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Hydrogen-bonding and protonation effects on the formation of charge transfer complex between *para*-benzoquinone and 2,6-dimethoxy phenol ☆

Prakriti Ranjan Bangal *

Microwave Spectroscopy Laboratory, ECMP Division, Saha Institute of Nuclear Physics, Sector-1, Block-AF, Bidhannagar, Kolkata 700064, West Bengal, India

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Abstract

Formation of CT complex of series of quinines of increasing basicity (chloranil to duroquinone) were checked systematically in methylenechloride with different aromatic donors in presence of hydroxylic additives of increasing hydrogen-bonding power (tetra-butyl-alcohol to hexafluoro-2-propanol) or acidity. The effect of the basic additives of increasing basicity (pyridine to 4-*N*,*N*-dimethylaminopyridine) was also observed. The formation constant (K_{CT}) of CT complex between *para*-benzoquinone and 2,6-dimthoxyphenol was enhanced approximately 50 times by TFA and approximately two times by HFIPA due to protonation and strong hydrogen-bonding interaction of BQ with TFA and HPIPA, respectively. Similarly, K_{CT} increased approximately six times by DMAPy due to hydrogen-bonding with DMOPh.

1. Introduction

Ground state electron donor–acceptor (EDA) or charge transfer (CT) complexes are very fundamental processes not only to living system leading to the natural phenomena like proton coupled electron transfer in excited state which occurs in Photosystem-II but also recently gaining very high importance as potentially high efficiency non-linear optical materials [1]. Such complexes have been [2–4] and are recently being [5–7] reported to act as reaction intermediates. Quinones are ubiquitous to living systems and represent important cofactors for electron transfer in photosynthesis and respiration [8]. Quinone–hydroquinone couples have been studied over many decades as the prototypical examples of organic redox system [9–11]. In addition to their intrinsic chemical interest, these studies are particularly important in view of the key biological functions of quinone based couples as electron–proton transfer agents in oxidative phosphorylation or photosyntheis [12–16]. Thus, it is necessary to understand as far as possible, the environmental factors which regulate the potential and formation of CT complex pathway with various electron donors which appear in quinone systems, both in vitro and in mitochondrial or photosynthetic membranes. Among these factors, we are particularly concerned in this Letter with hydrogen bonding as well as protonation which have been implicated in the biological function of the quinone systems [15] and on which surprisingly little systematic research has been done. Ground state hydrogen-bonding (HB) complexes are well known for many systems [17–19] but their importance on formation of CT complex are not yet known so far.

Since few decade solvent dependence of the CT absorption band between organic EDA complexes has

☆ Part of this work has been done in Brandeis University.

* Fax: +91 33 2337 4637.
E-mail address: prbangal@yahoo.com.

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been the subject of extensive investigations [20–27]. A large hypsochromic shift of the CT band with increasing solvent polarity was observed [20–22] due to the much stronger solvent stabilization of the ground state than that of excited state. A large bathochromic shift was also reported for the CT transition in complex of π electron donor with electron acceptor containing CO group in strongly hydrogen bonding solvents such as hexafluoro-isopropanol (HFIPA) or trifluoroaceticacid (TFA). But, unfortunately no work has yet been done investigating the effect of H-bonding agent both in donor site and in acceptor site on the position of equilibrium between the component species and complex. Indeed, references to the role of hydrogen-bonding in quinone CT complex are remarkably sparse [28], in view of the enormous literature on the subject. To further clarify the situation, I present spectrometric studies of quinines CT complex with aromatic donors in non-polar aprotic solvent from both sides, in which I systematically vary the acidity and hydrogen-bonding power of added hydroxylic reagents (increasing from tetrabutyl alcohol to hexafluoro-2-propanol (HFIPA)) and unambiguous protonating agent TFA as well as the basicity of the substitute *p*-benzoquinones (BQs) (from chloranil to duroquinone) in one side and on the other side, basicity or hydrogen-bond accepting power of added bases from pyridine to DMAPy.

2. Experimental

p-Benzoquinones were of best available grade (>97%) from Sigma, Aldrich and substituted as follows: tetrachloro (TCBQ, chloranil); 2,5-dichloro (DCBQ); 2,5-diphenyl (DPBQ); 2,5-dimethoxy (DMOBQ); 2,5-dimethyl (DMBQ); tetramethyl (TMBQ, duroquinone). Methelenechloride, spectroscopic grade (99.9%, Sigma-Aldrich) was used as solvent without further purification but dried under molecular sieives (4A, 8–12 mesh. Aldrich) preheated to 400 °C for 12 h prior to use. 1,1,1,3,3,3-hexa fluoro 2-propanal (99+%) (HFIPA); 2,2,2-trifluoroethanol (99.5+%) (TFE), trifluoroacetic-acid (99+%) (TFA) were from Aldrich.

Absorption spectra were recorded by Shimazu Spectrometer (Model PC-2101). Equilibrium constant K_{HB}, for formation of hydrogen-bond complexes were calculated from the effect of added reagent (ROH) on absorption spectra using the relation given by Mataga and Tsuno [29]

$$[1 - A_0/A]_\lambda/[\mathrm{ROH}] = -K + (\varepsilon_c/\varepsilon)K(A_0/A),$$

where ε_c and ε, respectively, denote the extinction coefficient of the complex and free molecule and A_0 and A are absorbances in absence and present of bonding agent whose total concentration is much greater than that of substrate. The intercept of the plot $(1-A_0/A)/[\mathrm{ROH}]$ vs. A_0/A is $-K$.

3. Results and discussions

3.1. Effect of hydrogen-bonding additives on quinones

All substituted *p*-BQs (chloranil to duroquinone) form H-bond or get protonated with C=O groups by hexafluoro-2-propanol (HFIPA) and TFA. The effect of strongly hydrogen bonding agent on the absorption spectra of all substituted BQs has very less effect. Upon addition of TFA/HFIPA, a slight increase in absorbance of π–π* (S_2–S_0) band of quinone are marked in methylenechloride. Other alcohols are much less effective in influencing quinone absorption. A representative Mataga plots [29] using the change of absorbance in the π–π* (S_2–S_0) band of unsubstituted 1,4-benzoquinone by TFA were non-linear (Fig. 1) and it indicated for separate two steps bonding (protonation) at the two quinone oxygens. The equilibrium constant of protonation K_P values were 5.5 and 107.5 M^{-1} for bonding of BQ to TFA. A linear Mataga plot was observed for binding of HFIPA to BQ, no distinct two steps bonding could be observed having hydrogen-bonding equilibrium constant K_{HB} equal to 4.1 M^{-1}. Similarly, K_{HB} values were calculated from linear Mataga plot for binding of TCBQ to TFA and HFIPA which were to be 1.84 and 0.54 M^{-1}. These H-bonding equilibrium constants are quite close, compared to the very large difference in the proton acidities of the additives: pK_a of TFA is 0.52, where as that of HFIPA is 9.3 [30]. In DMSO, respective pK_as are 3. 45 and 17.85 [31].

3.2. Charge transfer complex formation in pure media

All substituted BQ studied here have strong electron affinity and easily form CT complexes with good electron donor molecules. Different benzene derivatives such

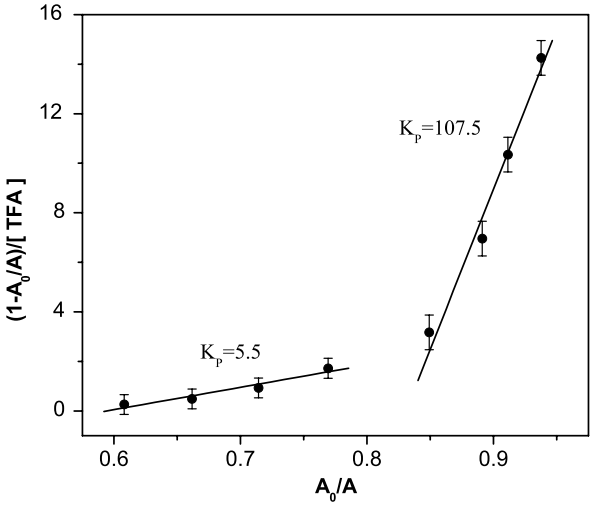

Fig. 1. Mataga plot of TFA + *p*-benzoquinone at 300 nm.

as nitrobenzene, methylebenzene, methoxybenzene and different substituted phenols have been checked to form CT complexes with the quinones. In all cases, complex formation is indicated by the appearance of a new broad band in the visible region of the absorption spectrum. As it can be expected the CT complex formation constant K_{CT} values slightly increases with decreasing solvent polarity and oxidation potential of electron donor molecules. Fig. 2 shows the CT complex absorption band of BQ and DMOPh peaking at 460 nm. For a given concentration of BQ, the intensity of absorption band increases as function of DMOPh. Benesi–Hilderbrand plot gives the formation constant and extinction coefficient of the complex 12.8 M^{-1} and 580 $M^{-1}\,cm^{-1}$, respectively.

3.3. Effect of hydrogen-bonding agent

Upon addition of weak hydrogen-bonding agents: ethanol, 2-propanol and tetra-butyl alcohol to methyelenechloride solution of all quinones studied do not show any effect in the formation of CT complex with the any aromatic donors reported. HFIPA is a stronger acid and hydrogen-bonding reagent than any other alcohol. On addition of HFIPA in the complex of quinones and aromatic donor in CH_2Cl_2, a little change of color was observed. The effect is more prominent for BQ and DMOPh pair. In presence of sufficient amount of HFIPA, the CT equilibrium constant K_{CT} of BQ and DMOPh increases twofold than that of without this additive. The peak position of the absorption band of CT complex shifts toward red on addition of HFIPA. For quinines with low basicity (TCBQ, DCBQ) or high basicity (DMOBQ, TMBQ), the effect of HFIPA on their CT complex with DMOPh and other donors is too low to measure in spectroscopic technique. The enhancement of CT complex formation between BQ and DMOPh is due to very strong hydrogen-bonding of BQ with HFIPA. The pK_a values of TCBQ and DCBQ should be lower than BQ which do not favor the protonation, only weak hydrogen-bonding interaction can be expected by HFIPA. TMBQ (duroquinone) is very weak base as indicated by its pK_a (=−1 [9]) in aqueous medium, its protonation by HFIPA is ruled out. The UV–Vis spectrum of TMBQ in methylenechloride shifts slightly to the red upon addition of HFIPA which is ascribed to hydrogen bonding between TMBQ and HFIPA and the hydrogen-bonding equilibrium constant for this system in CH_2Cl_2 is estimated from the shift in spectrum is to be 2.8 M^{-1}. So the enhancement of CT complex formation between BQ and DMOPh is due to the strong hydrogen-bonding interaction or protonation of BQ by HFIPA.

3.4. Effect of strong acid TFA

Now the effect of TFA, a strong acid on CT complex between quinines and the donor DMOPh in methylenechloride has been studied in details. It is important to note that TFA has significant effect on CT complex between all quinines and any aromatic donors studied here. A strong effect was monitored on addition of TFA in CT complex of BQ and DMOPh. Fig. 3 portraits the signature of the remarkable effect of it. For a given concentration of BQ and 1 M concentration of TFA, very less amount of DMOPh is required to reach the saturation condition. The equilibrium moved to the forward direction and the absorption band of CT

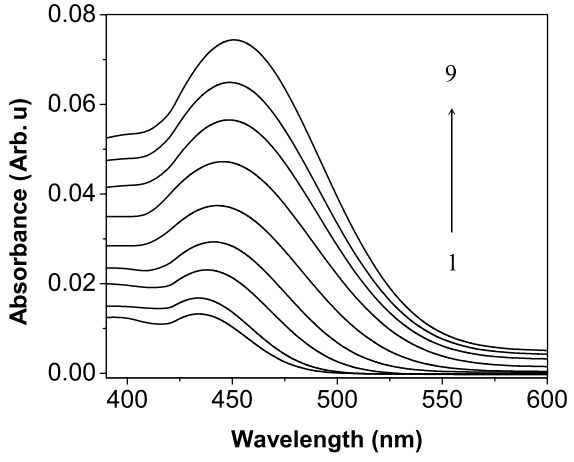

Fig. 2. Absorption spectra of CT complex as a function of DMOPh concentration at fixed concentration of *p*-benzoquinone (2.17×10^{-4} M) in CH_2Cl_2. Concentration of DMOPh is (1) 0, (2) 2.4 mM, (3) 7 mM, (4) 14.3 mM, (5) 24 mM, (6) 35.6 mM, (7) 47.5 mM, (8) 59.4 mM, (9) 71 mM. Uncertainty in measuring the DMOPh concentration ~±0.2 mM.

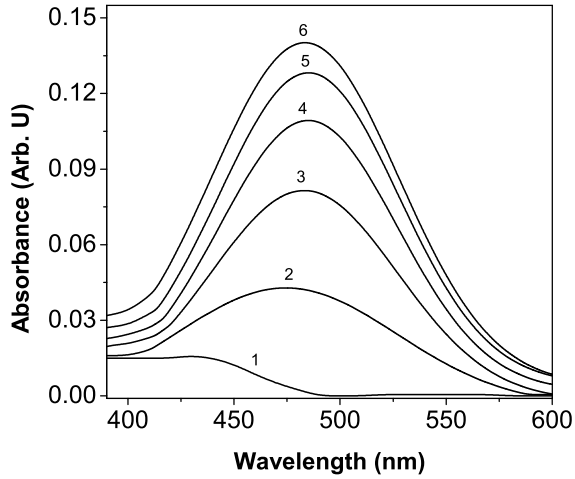

Fig. 3. Absorption spectra of CT complex as a function of DMOPh concentration at fixed concentration of *p*-benzoquinone (1.6×10^{-4} M) and TFA (0.9 M) in CH_2Cl_2. Concentration of DMOPH is (1) 0, (2) 1.0 mM, (3) 3.0 mM, (4) 5.0 mM, (5) 8.4 mM, (6) 15 mM. Uncertainty in measuring the DMOPh concentration ~±0.2 mM.

complex shifts to red peaking at 485 nm. In 1 M concentration of TFA the formation constant and extinction coefficient calculated to be 243 M^{-1} and 1218 M^{-1} cm^{-1}, respectively. On successive addition of TFA for given concentration of BQ and DMOPh, the peak position shifts towards red, extinction coefficient and equilibrium constant all increases (Table 1). Fig. 4 shows the change of K_{CT} as a function of TFA concentration and it is non-linear in nature which nicely corresponds to the two steps nature of Mataga plot (Fig. 1). For lower concentration region of TFA the change of K_{CT} is very fast and higher concentration region it is relatively slow. At about 1 M concentration of TFA the formation constant becomes constant which is approximately 20 times higher than that of in neutral solution and extinction coefficient (ε) increases around 2.5 times at 480 nm. It is important to mention here that the separation of K_{CT} and ε is bit tricky from Benesi–Hilderbrand plot. Hence, the product of K_{CT} and ε should be the good parameter to compare the effect of additives on CT complex formation by spectroscopic technique.

Table 1
Absorption peak position, extinction coefficient and equilibrium constant value of BQ–DMOPh CT complex at different TFA concentration in CH_2Cl_2 solution

TFA (mM)	λ_{max} (nm)	ε(M^{-1} cm^{-1}) (at 480 nm)	K (M^{-1})
0	460	580 ± 30	13.0 ± 1
4	462	631 ± 35	46.0 ± 2
22	467	766 ± 40	81.0 ± 4
54	475	950 ± 50	118 ± 5
108	477	1131 ± 55	147 ± 7
216	480	1168 ± 55	195 ± 10
433	483	1179 ± 55	229 ± 11
750	484	1217 ± 60	239 ± 12
1000	484	1218 ± 60	243 ± 12

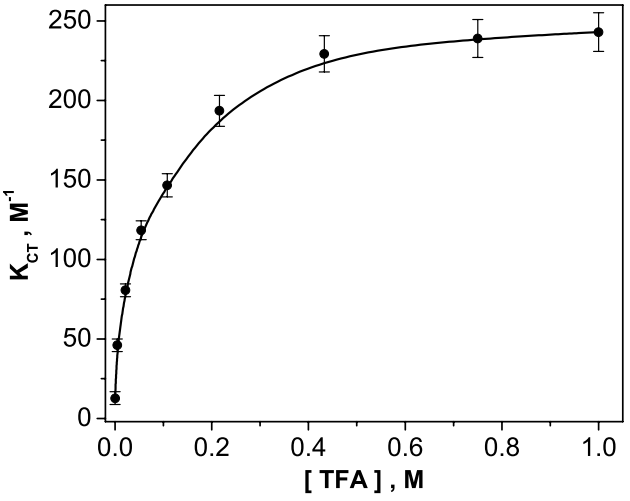

Fig. 4. Dependence of CT equilibrium constant of BQ and DMOPh on TFA concentration in CH_2Cl_2.

Considering $K_{CT}\varepsilon$ as the parameter of CT complex formation one can see that the effect of TFA on the BQ–DMOPh CT complex is approximately 50-fold enhanced. The negative pKa value of BQ (−7) [32] and TFA (0.52) shows the protonation of BQ by TFA is highly favorable and it is well supported from the change of absorption spectra of BQ which has been taken into account to calculate formation constant by Mataga plot (vide supra). This large effect of TFA on BQ–DMOPh complex is due to protonation of BQ by TFA. The effect of TFA on CT complex between weakly basic TCBQ and DMOPh is relatively poor, no effect could be monitored on lower concentration of TFA (0.3 M). K_{CT} increases approximately seven times on very high concentration of TFA (1 M) than that of in neutral solution where as change of extinction coefficient was not prominent. The protonation of TCBQ by TFA is highly unfavorable which is again supported by the lack of the significant change in absorption spectra of chloranil in CH_2Cl_2 upon addition of TFA up to 0.3 M. Irrespective of quinone basicity, all quinines get protonated by TFA and enhance the formation rate of CT complex finally. On the other hand, effect of TFA on TMBQ and DMOPh complex is very high as it can be expected. The K_{CT} of TMBQ–DMOPh complex increases approximately 10 times on addition of only 0.1 M TFA keeping the extinction coefficient same. TMBQ is very strongly basic quinone and easily get protonated by TFA resulting the strong enhancement of CT complex formation ability with DMOPh.

3.5. Effect of base (hydrogen-bonding acceptor)

Pyridine, lutidine, collidine and 4-*N*,*N*-dimethylamino pyridine (DMAPy) all four bases make hydrogen bonded complex with DMOPh. Fig. 5 shows the effect of strong base DMAPy on the overtone absorption spectrum of OH of DMOPh in CH_2Cl_2. On addition of DMAPy, overtone band intensity decreases sequentially and application of Mataga equation to the data gives a good line (Fig. 5, inset a). This results is suggestive to the fact that DMOPh and DMAPy form 1:1 complex in CH_2Cl_2 and from the intercept of the linear plot of Fig. 5 one can predict hydrogen-bonding equilibrium constant K_{HB} to be 3.6 M^{-1}. Hydrogen-bonding equilibrium constant of pyridine, lutidine and collidine with DMOPh is calculated to be 0.7, 1.2 and 1.4 M^{-1}, respectively. The effect upon addition of pyridine, lutidine or collidine on BQ and DMOPh mixture is very weak, a little increase of K_{CT} is observed on very high concentration of bases (1.5 M). But Fig. 5, inset b shows very strong effect of DMAPy on formation constant of BQ and DMOPh CT complex. Addition of 0.02 M DMAPy on the mixture of BQ–DMOPh, enhances the formation constant by approximately 3.5 times and extinction coefficient by 1.5 times and on 0.2 M concentration of

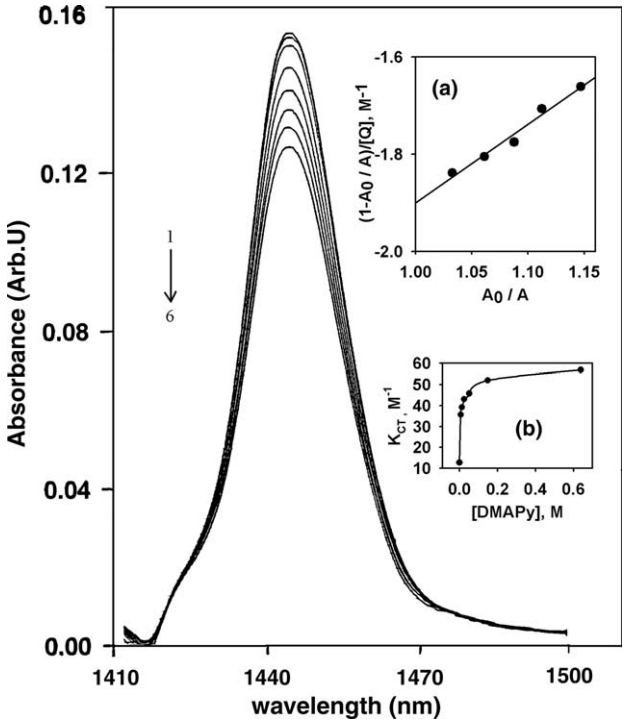

Fig. 5. Variation of overtone absorption band intensity of OH of DMOPh (1 M) by DMAPy. Concentration of DMAPy (1) 0, (2) 15, (3) 25, (4) 35, (5) 45, (6) 55 mM, respectively. Inset (a) is the Mataga plot of the absorption data and inset (b) is the variation of CT complex formation constant between BQ and DMOPh as function of DMAPy concentration.

DMAPy the value of K_{CT} get saturated. This results suggests that strongly bonded DMOPh–DMAPy pair serves as stronger electron donor moiety increasing the CT complex formation ability with quinines.

4. Conclusion

From the aforesaid results, it is conclude that strongly hydrogen bonded or protonated *para*-benzoquinine serves as strong electron acceptor increasing the ground state CT complex formation ability with aromatic donors.

Hydrogen-bonded 2,6-dimethoxyphenol base pair behaves as stronger donor than the neutral phenol and helps easy CT complex formation with quinines.

It is also concluded that proton coupled CT could occur in ground state at least for quinone and DMOPh pair. This proton coupled CT occurs in both ways, i.e. when proton of the additives coupled with quinone moiety and proton of phenol moiety coupled with DMAPy.

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