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Molecular Complexes of Paraquat(PQ) with Phenolic Drugs

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Abstract: *Molecular complexes of paraquat (PQ) with a few phenolic drugs viz., Pholidrin, p-Cresol, Tyrosine, Nylidrin, Isoxsuprine, Phenol and Salbutamol in alkaline medium, have been studied spectrophotometrically. The entire complexes exhibit one charge transfer band each in the region where neither of the components have any absorption. The stoichiomtry of each complex is found to be 1:1 from Job's method. The ionization potentials of the donors (drugs) have been determined from the position of CT band of PQ – drug complex. The stability constants of the complexes have been determined from Rose-Drago method. Extinction coefficients (ε), oscillatory strengths (f) and transition dipole moments (D) of CT complexes have also been determined. For a given complex the extinction coefficients, the oscillatory strengths and the dipole moments are found to be almost independent of temperature. The constancy of ε, f and D over the temperature range studied rules out the possibility of existence of the complexes other than 1:1 stoichiometry.*

Keywords: *Spectro photometer, Paraquat, CT complexes, Pholedrine, p-Cresol, Tyrosine, Nylidrine, Isoxsuprine, Salbutamol.*

I. Introduction

Paraquat (PQ) is an important biologically active molecule. It was proved to be herbicide and a weedicide either independently or mixed with other activating compounds. It is a chief component in the commercial herbicides (grammaxone) and weedol. Paraquat is a di-cation and possesses a strong electron acceptor character with an electron affinity[1] 1.24 eV. Although the biological activity of paraquat is known for a long time, its property of forming CT complexes, for the first time, was reported by Nakahara and Wang[2], using inorganic anions and anionic metal complexes as donors[3-6]. Later, the electron donor-acceptor interaction between some neutral organic donors and paraquat has been carried out by White[1]. Subsequently paraquat attracted the attention of many researchers in the field of molecular complexes and it has been shown to form CT complexes with a variety of electron donors[7-14]. The CT complexes of anilines, phenyl hydrazones, crown ethers, phenolates and purinates with PQ have already been reported [15,16]. The formation of molecular complex of PQ with thiafulvalenes was reported by Rahman *et al*.[17]. Continuing our studies on drugs chemistry, PQ as an acceptor has been tested for the formation of CT complexes. The successful results are reported in the present paper.

II. Experimental Procedure

Paraquat dichloride was prepared by the dimerisation of pyridine to 4,4'-bipyridyl, followed by quarternization with methyl chloride and isolation as the dihydrate1. Alternatively PQ dichloride was xtracted from the commercial herbicide (grammaxone) by repeated recrystallization from water, ethanol and ethanol-acetone mixture. Triply distilled water was used to prepare aqueous solution of NaOH to produce alkaline PQ solution where necessary. The samples of the drugs were purified by the methods available in literature till TLC pure [18]. NaOH, ethanol, acetone and methanol were of the highest purity (BDH). Solvents were used without any further purification (BDH Spectrograde). Phenolic drugs were converted into their anions on addition of calculated amounts of NaOH. The IR and UV spectra of the samples tallied well with those of reported in literature. The UV-Vis spectra of the complexes were recorded on Shimadzu-240 and Elico SL 210 UV-Visible double beam spectrophotometers using a matched pair of quartz cuvettes of 10 mm path length (Fig. 1). The concentration of PQ was held constant at 2×10^{-2} M while those of drugs varied between 3×10^{-3} and 9×10^{-2} M. The solutions concentration was kept constant at 2×10^{-3} M for the production of complex with optical density between 0.08 and 1.6 absorbance units. The absorption bands due to acceptor or donor individually have fallen to the base line much more before the wavelength of CT absorption, for example Salmeterol. However, the lower wavelength side of the CT bands is complicated by other absorption probably due to complexed donor. The complicated CT bands were analyzed by using the following relationship put forward by Briegleb and Czekella[19]:

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

Where ν_h and ν_l refer to the frequency at half the maximum intensity on the high and low frequency side of the peak located at ν_m.

The stability constants of the CT complexes were determined by using the following Rose-Drago[20] method
$K^{-1} = (d/\varepsilon) - ([Do] + [Ao]) + [Do][Ao]\,\varepsilon/d$
Where d is the absorption; ε, the molar extinction coefficient of the complex; [Ao] and [Do] are the initial concentrations of acceptor and donor respectively.

III. Results and Discussion

Colorless aqueous solution of Paraquat when mixed with donor in alkaline medium produce characteristic colors (orange red, light orange and light yellow). The production of characteristic colors is attributed to the formation of CT complexes between PQ and anions of drugs in aqueous solution. The entire complexes exhibit one charge transfer band in the region where neither the free donor nor acceptor have any measurable absorption in these regions (Fig. 1).The color changes observed and appearance of CT bands observed in their electronic spectra are attributed to the excitation of electron from the HOMO of donor to LUMO of acceptor. The positions of CT bands and other spectral characteristics are presented in Table 1. The position of CT bands (λ_{CT}) of drugs with PQ is found to be in the following order: Pholidrin>p-Cresol> Tyrosine> Nylidrin> Isoxsuprine > Phenol> Salbutamol.

The energies of the intermolecular charge transfer bands of the complexes (E_{CT}) in solution are calculated from the frequencies of absorption and the values are reported in Table 1. The E_{CT} values are in the order Phelidrin<p-Cresol<Tyrosine< Nylidrin< Isoxsuprine < Phenol< Salbutamol.

IV. Ionization potentials of donors

The energies of CT bands are linearly related to the ionization potentials of the donors as shown by following equation [15].
$h\nu_{CT} = aI_d - b$
where ν_{CT} is the frequency of the CT band; I_d, the ionization potential of donor; h, the Planck's constant; and a and b are constants depending on the acceptor and solvent. This relation is used for the determination of ionization potentials of the donors from the positions of CT bands. The values of the constants a and b of PQ complexes in aqueous medium, reported [15] as 0.976 and -4.5eV respectively, are used for calculation of ionization potentials of Pholidrin, p-Cresol, Tyrosine, Nylidrin, Isoxsuprine, Phenol and Salbutamol.

V. Stoichiometry of complexes

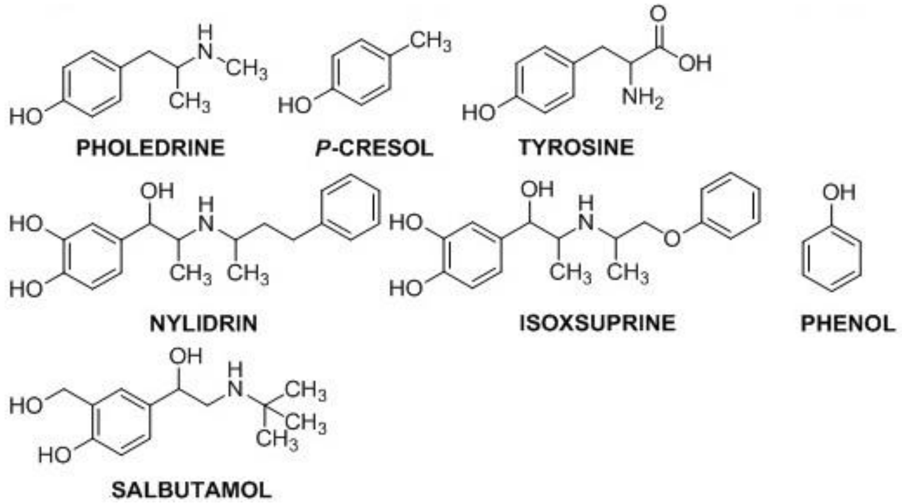
The stoichiometry of the complexes is determined by Job's continuous variation method using equimolar solutions of PQ and drugs. A maximum absorbance is observed at 0.5 mole fraction of the drug in each case and hence the complexes are inferred to have 1:1 composition. The intersection points of Rose-Drago plots also indicate a 1:1 stoichiometry for the complexes. It is observed that the molar extinction coefficient (ε) for a given complex remains approximately constant over the temperature range studied. The constancy of ε may also be taken as a further evidence in support of species with 1:1 stoichiometry in all the PQ-drug complexes.

VI. Extinction coefficients (ε), oscillatory strengths (f) and transition Dipole moments (D) of CT complexes

The extinction coefficients of the complexes are determined at different temperatures from the intersection points of Rose-Drago plots and are reported in Table 1. The extinction coefficient of a CT complex is found to be almost constant over the temperature range studied. The oscillatory strength (f) defined by Mullikan[21] is calculated using the following equation:
$f = 4.319 \times 10^{-9}\,.\varepsilon_{max}.\Delta\nu_{1/2}$
Transition dipole moments (D) of the complex as defined by Tsubomura et al.[22], have also been computed from the extinction coefficients and half–band widths and are reported in Table 1. The relationship used is given below:
$D = 0.09582\,(\varepsilon_{max}.\,\Delta\nu_{1/2}/\nu_{max})^{1/2}$
For a given complex the extinction coefficients, the oscillatory strengths and the dipole moments are found to be almost independent of temperature. The constancy of ε, f and D over the temperature range studied rules out the possibility of existence of the complexes other than 1:1 stoichiometry. The randomness observed in ε may be due to contact charge transfer transition and randomness in f and D may be due to randomness in ε together with uncertainties in the measurement of $\Delta\nu_{1/2}$ due to overlap of lower wavelength side of the CT band with the absorption due to donors.

VII. Formation constants and thermodynamic parameters of the complexes

The formation constants (K) of the complexes are determined by Rose-Drago method. The formation constants of the complexes increase with electron releasing ability of the donors and are in the order: Pholidrin> p-Cresol>Tyrosine> Nylidrin> Isoxsuprine >Phenol> Salbutamol. The thermodynamic parameters, viz. ΔHand ΔS are determined from the slope and intercept of the plot log K vs 1/T. The order of stability constants is parallel to those of wavelengths of absorption. ΔG values are calculated using the relation ΔG = ΔH-TΔS. The enthalpies of formation are below 10 K Cal $mole^{-1}$, a characteristic feature of weak CT complexes. The ΔH,ΔSand ΔG values are found to increase with increase in electron releasing ability of the substituent's (Table 2). A linear relationship is obtained between ΔHand ΔS for all the complexes. The negative enthalpies indicate that the complex formation is spontaneous while negative entropies indicate a loss in degree of freedom of the components upon complexation. The linear relation between -ΔH and -ΔS indicates that the complexation is unhindered by the substituent's present on benzene ring of the drug.



Spectral characteristics of CT complexes of PQ-Phenolate Drugs
Table No.1

Sl No.	Drugs	λ_{max}(nm)	E_{CT} (eV)	I.P. (eV)	$\nu_{CT}\times10^{-3}$ (cm^{-1})	ε_{max}	$\Delta\nu_{1/2}$	f	D
1	Pholedrine	480	2.559	7.223	20.833	260	11885	0.0133	1.173
2	p-Cresol	475	2.613	7.288	21.050	235	9953	0.0103	1.023
3	Tyrosine	462	2.686	7.363	21.646	220	10081	0.0096	0.970
4	Nylidrin	458	2.710	7.387	21.834	230	13068	0.0130	1.176
5	Isoxsuprine	455	2.728	7.406	21.978	280	12953	0.0157	1.284
6	Phenol	452	2.760	7.430	22.120	215	10128	0.0094	0.933
7	Salbutamol	448	2.771	7.449	23.230	215	10407	0.0097	0.959

Stability Constants and Thermodynamic Parameters of CT Complexes of PQ-Phenolate Drugs
Table No.2

		Stability constants (K) at various temperatures					-ΔH	-ΔS	-ΔG
S.No	Drugs	10^0C	20^0C	30^0C	40^0C	50^0C	Kcal mol^{-1}	Cal deg^{-1} mol^{-1}	Kcal mol^{-1}
1	Pholedrine	13.14	9.08	6.43	4.65	3.44	6.09	16.4	1.20
2	p- Cresol	12.31	8.67	6.25	4.60	3.45	5.77	15.4	1.18
3	Tyrosine	11.59	8.21	5.95	4.41	3.32	5.68	15.2	1.15
4	Nylidrin	12.83	8.91	6.33	4.60	3.41	6.12	16.2	1.19
5	Isoxsuprine	12.46	8.71	6.24	4.56	3.40	5.89	15.8	1.18
6	Phenol	10.48	7.50	5.49	4.10	3.12	5.51	14.8	1.10
7	Salbutamol	10.18	7.27	5.31	3.94	2.99	5.59	15.0	1.09

Fig.1 Charge transfer Spectra of PQ-Nylidrin

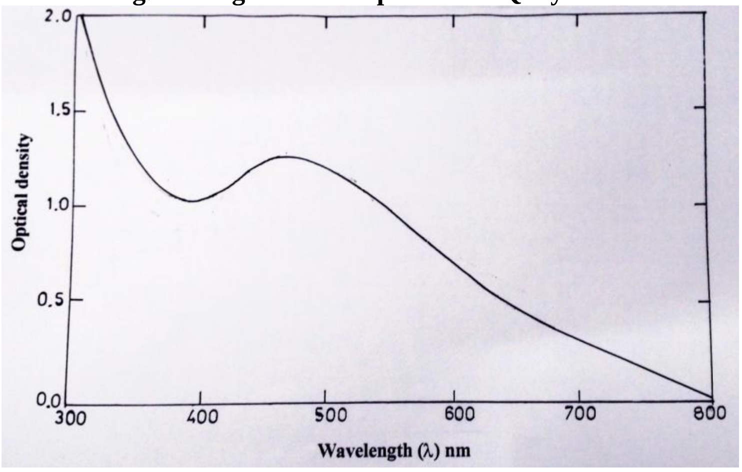
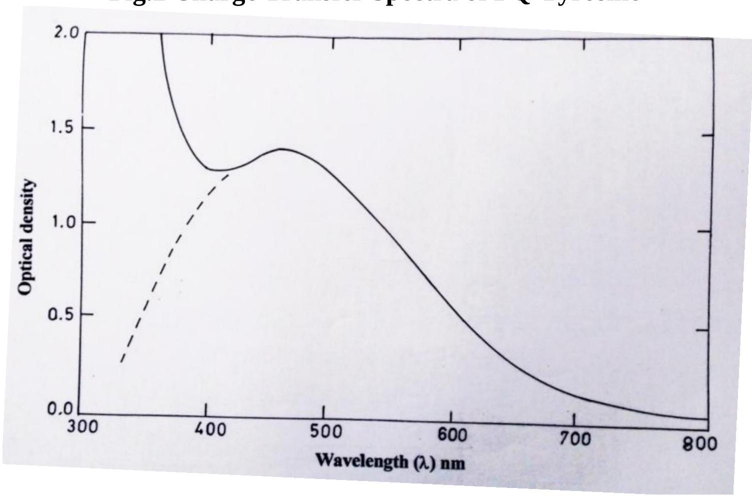


Fig.2 Charge Transfer Spectra of PQ-Tyrosine



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