Molecular complexes of phenols with DDQ

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Abstract. Molecular complexes of phenols with DDQ have been studied spectrophotometrically in the temperature range of 10–30°C in a solvent (CHCl₃) of low polarity under low donor concentrations. All the complexes exhibit one CT band each in the wavelength region where acceptor and donor do not have any absorption. The complexes are inferred to be of the π – π type and have *R_y* configuration in which the donor molecular orbital encompasses the substituent. The ionization potentials of the donors, the stability constants and thermodynamic parameters of the complexes have been evaluated.

Keywords. DDQ-phenols; CT complexes; configuration; stability constants.

1. Introduction

In continuation of our work on the donor abilities of phenols and their tendency to form charge transfer (CT) complexes with π acceptors¹, we considered it interesting to investigate the CT spectra, stabilities and thermodynamic parameters of CT complexes of phenols with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). Literature survey revealed that DDQ forms CT complexes with phenols and produces a characteristic colour in methanol^{2,3}, but the colour fades with time indicating that these complexes are unstable and soon turn into other products. It is for this reason that the characteristics of CT complexes, viz., positions of CT bands, stabilities and thermodynamic parameters have not yet been reported. Further, we noticed from literature^{4,5} that the CT complexes can be stabilized for a longer time in solvents of low polarity, at low temperatures and under low donor concentrations. To study this further we chose a low polar solvent, viz. CHCl₃, and recorded the spectra of these complexes at low temperatures using low concentrations of phenols. The results are reported here.

2. Experimental

The commercial sample of DDQ obtained from Aldrich was repeatedly recrystallized from benzene–chloroform (2:1) mixture (m.p. 213–214°C). Phenols (BDH-Analar) were purified by the methods available in literature⁶. Spectrograde chloroform (BDH) was used without further purification.

The UV-vis absorption spectra (figure 1) of the complexes were recorded on a Shimadzu-240 double beam spectrophotometer on fast scan speed in the temperature

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Figure 1. Charge transfer spectra of DDQ complexes with phenols and naphthols (1, α -naphthol; 2, β -naphthol; 3, *p*-methoxy phenol; 4, *p*-cresol; 5, *o*-cresol; 6, *m*-cresol; 7, *p*-chloro phenol; 8, *p*-bromo phenol and 9, phenol.)

range 10–30°C at 5°C intervals with an accuracy of $\pm 0.1^\circ\text{C}$ using a matched pair of quartz-stoppered cells of 10 mm path length. The studies at different temperatures were made in a thermostatted sample compartment by circulating water around the cuvettes. Stock solutions of donor and acceptors were prepared and were mixed just before recording the spectra. The concentration of DDQ varied between 1×10^{-4} and 5×10^{-4} M while that of donors between 0.005 and 0.15 M. Absorption bands due to the acceptor or donor alone have fallen to the base line much before the wavelength of CT absorption. However, the lower wavelength side of the CT band is further complicated by other absorptions, probably due to the complexed donor⁷. The complicated CT bands are analysed using the relation given by Briegleb and Czekalla⁸,

$$\nu_h - \nu_l / 2 (\nu_m - \nu_l) = 1.2, \quad (1)$$

where ν_h and ν_l refer to the frequency at half the maximum intensity of the high and low frequency sides of the peak located at ν_m . The formation constants (K) of the complexes were determined by using both Benesi–Hildebrand⁹ and Rose–Drago¹⁰ equations,

$$[A_0]/A = 1/K[D_0] \varepsilon + 1/\varepsilon, \quad (2)$$

$$K^{-1} = A/\varepsilon - ([A_0] + [D_0]) + [A_0][D_0]\varepsilon/A, \quad (3)$$

where K is the stability constant, A is absorbance and ϵ is molar extinction coefficient of the complex. $[A_0]$ and $[D_0]$ are initial concentrations of acceptor and donor respectively.

Stability constants are obtained from the ratio of intercept to slope and ϵ from inverse intercept of Benesi–Hildebrand plots (figure 2). They are also determined from the intersection points of the Rose–Drago plots. The values obtained by both the methods agreed well with each other. Thermodynamic parameters, viz. ΔH and ΔS , have been determined from the temperature variation of stability constants using van't Hoff's method and are reported in table 1 together with ΔG at 25°C. The stoichiometry of each of the complexes was determined by Job's continuous variation method and is found to be 1:1 (figure 3).

3. Results and discussion

Colourless solutions of DDQ and phenols in chloroform turned blue immediately after mixing. The colour changes are attributed to the formation of CT complexes between the DDQ and the phenols. All the complexes exhibit one CT band each in the range 525 to 680 nm. Appearance of CT bands is attributed to the excitation of electron from the highest occupied molecular orbital (HOMO) of donor to the lowest unoccupied molecular

Figure 2. Benesi–Hildebrand plots of CT complexes of DDQ with phenol at different temperatures.

Table 1. Charge transfer spectra, stability constants (K) and thermodynamic parameters of DDQ-phenol complexes.

ΔH and ΔG in k cal mol⁻¹; ΔS in cal deg⁻¹ mol⁻¹; ϵ in l mol⁻¹ cm⁻¹; λ in nm; IP in eV; K in l mol⁻¹. The values of stability constants (K) are accurate up to ± 0.25 .

Donor	λ CT	ϵ	IP	K °C at					ΔH	ΔS	ΔG
				10	15	20	25	30			
α -Naphthol	735	4590	7.64	156	103	71	48	34	13.0	35.9	2.31
β -Naphthol	693	4960	7.77	146	99	68	47	33	12.74	35.10	2.28
<i>p</i> -Methoxy phenol	680	5765	7.81	85	60	43	31	23	11.20	30.74	2.04
<i>p</i> -Cresol	595	4100	8.14	54	40	30	23	17	9.62	26.06	1.85
<i>o</i> -Cresol	580	3940	8.22	50	37	28	21	16	9.54	25.92	1.81
<i>m</i> -Cresol	570	3960	8.26	33	26	20	16	13	8.20	22.02	1.64
<i>p</i> -Chlorophenol	560	3050	8.32	23	19	15	12	10	7.10	18.83	1.49
<i>p</i> -Bromophenol	550	2950	8.37	20	16	13	11	9	6.95	18.59	1.41
Phenol	537	2400	8.44	12	10	8.7	7.5	6.3	5.68	15.08	1.18

Figure 3. Job's continuous variation plot of DDQ with *p*-methoxyphenol $[D_0] = [A_0] = 2.0 \times 10^{-3}$ M.

orbital (LUMO) of the acceptor. Here it is interesting to note that phenols exhibit two CT bands with TCNE. The higher and lower wavelength bands were attributed to excitation of electron from ultimate (ψ_s) and penultimate (ψ_{as}) molecular orbitals of the donor thus

forming complexes with two different configurations viz., R_x and R_y . In order to determine the configuration of the phenols-DDQ complexes, the ν_{CT} of phenols-DDQ are plotted against those of R_x and R_y configurational complexes of phenols-TCNE. A linear relationship is observed between the ν_{CT} of phenols-DDQ and the ν_{CT} of R_y configuration of phenols-TCNE while that of R_x configuration exhibited a scatter. A linear relation is observed only when the same orbital of donors is involved in the formation of complexes with two different acceptors. It is therefore inferred that in phenol-DDQ complexes also the ψ_s orbital acts as a donor level and forms complexes with R_y configuration in which the energy of the CT transition is affected by the substituents as this level encompasses the substituent¹ (figure 4). The absence of R_x configurational complex implies that the R_y configuration is more stable than the R_x configuration. This is reasonable because in R_y configuration the C=O of DDQ and the O-H of phenol lie parallel and may form hydrogen bonding which significantly favours this configuration over the other.

3.1 Effect of substituents on CT bands

The position of CT band of phenol-DDQ (530 nm) is shifted to longer wavelengths by the substituents present in the phenol ring and the shifts are in the following order.

α -naphthol > β -naphthol > *p*-methoxy phenol > *p*-cresol > *o*-cresol > *m*-cresol > *p*-chloro phenol > *p*-bromo phenol > phenol.

The effect of substituents on the position of the CT band is attributed to the interaction of substituents with the π orbitals of the benzene ring of phenol. The conjugative interaction of naphthalene, the mesomeric effect of OCH_3 , hyperconjugative effect of CH_3 and inductive effect of halogen groups all perturb the resonance in the benzene ring and boost the energy of the donor ψ_s level and bring it closer to the LUMO of DDQ and thus cause a bathochromic shift in the CT band.

3.2 Ionisation potentials of the donor

The ionisation potentials of the phenols were calculated from the following equation¹¹,

$$h\nu_{CT} = 0.77 I_D - 4.19, \quad (4)$$

and are reported in table 1.

Figure 4. The ψ_s and ψ_{as} molecular orbitals of benzene.

The values of ionization potentials obtained in this study are comparable to those obtained from the CT spectra of phenols-TCNE complexes and the photoionization method. They are however lower compared to those obtained from the electron impact method. The ionisation potential of phenol is very close to that obtained from photoelectron spectroscopy for the electrons in π -HOMO and far lower than those of electrons in other orbitals^{12,13}. This supports our assumption that electron donation takes place from the ψ_s molecular orbital.

3.3 Formation constants and thermodynamic parameters

The stabilities of complexes increase with increasing electron-releasing ability of the substituents in the benzene ring and are in the sequence:

α -naphthol > β -naphthol > *p*-methoxy phenol > *p*-cresol > *o*-cresol > *m*-cresol > phenol > *p*-chloro phenol > *p*-bromo phenol.

The formation constants of α -naphthol and β -naphthol complexes are greater than that of phenol complex and are in the order: α -naphthol > β -naphthol > phenol. The logarithmic functions of formation constants bear a linear relationship with the Hammett σ_p constants (figure 2).

It is interesting to note that the stability constants of the phenols-DDQ complexes are found to be greater than those of the corresponding phenols-TCNE complexes¹ and they are also greater than the correspondingly substituted benzenes-DDQ complexes, while the stabilities of α -naphthol and β -naphthol-DDQ complexes are greater than that of naphthalene-DDQ¹⁴. The higher stability of DDQ complexes over those of TCNE may be due to the greater electron affinity of DDQ over the TCNE. The greater stability of the phenols-DDQ over the benzenes-DDQ may be due to greater polarity of phenols over benzenes as discussed elsewhere¹.

Thermodynamic parameters viz. ΔH , ΔS and ΔG of the complexes have been determined from the variation of K with temperature (table 1). Plots of $\log K$ vs $1/T$ give straight lines, from the slope and intercept of which ΔH and ΔS can be evaluated. The ΔG values are calculated from the equation

$$\Delta G = \Delta H - T \Delta S, \quad (5)$$

and are reported at 25°C. The ΔH values are found to be about 10 K cal mol⁻¹ a characteristic feature of CT complexes. The negative enthalpies show that the complex formation is spontaneous, while negative entropy indicates a decrease in the degree of freedom of the components upon complexation. The plot of ΔH vs ΔS which is a straight line indicates that the complex formation is sterically unhindered. This favours a sandwich structure for the complexes in which the π orbital of donor and π^* orbital of acceptor can have greater possible overlap¹⁵.

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