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FORMATION AND TRANSFORMATION OF CHARGE-TRANSFER COMPLEXES OF PIPERIDINES WITH 1,4-BENZOQUINONE HOMOLOGUES

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Electronic absorption spectra of molecular complexes formed between methyl substituted piperidines as electron donors and 1,4-benzoquinone homologues as electron acceptors are reported in chloroform medium. The stability constants of the complexs of piperidine with different benzoquinones are nearly proportional to the strength of the acceptor. The 1 : 1 complexes formed between donor and acceptor are sufficiently stable in excess concentrations of the acceptor, but transform to disubstituted products with excess donor concentrations. The ionisation potential of the donors and the electron affinity of the acceptors are evaluated from the spectral data of the complexes.

Key Words : Charge-Transfer Complexes; Piperidine; Benzoquinone; Electronic Absorption Spectra; Electron Affinity

INTRODUCTION

STUDIES on the molecular interaction of piperidine and its methyl derivatives as typical strong electron donors with some organic π-acids were reported[1-8] by us earlier. These studies indicate that the charge-transfer(CT) complexes formed by the electron donor-acceptor(EDA) interactions are strong. The strength of the acceptor depends on the nature of the substituents and the extent of CT on the acceptor and donor moieties.[9]

To understand the dependence of the CT transition energy on the substituents of the acceptor, the authors undertook the study of the EDA interactions of piperidine (PD) with 1,4-benzoquinone (BQ) homologues. This study is aimed at predicting the position and results of the equilibria of the CT complexes of PD with various BQs and to find out the final products of the transformation reaction of CT complexes. The investigations in chloroform medium are reported and the results are discussed in the present paper.

EXPERIMENTAL

Chemicals and Solvents

BQ[1] and its monochloro derivative[10] were prepared and purified as in the literature. Methyl-BQ 2,5-dichloro-BQ and 2,6-dichloro-BQ were supplied by

Bio-organics (India) and 2,3,5,6-tetrachloro-BQ by Merck (FRG) and were recrystallised three time each from ethanol. Their purity was checked chromatographically. Chloroform, Glaxo spectrograde (India) was used after further purification by standard methods.[11] PD and methyl substitued PDs were obtained from Fluka (Switzerland), except 3,5-dimethyl-PD which is obtained from EGA (FRG), and were purified by repeated distillation. Other chemicals and solvents used were of sufficient purity for spectroscopic studies.

Position and Results of Equilibrium

The mole-ratio[12] and the continuous variation[13] methods were employed for determining the composition of the complexes. Coleman *et al.*[14] plots were drawn for the verification of the single absorption of the CT complexes. Keeping the concentration of the acceptor constant at 4×10^{-4} mol dm^{-3} and varying the concentration of PD between 4×10^{-4} to 8×10^{-4} mol dm^{-3}, the method of Seal *et al.*[15] was adopted for the evaluation of the results of the equilibrium. The maximum absorbance values were measured at the absorption maximum (λ_{CT}) of each CT complex. The half width of the CT bands were obtained at the half intensity of the λ_{CT}.

Isolation of Final Products

The reaction mixture with excess donor in chloroform was refluxed for 30 min at 50 °C. The disappearance of the CT complex spot on a tlc plate was tested eluting with hexane-chloroform (50/50, v/v) mixed solvent. The mixture was then subjected to fractionation on a column, containing silica gel. The solid product was isolated under normal pressure and temperature, and dried.

Instruments and Spectra

Carl Zeiss specord and spekol spectrophotometers were used with 1cm matched cells for recording the absorption spectra and absorption measurements. IR spectra were recorded in KBr medium on a Perkin-Elmer 237 IR spectrophotometer and proton NMR spectra on a Perkin-Elmer R-32 NMR spectrometer operated at 90MHz. $CDCl_3$ was used as solvent for the NMR spectra with TMS as internal reference.

Results and Discussion

Electronic Spectral Data

PD on mixing with each of all BQs in chloroform exhibits new, moderately intense and broad absorption bands in the visible region, characteristic of CT Complexes.[16] The new absorption bands are separated well from those of either of the components. The donor is saturated and in free donor, the possible transition is $n \rightarrow \sigma^*$, while in benzoquinones an allowed high energy $\pi \rightarrow \pi^*$ and a relatively forbidon low energy $n \rightarrow \pi^*$ transitions. But the new absorption in the present electron donor-acceptor (EDA) system is assigned to an inter-

molecular $n \rightarrow \pi^*$ transition, from the HOMO of donor to the LUMO of acceptor. While the effect of PD substituent on the absorption maximum of the CT complex is almost negligible reflecting in the non-aromaticity of the donor, the substituents on BQ have considerable effect on the electronic transition of the complexes; the methyl group leading to a bathocromic shift and the chloro group leading to a hypsocromic one, conforming the expected mesomerie effect. The accepting ability of BQ is enhanced in its complexes with PD by the presence of chloro substituents (Table I), indicating the trend reported earlier.[9,16] The plot of the absorption maxima of CT complexes of PDs with tetrachloro-1,4-BQ *versus* those with tetrachloro-1,2-BQ in Fig. 1 yields a straight line with a slope of unity, indicating the formation similar type of complexes with both acceptors.

TABLE I

Absorption maxima (λ_{CT}), *half width of the CT band* ($\Delta\ \nu_{CT}$), *molar absorptivity* (ϵ), *equilibrium constant* (K), *oscillator strength* (f) *and transition dipolement* (μ_{en}) *values for the complexes of PB with BQs*

Benzoquinone Substituent	λ_{CT} nm	$\Delta\ \nu_{CT}$ cm^{-1}	ϵ $dm^3\ mol^{-1}\ cm^{-1}$	K $dm^3\ mol^{-1}$	f	μ_{en} debye
Parent	508	6008	1820 ± 60[a]	2110 ± 80[a]	0.071	2.76
Methyl	491	6141	1840 ± 60	1770 ± 70	0.073	2.78
Chloro	522	5674	2060 ± 110	2700 ± 120	0.076	2.92
2,5-Bichloro	530	5609	2150 ± 140	3190 ± 150	0.077	2.97
2,6-Dichloro	542	5404	2310 ± 170	3280 ± 180	0.081	3.08
Tetrachloro	576	5231	3690 ± 220[b]	4410 ± 250	0.129	4.29

[a]Reference 1. [b]Reference 5.

Stability Parameters

The composition of all CT complexes is found to be 1 : 1 of the components. Single absorption of the CT complex is verified in all cases and a representative plot is given in Fig. 2 for the CT complex formed between PD and tetrachloro-BQ. As mentioned earlier[5] many usual methods for the evaluation of the results of equilibrium[17–22] failed, but the method described by Seal *et al.*[15] is practicable. Values of molar absorptivity, equilibrium constant and half width of the CT bands are listed in Table I. The oscillator strength and the transition dipole moment values are derived as mentioned earlier[2] and are also listed in Table. 1. The results on the intensity and stability of the CT complexes of PD are in order : tetrachloro-BQ > 2,6-dichloro-BQ > 2,5-dichloro-BQ > chloro-BQ > BQ > methyl-BQ, which in turn is attributed to the electron affinity of benzoquinones on the Briegleb's scale,[23] corroborating the Mulliken's theory of intermolecular CT transistions.[24]

Transformation of CT Complexes

Complexes of equimolar concentrations of acceptor or with excess concentrations of acceptor are sufficiently stable, but in excess donor concentrations, these

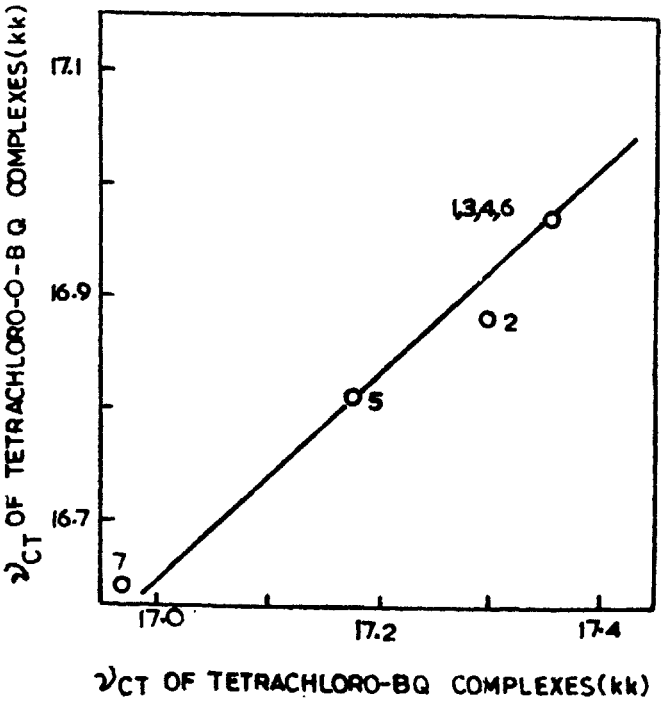

FIG 1 Plot of ν_{CT} of the complexes of piperidines (numbers as indicated in Table II) with tetrachloro-1,4-BQ *vs* those of tetrachloro-1,2-BQ in chloroform.

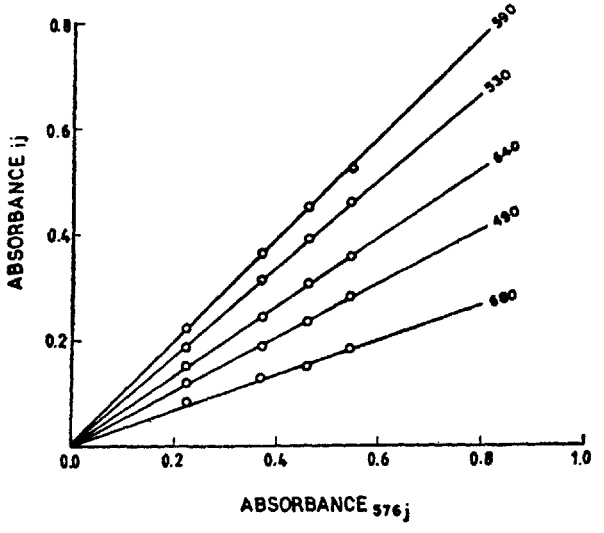

FIG 2 Coleman, Varga and Mastin plots for the complex of piperidine with tetrachloro-BQ in chloroform.

transform to yellow coloured species in solution, having the absorption in the lower wavelength region. The halogen atoms of haloquinones are known to be very reactive[25,26] and are easily replaceble by the amino group. PD, with a pK value of 11.2,[27] is a strong base and its driving force in the EDA interactions may favour the necleophilic substitution. The transformation is also observed with BQ as acceptor,[1] on the other hand the CT complex of PD with methyl-BQ is stable even in the presence of excess concentrations of PD. As such the apparent molar absorptivity and the oscillator strength values (Table I) for PD complex of methyl-BQ are probably relatively high and does not follow the trend of the electron affinity of the acceptors.

Characterisation of Products

The IR data indicate all frequencies pertinent to the components of the products, except the NH stretching of PD[28] at $\sim$ 3200cm^{-1}, and are similar to those reported for dipiperidinobenzoquinones.[29] The absence of the $>$NH group in the final products is also indicated by the proton NMR. Further, it is found that the proton NMR data (Chemical shifts in δ scale, downfield from TMS internal reference) of the products of PD with chloro and 2,5-dichloro-BQ are similar, having resonances at 5.34 (for 2H on quinone), 3.43 (α-H of PD) and 1.65 (β, γ-H of PD) and are consistent with the results for 2,5-dipiperidino-BQ.[1,30] The spectrum of the product with 2,6-dichloro-BQ has exhibited similar pattern of resonances with chemical shifts at 5.52, 3.40 and 1.71, respectively, indicating the probable formation of a 2,6-disubstituted product, 2,6-dipiperidinon-BQ. The product with tetrachloro-BQ, as reported earlier,[2] exhibited only the resonances of α-H and β, γ-H of PD only. This is due to the absence of quinone protons. Elemental analysis conforms to disubstitution in all cases.

Ionisation Potential of the Donors (I^D)

The spectral data of the EDA interactions are reported to be useful for obtaining the I^D values.[24] Using the electronic absorption spectra of the CT complexes of tetrachloro-BQ in dichloro-methane medium, Aloisi and Pignataro[31] proposed the utility of Equation 1 for the I^D values.

$$I^D = 5.0 + 1.55 \times 10^{-4}\, \nu_{CT} \qquad \ldots(1)$$

From the ν_{CT} values, the I^D values are calculated and listed in Table II. The I^D value of PD, calculated from the spectral data, is in close agreement with the experimentally derived one, 7.7eV.[32] The similarity of the I^D values of PD homologues is expected due to the alicyclic nature of the donor. However, relatively low values for N-methyl, 2-methyl and 2,6-dimethyl-PDs are indicative of their higher basicity.

Electron Affinity of the Acceptors (E^A)

The approximate relationship[24] of the excitation energy ($h\nu_{CT}$), I^D and E^A may be given as in equation 2.

TABLE II

Ionisation potential of piperidines calculated from the absorption maxima (ν_{CT}) values of tetrachloro-1,4-benzoquinone complexes in dichloromethane medium

S. No.	Piperidine substituent	ν_{CT} *kk*	Ionisation potential	
			eV	KJ mol^{-1}
1	Parent	17.48	7.67	736
2	2-Methyl	17.39	7.66	735
3	3-Methyl	17.48	7.67	736
4	4-Methyl	17.48	7.67	736
5	2,6-Dimethyl	17.24	7.64	733
6	3,5-Dimethyl	17.45	7.67	736
7	N-Methyl	17.07	7.61	731

$$h\nu_{CT} = I^D - E^A - C, \qquad \ldots(2)$$

where C is the stabilisation energy, which can be taken as a constant.

In a simple application for two acceptors, a and b, equation 2 can be written as

$$(h\nu_{CT})_a - (h\nu_{CT})_b = E_b^A - E_a^A + C_b - C_a \qquad \ldots(3)$$

If $C_b - C_a$ is assumed to be zero, equation 3 further simplities to equation 4.

$$(h\nu_{CT})_a - (h\nu_{CT})_b = (E^A)_b - (E^A)_a \qquad \ldots(4)$$

Utilising equation 4 and taking tetrachloro-BQ ($E^A = 1.37$eV) as a reference acceptor, Briegleb[23] and Venuvanalingam *et al.*[33] have calculated the E^A values of some quinones and quinonechlorimides. However, E^A values of 2.60[34]; 2.76[35] and 2.45eV[36] are also reported for tetrachloro-BQ. Farragher and Page method,[36] involving the direct electron capture, is the most reliable one for the E^A values,[37–39] but is limited only for BQ and its tetrachloro derivative.

From the difference of these two E^A values of BQ and tetrachloro-BQ and from the $h\nu_{CT}$ values of the PD complexes of these two acceptors in chloroform, a difference the stabilisation energy, $C_a - C_b = 0.79$eV is obtained. This energy difference is too significant to be neglected, particularly in strong EDA interactions, where the overlap parameter will generally be of higher magnitude. Using equations 3 and 5 and the proportional differences of the CT excitation energy of the complexes of PD with BQ homologues, the relative E^A values of quinones can be calculated.

$$C_Q - C_{BQ} = \frac{[(h\nu_{CT})_Q - (h\nu_{CT})_{BQ}] \times 0.79}{[(h\nu_{CT})_{BQ} - (h\nu_{CT})_{\text{tetrachloro-BQ}}]} \qquad \ldots(5)$$

The relative E^A values of BQ homologues thus calculated are listed in Table III.

TABLE III

Electronic excitation energy of piperidine complex of benzoquinone ($h\nu_{CT}$) in chloroform and the electron affinity of benzoquinones

Benzoquinone Substituent	$h\nu_{CT}$ eV	Electron affinity		
		Present values		Briegleb's[23]
		eV	KJ mol^{-1}	eV
Parent	2.44	1.37[a]	132	0.77
Methyl	2.52	1.07	103	0.66
Chloro	2.37	1.63	157	1.00
2,5-Dichloro	2.34	1.74	168	1.15
2,6-Dichloro	2.29	1.93	185	1.20
Tetrachloro	2.15	2.45[a]	235	1.37

[a]From the results of Farragher and Page.[36]

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REFERENCES

1 U Muralikrishna and M Krishnamurty *Indian J Chem* **21A** (1982) 1018; **22A** (1983) 858
2 U Muralikrishna, Y V S K Seshasayi and M Krishnamurthy *J Indian chem Soc* **60** (1983) 447, 1048
3 U Muralikrishna and M Krishnamurthy *Indian J Chem* **22A** (1983) 512; **25A** (1986) 949
4 U Muralikrishna and M Krishnamurthy *Spectrosc Lett* **16** (1983) 711
5 U Muralikrishna, Y V S K Seshasayi and M Krishnamurthy *Natl Acad Sci Lett* **6** (1983) 383
6 U Muralikrishna and M Krishnamurthy *Spectrochim Acta* **40A** (1984) 65
7 U Muralikrishna, Y V S K Seshasayi and M Krishnamurthy *React Kinet Catal Lett* **24** (1984) 193
8 U Muralikrishna, M Krishnamurthy and N S Rao *Indian J Chem* **23A** (1984) 77; *Analyst* 109 (1984) 1277
9 G Briegleb (*Elektronon Donator-Acceptor Komplexe* Springer-Verlag Berlin (1961)
10 J W Conant and L F Fieser *J Am chem Soc* **45** (1923) 2195
11 J A Riddick and W B Bunger *Techniques of Chemistry*, Vol **2** Wiley-Interscience New York (1970) 771
12 J H Yoe and A L Jones *Ind Eng Chem Anal Edn* **16** (1944) 111
13 P Job *Ann Chim (Paris)* **9** (1928) 113
14 J S Coleman, L P Varga and S H Mastein *Inorg Chem* **9** (1970) 1015
15 B K Seal, A K Mukharjee and D C Mukherjee *Bull chem Soc Japan* **52** (1979) 2088
16 M Tamres and J Yarwood *Spectroscopy and Structure of Molecular Complexes (Ed)* J Yarwood Plenun Press London (1973) 217
17 H A Benesi and J H Hildebrand *J Am chem Soc* **71** (1949) 2703

18 R Foster, D L Hammic and A A Wardley *J chem Soc* (1953) 3817
19 P H Emslie, R Foster and R Pickles *Canad J Chem* **44** (1966) 9
20 N J Rose and R S Drago *J Am chem Soc* **81** (1959) 6138, 6141
21 F J C Rossotti and H S Rossotti *The Determination of Stability Constants and Other Equilibrium Constants in Solution* McGraw-Hill New York (1961)
22 R Foster (Ed) *Molecular Complexes* Vol 2 Elek Science London (1974) 107
23 G Briegleb *Angew Chem* **76** (1964) 326; *Angew Chem int Edn Engl* **3** (1964) 617
24 R S Mulliken and W B Person *Molecular Complexes* Interscience New York (1969)
25 D Buckley, H B Henbest and P Slade *J chem Soc* (1957) 4891
26 B K Das and B Majee *J Indian chem Soc* **45** (1968) 1055
27 I L Finar *Organic Chemistry Vol* **1** ELBS London (1985) 840
28 D Vedal, O H Ellestard, P Klaboe and G Hagen *Spectrochim Acta* **32A** (1976) 877
29 K Wallenfels and W Draber *Tetrahedron* **20** (1964) 1889
30 S Dhane, J Ranfi and H Paul *Tetrahedron Lett* (1964) 3355
31 G G Aleisi and S Pigrataro *J chem Soc Faraday Trans* 2 **69** (1973) 534
32 K Higasi, I Cmura and T Isuchiya *Monograph Series Res Inst Appl Electric* Hokkaido University No 4 (1954)
33 P Venuvanalingam, U C Singh and N R Subbaratnam *Spectrochim Acta* **37A** (1981) 1
34 M Batley and I M Lyons *Nature* **196** (1962) 537
35 C D Cooper, W F Pery and R M Comption *J chem Phys* **69** (1978) 2369
36 A L Farragher and F M Page *Trans Faraday Soc* **62** (1966) 3072
37 K M C Davis, P R Hammond and M E Peover *Trans Faraday Soc* **61** (1965) 1516
38 G Saito and Y Matsunaga *Bull Chem Soc Japan* **44** (1971) 1788
39 R Foster and C A Fyfe *The Chemistry of Quinonoid Compounds* (*Ed* : S Patai) John Wiley New York (1974) 257