



## STABILITY CONSTANTS OF MOLECULAR COMPLEXES OF PARAQUAT WITH CATECHOL

T. Charan Singh\*

Department of Chemistry, G. Narayanamma Institute of Technology and Science  
(for Women) Shaikpet, Hyderabad.

Article Received on  
21 February 2022,

Revised on 11 March 2022,  
Accepted on 01 April 2022

DOI: 10.20959/wjpps20224-23199

### \*Corresponding Author

**Dr. T. Charan Singh**

Department of Chemistry,  
G. Narayanamma Institute  
of Technology and Science  
(for Women) Shaikpet,  
Hyderabad.

### ABSTRACT

Molecular complexes of paraquat (PQ) with a Catecholic drug in alkaline medium, has been studied spectrophotometrically. The entire complexes exhibit one charge transfer band each in the region where neither of the components have any absorption. The stoichiometry 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 ( $\epsilon$ ), 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  $\epsilon$ ,  $f$  and  $D$  over the temperature range studied rules out the possibility of existence of the complexes other than 1:1 stoichiometry.

**KEYWORDS:** Paraquate, Catecholic drugs, CT complexes.

### 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.<sup>[1]</sup> 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<sup>[2]</sup>, using inorganic anions and anionic metal complexes as donors.<sup>[3-6]</sup> Later, the electron donor-acceptor

interaction between some neutral organic donors and paraquat has been carried out by White.<sup>[1]</sup> 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.<sup>[7-14]</sup> The CT complexes of anilines, phenyl hydrazones, crown ethers, phenolates and purinates with PQ have already been reported.<sup>[15,16]</sup> The formation of molecular complex of PQ with thiafulvalenes was reported by Rahman *et al.*<sup>[17]</sup> 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.

### Experimental procedure

Paraquat dichloride was prepared by the dimerisation of pyridine to 4,4'-bipyridyl, followed by quaternization with methyl chloride and isolation as the dihydrate. Alternatively PQ dichloride was extracted 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.<sup>[18]</sup> NaOH, ethanol, acetone and methanol were of the highest purity (BDH). Solvents were used without any further purification (BDH Spectrograde). Catecolic 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  $2 \times 10^{-2}$  M while those of drugs varied between  $3 \times 10^{-3}$  and  $9 \times 10^{-2}$  M. The solutions concentration was kept constant at  $2 \times 10^{-3}$  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 analysed by using the following relationship put forward by Briegleb and Czekella.<sup>[19]</sup>

$$(v_h - v_l)/2(v_m - v_l) = 1.2$$

Where  $v_h$  and  $v_l$  refer to the frequency at half the maximum intensity on the high and low frequency side of the peak located at  $v_m$ .

The stability constants of the CT complexes were determined by using the following Rose-Drago<sup>[20]</sup> method.

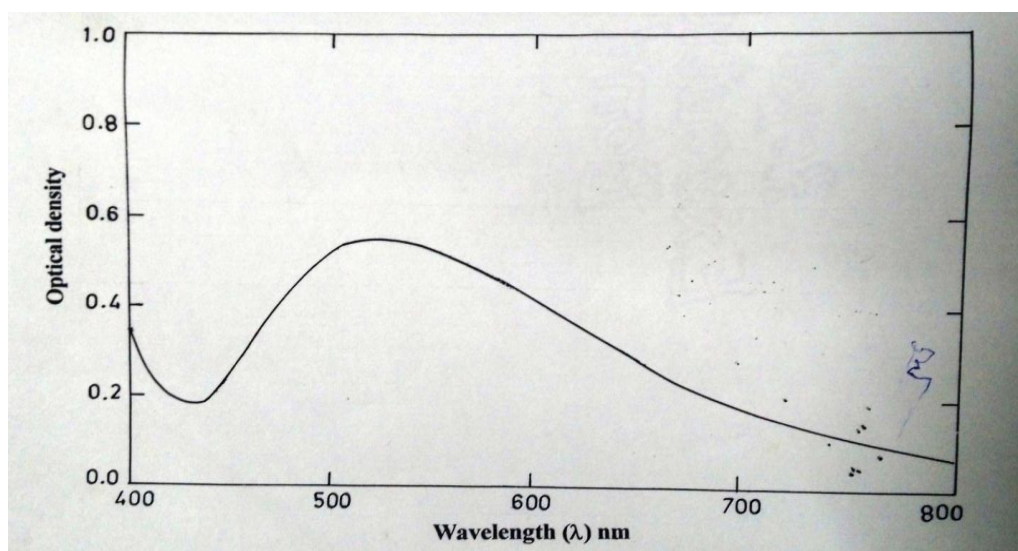
$$K^{-1} = (d/\epsilon) - ([Do] + [Ao] ) + [Do] [Ao] \epsilon/d$$

Where  $d$  is the absorption;  $\epsilon$ , the molar extinction coefficient of the complex;  $[Ao]$  and  $[Do]$  are the initial concentrations of acceptor and donor respectively.

## 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 ( $\lambda_{CT}$ ) of Catechol drug with PQ is found at 475 nm.

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.



**Fig. 1: Charge Transfer Spectra of PQ-Catechol.**

### Ionization potentials of donors

The energies of CT bands are linearly related to the ionization potentials of the donors as

shown by the following equation.<sup>[15]</sup>

$$h\nu_{CT} = aI_d - b$$

where  $\nu_{CT}$  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<sup>[15]</sup> as 0.976 and -4.5eV respectively, are used for calculation of ionization potentials of Catechol.

### 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 ( $\epsilon$ ) for a given complex remains approximately constant over the temperature range studied. The constancy of  $\epsilon$  also be taken as a further evidence in support of species with 1:1 stoichiometry in all the PQ- drug complexes.

### Extinction coefficients ( $\epsilon$ ), 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<sup>[21]</sup> is calculated using the following equation.

$$f = 4.319 \times 10^{-9} \cdot \epsilon_{\max} \cdot \Delta\nu^{1/2}$$

Transition dipole moments ( $D$ ) of the complex as defined by Tsubomura *et al.*<sup>[22]</sup>, have also been computed from the extinction coefficients and half-band widths and are reported in Table 1. The relationship used is given below.

$$D = 0.09582 (\epsilon_{\max} \cdot \Delta\nu_{1/2} / \nu_{\max})^{1/2}$$

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  $\epsilon$ ,  $f$  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  $\epsilon$  may be due to contact charge transfer transition and randomness in  $f$  and  $D$  may be due to randomness in  $\epsilon$  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.

### Formation constants and thermodynamic parameters of the complexes

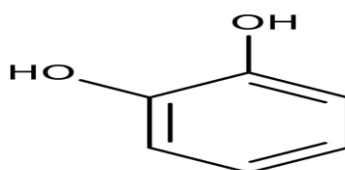
The formation constants ( $K$ ) of the complexes are determined by Rose-Drago method. The formation constants of the complexes increase with electron releasing ability of the donors.

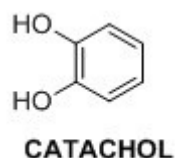
The thermodynamic parameters, viz.  $\Delta H$  and  $\Delta S$  are determined from the slope and intercept of the plot  $\log K$  vs  $1/T$ . The order of stability constants is parallel to those of wavelengths of absorption. The  $\Delta G$  values are calculated using the relation  $\Delta G = \Delta H - T\Delta S$ . The enthalpies of formation are below 10 K Cal mole<sup>-1</sup>, a characteristic feature of weak CT complexes. The  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  values are found to increase with increase in electron releasing ability of the substituent's (Table 2). A linear relationship is obtained between  $\Delta H$  and  $\Delta S$  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  $\Delta H$  and  $\Delta S$  indicates that the complexation is unhindered by the substituents present on benzene ring of the drug.

### Spectral characteristics of CT complex of PQ with Catechol

Table 1

Sl No.	Drugs	$\lambda_{\max}$ (nm)	E <sub>CT</sub> (eV)	I.P. (eV)	$\nu_{CT} \times 10^{-3}$ (cm <sup>-1</sup> )	$\epsilon_{\max}$	$\Delta\nu_{1/2}$	f	D
1	Catechol	475	2.613	7.288	21.050	240	99 90	0.0 104	1.0 23





### Stability Constants and Thermodynamic Parameters of CT Complex of PQ with Catechol Drug

Table 2

S. No	Drugs	Stability constants (K) at various temperatures					-ΔH Kcal mol <sup>-1</sup>	-ΔS Cal deg <sup>-1</sup> mol <sup>-1</sup>	-ΔG Kcal mol <sup>-1</sup>
		10 <sup>0</sup> c	20 <sup>0</sup> c	30 <sup>0</sup> c	40 <sup>0</sup> c	50 <sup>0</sup> c			
1	Catechol	13.06	9.15	6.56	4.81	3.59	5.86	15.6	1.21

### ACKNOWLEDGEMENTS

Author is thankful to Late Prof. G Venkateshwarlu, Head, Department of Chemistry, Osmania University for his helpful suggestions. He is also thankful to G. Anjaiah and Mr. Rakesh Goud Battini Asst. Prof Chemistry.

### REFERENCES

- White B G, *Trans Faraday Soc*, 2000; 1969: 65.
- Nakahara A & Wang J H, *J Phys Chem*, 1963; 67: 496.
- Oliveira L A & Haim A J, *J Am Chem Soc*, 1982; 104: 3363.
- Ebbesen T W & Ferraudi G, *J Phys Chem*, 1983; 87: 3717.
- Bertolotti S G, Cosa J J, Gsponer H E & Previtali C M, *Can J Chem*, 1986; 64: 845.
- Bertolotti S G, Cosa J J, Gsponer H E & Previtali C M, *Can J Chem*, 1987; 65: 2425.
- Haque R & Lilley S, *J Agricult Food Chem*, 1972; 20: 57.
- Macfarlane A J & Williams R J, *J Chem Soc (A)*, 1969; 1517.
- Ledwith A & Woods H J, *J Chem Soc, (C)*, 1970; 1422.
- Anjaiah G, Veeraiah T & Venkateshwarlu G, *Indian J Chem*, 2003; 42A: 2781.
- Cserhati T & Valko K, *J Liquid Chromatography*, 1991; 14: 20.
- Kunkely H & Vogler A, *Inorg Chem Commun*, 2000; 3(5): 205.
- Verhoeven J W, Marie A, Schoff V, Masson A & Schwyzer R, *Helvetica Chimica Acta*, 1974; 37(8): 2503.
- Cserhati T, Szogyi M & Szigeti Z, *Chromatography*, 1988; 26(1): 305.
- Charn Singh T, Vinod Kumar T & Venkateshwarlu G, *Indian J Chem*, 1999; 38A: 331.

16. Shijun L I, Zheng Bo, Huang FeiHe, Zakharov Lev N, Slebodnick Carla, Rheingold Arnold L & Gibson Harry W, *Science China Chem*, 2010; 53: 858.
17. Bilkish Rahman, Hiroki Akautsu, Jun-ichi Yamada & Shin'ichi Nakatsuji, *Molecules*, 2007; 12: 853.
18. Smith R M, *Handbook of Analytical Separations*, edited by K Valko (Elsevier, Amsterdam, The Netherlands), 2000; 471.
19. Briegleb G & Czekella J, *Z Physik Chem*, 1960; 24: 37.
20. Drago R S & Rose N J, *J Am Chem Soc*, 1951; 81: 6141.
21. Mulliken R S, *J Am Chem Soc*, 1950; 72: 600.
22. Tsubomura H & Lang R, *J Am Chem Soc*, 1961; 83: 2085.