Asian Journal of Chemistry Vol. 16, No. (2) (2004), 699–705

Studies on the Charge-transfer Complexes of 2,6 Dichloro-*p*-benzoquinone with Phenols

K.P. SRIVASTAVA
University Department of Chemistry, Rajendra College, J.P. University
Chapra-841 301, India
e-mail: kpsri@sify.com

The molecular complexes of 2,6-dichloro-*p*-benzoquinone with phenol and cresols have been studied using electronic absorption spectroscopy in carbon tetrachloride medium under high donor concentrations at different temperatures. All the complexes exhibit one charge transfer band each in the wavelengths region where acceptor and donor do not have any absorption. All the complexes are inferred to be of the π-π type with the 1 : 1 stoichiometry and have R_y configuration. The stability constants and thermodynamic parameters of the charge transfer complexes have been evaluated from the position of the CT bands. Further, the attempts have been made to determine the ionization potentials of the donors from the energies of the CT bands.

Key Words: Charge-transfer studies, Phenols, Cresols, 2,6-Dichloro-*p*-benzoquinone, Stability constant, Hyper-conjugative effect, Bathochromic shift.

INTRODUCTION

The formation of electron donor-acceptor (EDA) complexes or molecular complexes has long been recognized[1–4]. The charge transfer (CT) complexes of derivatives of *p*-benzoquinone and different kinds of donors have been of particular interest to workers[5–9] in recent years. The extensive works have been carried out to determine the stability constants (K_{AD}) and molar absorptivities (ε_{AD}) of the EDA complexes with their stoichiometry.

The main objective in the present work is to investigate the formation of 1 : 1 stoichiometric molecular complexes between 2,6-dichloro-*p*-benzoquinone and phenol and cresols by studying their electronic absorption spectra. The experimental CT transition energies of the CT complexes have been shown to follow a systematic trend with change in position of the CH_3 group attached to the aromatic ring. Since the CT complexes of mentioned acceptors and donors can be stabilized in non-polar solvents and under high donor concentrations, so for this study, further we chose CCl_4 as solvent and recorded the electronic absorption spectra of these complexes using high concentrations of phenols and cresols.

The calculated stability constants, thermodynamic parameters and ionization

potentials of donors from CT spectra of molecular complexes in CCl_4 medium have been reported here.

EXPERIMENTAL

The stability constants and thermodynamic parameters of the CT complexes were determined by spectrophotometric method. Absorbance measurements were recorded in a Systronics UV-Vis. spectrophotometer Type-119 PC based (wavelength range 2001000 nm and band width 2 nm) using 1 cm matched pair of quartz cuvettes.

The solvent CCl_4 (AnalaR) was purified by distillation (B.P. = 76°C) and 2,6-dichloro-*p*-benzoquinone (BDH) was recrystallized from ethanol, pale yellow crystals were obtained (m.p. = 120°C). Phenols (BDH-Analar) were purified by the methods available in literature[10].

The stock solution of each donor and acceptor compounds were prepared freshly by dissolving their appropriate amount in CCl_4. The prepared solutions of acceptor and donors were mixed just before recording the spectra. The colour changes observed on mixing the donors and acceptor indicated the formation of molecular complexes.

For quantitative studies on the EDA complex formation the spectra of a series of the mixtures of each donor with mentioned acceptor were subsequently obtained [Fig. 1].

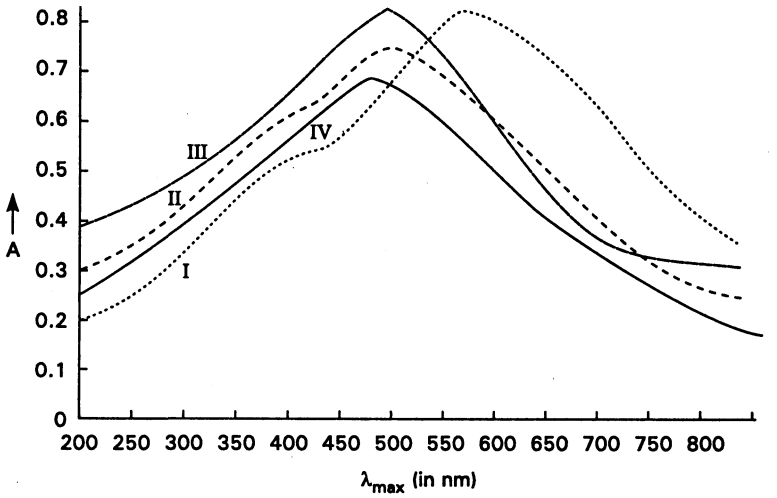


Fig. 1 CT spectra of 2,6-dichloro-*p*-benzoquinone with phenols [I = *p*-cresol, II = *o*-cresol, III = *m*-cresol, IV = phenol]

The absorbances were measured with a number of initial concentrations of donor keeping always $[D_0] \gg [A_0]$. The results are shown in Table-1.

TABLE-1
ABSORBANCE (A) DATA OF THE DONOR-ACCEPTOR MIXTURES MEASURED AGAINST SOLVENT (CCl_4) AS BLANK

$[D_0]$	$[A_0]$	A	λ_{CT}	K_{AD}
(a) *p*-cresol + acceptor				
0.091	0.00064	0.201		
0.117		0.303		
0.151		0.510	538 nm	6.41
0.227		0.665		
0.500		0.896		
(b) *o*-cresol + acceptor				
0.090	0.00064	0.338		
0.125		0.428	529 nm	4.12
0.161		0.500		
0.222		0.600		
0.384		0.774		
(c) *m*-cresol + acceptor				
0.106	0.00064	0.395		
0.135		0.471	514 nm	3.01
0.166		0.544		
0.222		0.662		
0.370		0.875		
(d) phenol + acceptor				
0.07	0.00064	0.274		
0.10		0.371	490 nm	2.88
0.14		0.401		
0.17		0.530		
0.21		0.607		

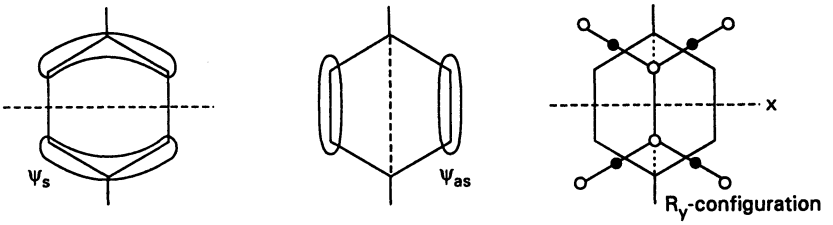
RESULTS AND DISCUSSION

All the complexes exhibit one CT band each in the range 490–538 nm. These CT bands appear due to excitation of electron from the highest occupied molecular orbital (HOMO) of donors to the lowest unoccupied molecular orbital (LUMO) of the acceptor[11, 12]. The HOMO of phenols may be symmetrical (Ψ_s) and unsymmetrical (Ψ_{as}) molecular orbitals. These result from the linear combination of atomic orbitals (LCAO) of benzene. The Ψ_s and Ψ_{as} as are expressed as :

$$\Psi_s = \frac{1}{\sqrt{12}}(2\Psi_1 + \Psi_2 - \Psi_3 - 2\Psi_4 - \Psi_5 + \Psi_6)$$

$$\Psi_{as} = \frac{1}{2}(\Psi_2 + \Psi_3 - \Psi_5 - \Psi_6)$$

The Ψ_s MO has a transverse nodal plane but the Ψ_{as} MO has a longitudinal nodal plane. Graphically the Ψ_s and Ψ_{as} MO may be represented as:



The application of maximum overlap principle[13] shows that the mentioned molecular complexes have R_y configuration as expected above.

The formation of longer wavelength CT bands for all investigated molecular complexes further predicts their R_y configuration[14]. It is therefore inferred that in phenols acceptor complexes the Ψ_s MO acts as a donor level and forms complexes with R_y-configuration. The ν(C=O) of *p*-benzoquinone and ν(O—H) of phenol lie parallel in R_y-configuration and may form H-bonding which significantly favours this configuration.

Effect of methyl group and its position on CT bands

The position of CT band of phenol-2,6-dicholoro-*p*-benzoquinone (490 mm) is shifted to longer wavelength by the presence of CH_3 group and its different position in the benzene ring of phenol. This arises due to donation of electron of Ψ_s orbital of donors which encompasses the CH_3 group. The shifts are in the order

p-cresol > *o*-cresol > *m*-cresol > phenol

The hyperconjugative effect of CH_3 perturbs the resonance in the benzene ring and boosts up the energy of the Ψ_s orbital of donors and brings it closer to the LUMO of acceptor and, therefore, shifts the CT band to longer wavelength (bathochromic shift).

Formation constants or stability constants of the CT complexes

The formation constants or stability constants (KAD) of the CT complexes under investigation were determined by using Benesi-Hildebrand equation[15] and also from Rose-Drago equation[16] from the absorption measurement of CT bands.

$$\frac{[A_0]}{A} = \frac{1}{K_{AD}[D_0]\varepsilon} + \frac{1}{\varepsilon} \quad \text{(i)}$$

$$K_{AD}^{-1} = \frac{A}{\varepsilon} - \frac{([A_0] + [D_0] + [A_0][D_0]\varepsilon)}{A} \quad \text{(ii)}$$

where K_{AD} is the stability constant, A is the absorbance and ε is the molar absorptivity of the molecular complex. $[A_0]$ and $[D_0]$ are the initial concentrations of acceptor and donor respectively.

The stability constants were obtained from the ratio of intercept to slope and ε from inverse intercept of Benesi-Hildebrand plots (Fig. 2).

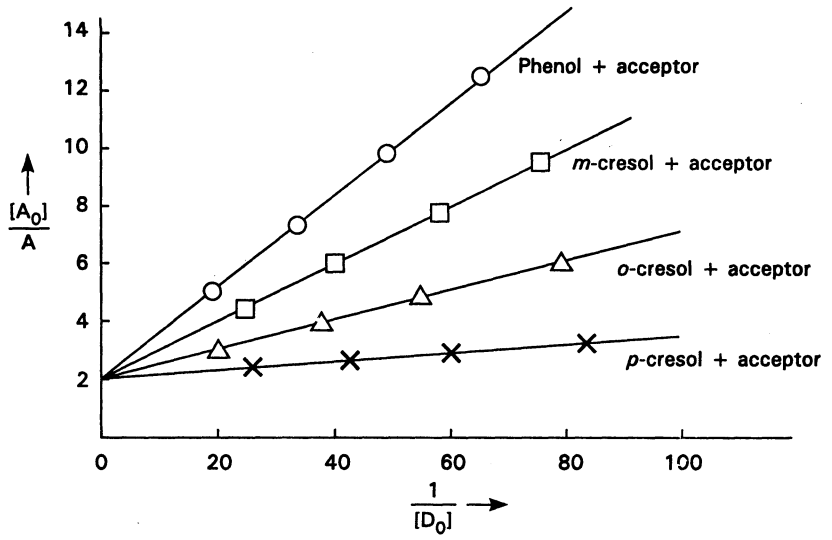


Fig. 2 Benesi-hildebrand plot for CT complexes in CCl_4 medium

The K_{AD} were also evaluated from the intersection points of the Rose-Drago plots which agreed with results of the Benesi-Hildebrand plots.

The linearity of Benesi-Hildebrand plots indicated the formation of molecular complexes of 1 : 1 stoichiometry which was further verified by Job's continuous variation method.

The stability of CT complexes under investigation is due to high energy and greater donor ability of Ψ_s orbital. The donor ability of phenols is in the order

p-cresol > *o*-cresol > *m*-cresol > phenol

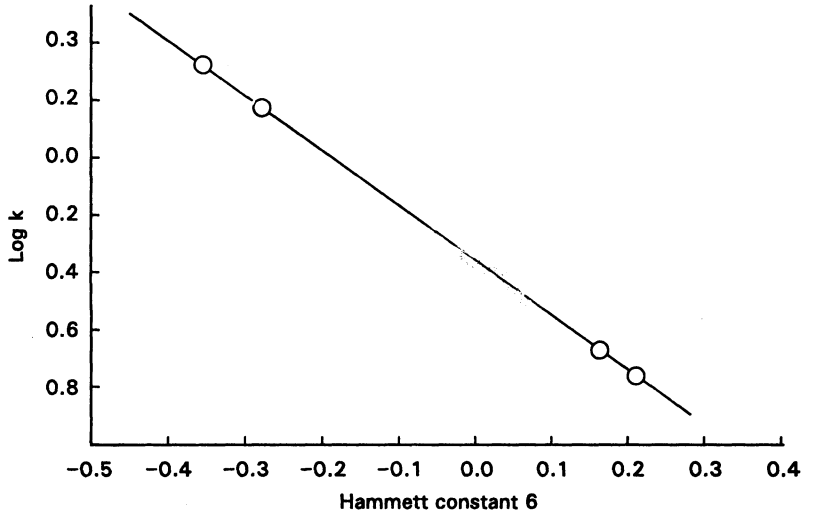


Fig. 3 A plot of log k *vs.* σ of R_y-configuration of CT complexes

as predicted by values of their ionisation potentials, (Table-2). The stability constants of the molecular complexes are in the same order, which certifies that the order of stability of complexes are based on I.P. values. This order of stability of molecular complexes was verified by linearity of logarithmic functions of K_{AD} with the Hammett constants (6p) (Fig. 3).

TABLE-2
CT SPECTRA, FORMATION CONSTANTS AND THERMODYNAMIC PARAMETERS OF 2,6-DICHLORO-*p*-QUINONE-PHENOLS COMPLEXES

Donor	λ_{CT} (nm)	ε_{AD} ($L\ mol^{-1}cm^{-1}$)	I_D (ev)	K_{AD} at 298 K ($L\ mol^{-1}$)	ΔH ($kcal\ mol^{-1}$)	ΔS ($kcal\ mol^{-1}\ K^{-1}$)	ΔG ($kcal\ mol^{-1}$)
p-cresol	538	5827	8.44	6.41	5.289	0.02145	–1.1029
o-cresol	529	5236	8.48	4.12	3.665	0.01512	–0.8405
m-cresol	514	4240	8.57	3.01	2.892	0.01189	–0.6510
phenol	490	2830	8.73	2.88	2.313	0.00987	–0.6279

This stability of CT complexes, besides the ionization potential of the donors (I_D), also depends upon the polarizability, dipole moment of donors and polarizing power of acceptor. The non-bonded electrons of oxygen interact with benzene ring and cause greater polarity in them. The dipolar phenols form stable complexes with the mentioned acceptor by dipole-dipole interaction.

Thermodynamic parameters of CT complexes

The thermodynamic parameters, *viz.*, ΔH and ΔS connected with the complex formation for the different CT complexes have been determined from the temperature variation of stability constants using van't Hoff's method. The values of ΔG at 25°C for CT complexes under investigation are reported in Table-2.

The negative values of ΔH show that the formation of CT complexes was spontaneous. Further, the decrease in the degree of freedom of the components on complexation is shown by the negative values of ΔS.

The linearity of the plot of ΔG *vs.* ΔS indicated the greater overlap of π-HOMO donors with π^*-LOMO of acceptor which favoured the sandwich structure of the molecular complexes[13].

Calculation of ionization potential of donor

Attempts have been made to determine the ionization potential (I_D) of donor phenols using the following equation[17] from the energies of the CT transitions.

$$h\nu_{CT} = 0.77I_D - 4.19 \text{ electron volt per molecule.}$$

The values of I_D obtained are recorded in Table-1.

The values of ionization potentials of donor determined in this study are close to that obtained from the electron impact method and photo-electron spectroscopy[18], for electron in the π-HOMO. These ionization potentials support our assumption that the removal of electron occurs from the ultimate Ψ_s molecular orbitals of the phenols[19].

Conclusions

The following main conclusions were drawn from the present study:

(1) Each donor formed a molecular complex with 2,6-dichloro-*p*-benzoquinone by dipole-dipole interactions and the CT bands arise due to excitation of electron from ultimate Ψ_s molecular orbital of donors to LUMO of the acceptor.

(2) All the CT complexes were π-π type with R_y configuration and 1 : 1 stoichiometry.

(3) The bathochromic shifts of the CT band is in the order

p-cresol > *o*-cresol > *m*-cresol > phenol

which is inconsistent with the ionization potential order and values of stability constants of the molecular complexes.

REFERENCES

1. G. Briegleb, Electron Donoor-Acceptor Complexes, Springer-Verlag, Berlin (1961).
2. L.J. Andrews and R.M. Keefer, Molecular Complexes in Organic Chemistry, Holden Day Inc. (1964).
3. R. Foster, Organic Charge Transfer Complexes, Wiley-Interscience, New York (1969).
4. R.S. Mulliken and W.B. Person, Molecular Complexes, Wiley-Interscience, New York (1969).
5. S.N. Singh, Ph.D. Thesis, B.R.A. Bihar University, p. 88 (1993).
6. B.K. Seal, Indian J. Chem., **37A**, 865 (1998).
7. G. Venkateshwarlu, *Indian J. Chem.*, **37A**, 1119 (1998).
8. T.V. Kumar, *Proc. Indian Acad, Sci.*, **112**, 119 (2000).
9. T.J. Marks, *J. Am. Chem. Soc.*, **115**, 682 (1993).
10. A.S. Vogel, A Text Book of Practical Organic Chemistry, 4th Edn., ELBS, p. 739 (1978).
11. E.M. Voigt, *J. Am. Chem. Soc.*, **86**, 3611 (1964).
12. G.G. Aloisi, Chem. Soc. Faraday Trans., I **73**, 95 (1977).
13. R.S. Mulliken, *J. Chem. Phys.*, **51**, 341 (1954).
14. A. Zweig, *J. Phys. Chem.*, **67**, 506 (1963).
15. H.A. Benesi and J.H. Hildebrand *J. Am. Chem. Soc.*, **78**, 2703 (1949).
16. N. Rose and R.S. Drago, *J. Chem. Soc.*, **81**, 6138 (1951).
17. S. Gautier, *Can. J. Chem. Soc.*, **107**, 862 (1982).
18. H. Agren and H.S. Bagus, *J. Am. Chem. Soc.*, **107**, 134 (1985).
19. A.D. Baker, D. May and D.W. Turner *J. Chem. Soc. (B)*, 22 (1968).

(*Received*: 26 May 2003; *Accepted*: 01 December 2003) AJC-3255