems and in the formation of charge-transfer salts. Derivatives of this molecule have been recognized as important electron transfer agents in biology. Charge-transfer complex of 2,2',5,5'-tetrathiafulvalene and p-benzoquinone were found to crystallize having mixed stacks (5). Tetrathiafulvalene (TTF) spontaneously forms a series of unusual charge-transfer complexes with o-chloranil (CA) (6). Charge-transfer (CT) complex of o-toluidine (o-Tol) with the π-acceptor tetrachloro-p-benzoquinone (p-chloranil; CHL) has been synthesized and characterized, along with the products of the elimination reaction of o-toluidine (o-Tol) with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) and 7,7,8,8-tetracyanoquino-dimethane (TCNQ) (7). Electron donor–acceptor (EDA) complex formation between o-chloranil and a series of anilines has been studied in CCl₄ medium (8). Infrared and polarographic analyses of 1 : 1 molecular complexes of p-benzoquinone with aromatic amines have been carried out (9). Charge-transfer interactions between aromatic amines and trinitrobenzene have been utilized for the distinction and determination of some primary, secondary, and tertiary aromatic amines (10). Ultrasonic velocity (u), density (ρ) and coefficient of viscosity (η) were used in measuring primary amine and acetophenone, 4-chloro-acetophenone and 4-methyl acetophenone...
in n-hexane medium, the formation of charge transfer complexes through hydrogen bonding between primary amine and aromatic ketones. The formation constants of the charge transfer complexes determined using Benesi–Hildebrand equation (spectroscopic method) are comparable with those obtained using Kannappan equation (ultrasonic method) (11). The interactions of two dye ions, thionine and toluidine blue with a variety of amines have been studied in methanol. The equilibrium and spectroscopic data have been interpreted in terms of a charge-transfer interaction between the dye ions and amines (12). The charge transfer complex formation between the studied amine drugs and tetracyanoethylene; and 7,7,8,8-tetracyanoquinodimethane (13). Charge-transfer (CT) complexes formed between aromatic thiol donors (thiophenol (TP), benzene-1,4-dithiol (BDT), p-aminothiophenol (ATP), p-hydroxythiophenol (HTP), and p-toluenethiol (TTP)) and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) as an acceptor were studied spectrophotometrically in dichloromethane (14). The molecular interactions between aniline, p-toluidines, benzidine and p-phenylenediamine as electron donors and 7,7,8,8-tetracyanoquinodimethane (TCNQ) as acceptor have been investigated by spectrophotometric method (15). A variety of electron donating compounds (anilines) have been reported to yield charge-transfer complexes leads to their utility in the development of simple and convenient colorimetric methods (16). The formation of charge-transfer complexes has been studied by conductometric measurements, in the systems diphenyl-amine-2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), 1,10-phenanthroline-DDQ, thiourea—DDQ and N,N-dimethylaniline-DDQ in methanol (17).

This paper presents the studies of the charge transfer complexes produced by the reaction of o-tolidine (o-Tol) and p-toluidine (p-Tol) with p-benzoquinone (p-Bq). The reactions of both (o-Tol) and (p-Tol) with π-acceptors to form stable CT-complexes (18). It was proved that a proton transfer from two different donors (o-Tol has two - NH₂ groups and p-Tol has one - NH₂ group) to π–acceptors (19). Charge transfer complex formed between (p-Tol) and chloranil. Showed that an interaction was associated with a proton migration from the donor to acceptor followed by intermolecular hydrogen bonding (20). The mechanism and structure of the reaction product have been discussed, the conductivity of the complexes was measured (20). The charge transfer complexes of the donor (p-Tol) with π–acceptor picric acid have been studied spectrophotometrically in various solvents such as carbon tetrachloride, chloroform, dichloromethane, acetone, ethanol, and methanol at room temperature (21).

**EXPERIMENTAL**

**Synthesis and characterization of the CT-complexes**

**Materials**

-o-toluidine, p-toluidine and solvent were of the highest purity (Merck). p-benzoquinone was further purified.

**Synthesis of CT complexes**

A yellow solution of the p-benzoquinone (1 mmol) in methanol was added separately to each of the two colorless solutions of o-toluidine and p-toluidine (1 mmol) in methanol at room temperature, then stirred for about 3h. The mixtures were kept overnight where the CT complexes were precipitated. The black precipitates formed in both cases were filtered off, washed with
diethyl ether and dried in vacuum over CaCl₂.

**Preparation of solutions**

The reaction between donors and p-benzoquinone in methanol solvent was carried out as follows: the concentration of donors \([D]_o\) were kept fixed at \(1 \times 10^{-4}\) mol/L, whereas that the concentration of the p-benzoquinone \([A]_o\) was changed over a wide range from \(0.25 \times 10^{-4}\) – \(3.00 \times 10^{-4}\) mol/L.

**Analysis and physical measurements**

Melting points were taken in open capillary on an electrically heated metal. IR-spectra, as KBr discs, were recorded on a Gensis II FT-IR spectrophotometer (400–4000 cm\(^{-1}\)). Microanalysis for carbon, hydrogen and nitrogen were measured. All Analysis were carried out at the Micro analytical centers, Cairo University, Cairo, Egypt. The results of the elemental analyses, formula and (mp, \(^\circ\)C) are given in Table 1. Electronic spectra were recorded at room temperature via both Shimadzu UV-Spectrophotometer model 1601 PC with quartz cell of 1 cm path length and Jenway 6405 Spectrophotometer each for certain reactions.

**RESULTS and DISCUSSION**

**Absorption Spectra**

The electronic spectra of the o-toluidine (o-Tol) and p-toluidine (p-Tol) as a donors with p-benzoquinone (p-Bq) as \(\pi\)-acceptor and their CT complexes are shown in Figure 1. The spectra in each cases of the (p-Bq)-donors systems have definite bands at 295 nm for (o-Tol-p-Bq) and 287 nm for [(p-Tol)(p-Bq)]. The absorbance was contributed by complexes, since both donor and acceptor alone did not absorb in this region (22).

The absorption bands were characteristic of an intermolecular charge transfer involving the overlap of the lowest unoccupied molecular orbital (LUMO) of the acceptor with the highest occupied orbital (HOMO) of the donor (Scheme 1). The donors are relatively electron rich and p-Bq is relatively electron poor compound, they tend to associate with one another in a loose interaction known as electron-donor-acceptor (EDA) complexes. The low energy absorptions observed in solutions containing both a donor and an acceptor have been described by Mulliken (23) as charge transfer transitions involving the excitation of an electron on the donor to an empty orbital on the acceptor.

**Spectrophotometric study of equilibrium constant of the charge transfer**

The modified Benesi-Hildebrand equation (24) used to determine the value of the equilibrium constant, \(K_{ct}\) (Lmol\(^{-1}\)), and the extinction coefficient, \(\varepsilon_{ct}\) (Lmol\(^{-1}\)cm\(^{-1}\)) for the complex formed in solution (Table 2). This equation can be written as follows:

\[
\frac{[A]_o [D]_o}{A} = \frac{[A]_o + [D]_o}{\varepsilon_{ct}} + \frac{1}{K_{ct} \varepsilon_{ct}}
\]

Where \([A]_o\) and \([D]_o\) are the initial concentrations of acceptor and donor, respectively, while A is the absorbance at the mentioned CT bands. On plotting the values of \([A]_o [D]_o\)/ A values against the \([A]_o + [D]_o\) values, a straight lines were obtained with a slope of \(1/ \varepsilon_{ct}\) and intercept of \(1/K_{ct} \varepsilon_{ct}\) (Figure 2). Generally, these complexes have a high equilibrium constant and extinction coefficient. These high values of \(K_{ct}\) confirm the expected high stabilities of the CT-complexes because of the extensive donation from the o-Tol and p-Tol due to the amino and methyl groups. The
equilibrium constants also depend on the nature of the acceptor.

**Determination of transition energy (E_{ct}) and standard free energy (\Delta G^o)**

The energy of the \( \pi - \pi^* \) interaction (E_{ct}) reported in Table 2 have been calculated using the following equation (25):

\[
E_{ct} = \frac{1243.667}{\lambda_{ct}} \text{ nm}
\]

The standard free energy of complex (Table 2) was calculated from the equilibrium constant by the following equation (26):

\[
\Delta G^o = - RT \ln K_{CT}
\]

**Stoichiometry of complex**

From Job's method of continuous variation (27), a stoichiometry of 1:1 was obtained for the CT complexes of donors with \( p \)-benzoquinone as illustrated in Figure 3. In this method, a series of solutions was prepared by mixing equimolecular solutions of donor and acceptor in varying proportion while keeping the total molar concentration constant. The stoichiometry of the CT complexes was determined graphically by plotting the mole fraction of donor on the abscissa against the absorbance on the ordinate. Graphical representation of the results obtained by this method show symmetrical curves with a maximum at a mole fraction \( \approx 0.5 \), indicating the formation of 1:1 CT complexes in all cases. A application of a molar ratio method (28) is determined by the inflection point in a plot of the absorption versus the molar ratio of the reactants. The intersections of the obtained straight lines indicate the molar ratio of the complexes (Figure 4). These results also prove the formation of the 1:1 CTCs. The elemental composition indicated in Table 1, suggested that the charge transfer complexes formed was a 1:1 stoichiometry of the reactants molecules.

**Conductivity**

The experimental data of conductivity measurement of the complexes are represented in Fig. 5. The conductivity of the \([(o-Tol)(p-Bq)]\) and \([(p-Tol)(p-Bq)]\) charge transfer complex were found to be \( \sigma_{RT} = 0.07 \times 10^{-6} \) and \( 0.05 \times 10^{-6} \) S cm\(^{-1} \) respectively. The d. c. electrical of the complexes increases as the temperature increases, indicating semiconducting behavior.

**Infrared spectra**

The possibility of a donation from the \( o \)-toluidine and \( p \)-toluidine to \( p \)-benzoquinone exists either by hydrogen bonding between O atom of \( p \)-Bq and H atom of the \( \text{NH}_2 \) group of donors or \( \pi \)-electron from the aromatic ring (17,29). There were shifting for the peaks towards the lower wavenumbers (Table 3). This shift assures that the donation process has been carried out by \( \text{NH}_2 \) group in the two cases. Also, there was a shift in the intensity of the aromatic character peaks for both the donors and the acceptor, resulted from the \( \pi - \pi^* \) CT complexes which were originally formed via benzene rings (electron rich group of \( o \)-Tol or \( p \)-Tol and electron acceptor as \( p \)-Bq) (30). The infrared spectrum of the \( o \)-Tol and \( p \)-Tol exhibits a group of bands at 3475- 3338 and 3417- 3333 cm\(^{-1} \) respectively, which are assigned to the stretching vibrations \( \nu (\text{N-H}) \). In the spectrum of CT complex, it was observed that there is a shift in their bands to lower frequencies 3242 – 3055 and 3231 cm\(^{-1} \) of \( o \)-Tol and \( p \)-Tol respectively. However, the majority of evidences suggest that the
nitrogen atom is a preferred donor site (31). The structures of donors, acceptor and proposed CT complexation are given in Scheme 2.

CONCLUSION

In conclusion, charge transfer complexes were synthesized and confirmed by elemental analysis and Infrared spectrophotometry. Charge transfer interaction between the donors (o-toluidine and p-toluidine) and acceptor (p-benzoquinone) were studied spectrophotometrically. The stoichiometry of the products was found to be 1:1 in two cases. Accordingly, the formed CT-complexes have the formulas [(o-Tol)(p-Bq)] and [(p-Tol)(p-Bq)]. The equilibrium constant of the CT complex, the extinction coefficient and the free energy, the electrical conductivity of the complexes were calculated.

REFERENCES


Table 1 Physical parameters data of charge transfer complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Formula</th>
<th>(M_w)</th>
<th>mp.</th>
<th>Elemental analysis a</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>%C</td>
</tr>
<tr>
<td>[(o-Tol)(p-Bq)]</td>
<td>C_{18}H_{20}N_2O_2</td>
<td>296.37</td>
<td>236</td>
<td>72.95 (72.11)</td>
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<td>[(P-Tol)(p-Bq)]</td>
<td>C_{13}H_{13}NO_2</td>
<td>215.26</td>
<td>135</td>
<td>72.54 (72.98)</td>
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a Calculated ( found )

Table 2 Physical parameters data of the CT complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ_{ct} (nm)</th>
<th>K_{ct} (mol^{-1})</th>
<th>ε_{ct} (mol^{-1} cm^{-1})</th>
<th>E_{ct} (K cal mol^{-1})</th>
<th>ΔG* (K cal mol^{-1})</th>
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<tr>
<td>[(o-Tol)(p-Bq)]</td>
<td>295</td>
<td>13.849 x10^3</td>
<td>16.949 x10^3</td>
<td>4.216</td>
<td>5.646</td>
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<tr>
<td>[(p-Tol)(p-Bq)]</td>
<td>287</td>
<td>10.277 x10^3</td>
<td>8.696 x10^3</td>
<td>4.333</td>
<td>5.370</td>
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</table>
**Fig. 1** Electronic absorption spectra of A-[(o-Tol)(p-Bq)], B-[(p-Tol)(p-Bq)] where 1–acceptor (1x10^-7 M), 2–donor (1x10^-4 M) CT complex (1x10^-4 M).

**Fig. 2** Relation between [A]_o + [D]_o x 10^-6 values against [A]_o + [D]_o values: A-[(o-Tol)(p-Bq)] and B-[(p-Tol)(p-Bq)].

**Scheme 1** Charge transfer transitions for HOMOs of the donors and LUMOs of the acceptor.
Fig. 3 Job's method of continuous variation for the CT complexes: A- [(o-Tol)(p-Bq)] and B– [(p-Tol)(p-Bq)], total concentration =1x10^{-4} M

Fig. 4 Stoichiometric ratio using molar ratio method, A-[(o-Tol)(p-Bq)] and B–[(p-Tol)(p-Bq)]
Fig. 5 Temperature versus conductivity plot for CT – complex: A- [(o-Tol) (p-Bq)] and B- [(p-Tol)(p-Bq)]

Scheme 2 Mode of the charge transfer complexes: A-[(o-Tol) (p-Bq)] and B-[(p-Tol) (p-Bq)]
### Table 3 Infrared frequencies and tentative assignments for CT complexes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\nu$ (N-H)</th>
<th>$\nu$ (OH)</th>
<th>$\nu$ (C=O) + $\nu$ (C=C) + $\delta$ (NH$_2$)</th>
<th>Hydrogen bond</th>
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<td><em>p</em>-Bq</td>
<td>1680 vs</td>
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<td></td>
<td>1410 vs</td>
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<td></td>
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<td>1220 vs</td>
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<tr>
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<td>3475 s</td>
<td>1625 vs</td>
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<td>1573 s</td>
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<td>3375 s</td>
<td>1520 w</td>
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<td></td>
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<td>1489 vs</td>
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<td>1625 vs</td>
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<td></td>
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<td>1510 vs</td>
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<td>1778 vv</td>
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<td>1629 vs</td>
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