

Molecular complexes of paraquat with anilines

P PADMA, T VINOD KUMAR, T CHARAN SINGH and
G VENKATESHWARLU*

Department of Chemistry, Nizam College, Hyderabad 500001, India

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Abstract. The UV–VIS spectra of molecular complexes of paraquat with ring and N-substituted anilines have been recorded in methanol and 50% v/v aqueous methanol. All the complexes exhibited well-resolved charge transfer bands in the wavelength region where neither of the components have any absorption. The energies of charge transfer bands of the substituted aniline–paraquat complexes bear linear relationships with the ionization potentials obtained from the substituted aniline–TCNE complexes, indicating π – π interaction between paraquat and the donors. Both ring and N-substituents have effects on the positions of the CT bands as well as on the stabilities of the complexes. The positions of the CT bands are shifted to shorter wavelengths and the stabilities of the complexes decrease on going from methanol to aqueous methanol.

Keywords. Molecular complexes; π – π interaction; substituent effect; stability constants; thermodynamic parameters.

1. Introduction

1,1'-Dimethyl-4,4'-bipyridinium dichloride (Paraquat, PQ) was shown to form charge transfer complexes with inorganic anions (Ebbesen and Ferrandi 1983; Hoffman *et al* 1983; Bertolotti *et al* 1986, 1987) as well as with neutral organic donors (White 1969; Martens and Verhoeven 1981; Fornasiero and Grieser 1990; Yoon and Kochi 1991) owing to its strong electron-acceptor property. However, studies on CT complexes of paraquat with anilines are few, although anilines were shown to form CT complexes with a variety of electron acceptors e.g. TCNE (Isaacs 1966), chloranil (Carper *et al* 1965), and TNB (Foster and Hammick 1954). The positions of the CT bands of aniline, *o*-phenylenediamine (OPD) and *p*-phenylenediamine (PPD) with PQ, in methanol, were reported by White (1969) together with the stabilities of PQ-OPD and PQ-PPD complexes. The CT spectrum of PQ-PPD was also reported by Poulos *et al* (1981), in CH₃CN, in connection with study of its flash photolysis.

This prompted the present authors to carry out a systematic study of the CT complexes of PQ with ring and N-substituted anilines. The results of the study are reported in the present communication.

*For correspondence

2. Experimental

2.1 Materials

Paraquat was prepared by the dimerisation of pyridine to 4,4'-bipyridyl, followed by quarternization with methyl chloride and isolation as the dihydrate (White 1969). Commercial anilines (BDH, AR grade) were purified by the methods available in the literature and are TLC pure. Spectrograde (BDH) methanol was used without further purification. Triply distilled water was used to prepare 50% v/v aqueous methanol.

2.2 Methods

The UV-VIS absorption spectra (figure 1) were recorded on a Shimadzu-240 double beam spectrophotometer in the temperature range of 10–40°C at 5°C intervals and an accuracy of $\pm 0.1^\circ\text{C}$, using a matched pair of quartz-stoppered cells of 10 mm path-length. The instrument is fitted with a thermostated sample compartment. Temperatures above 25°C were attained by heating the sample compartment while lower temperatures were brought about by circulating cold water. Each sample is allowed to equilibrate for at least ten minutes before measuring the absorbance. The concentration of PQ was held constant at 5×10^{-3} M, while that of the anilines varied between 0.2 M and 1.5 M. The formation constants of the complexes were determined by the Benesi-Hildebrand (1949) method, from the absorption measurements on the charge transfer bands, whereas the thermodynamic parameters viz. ΔH and ΔS , were determined from the temperature variation of formation constants using van't Hoff's

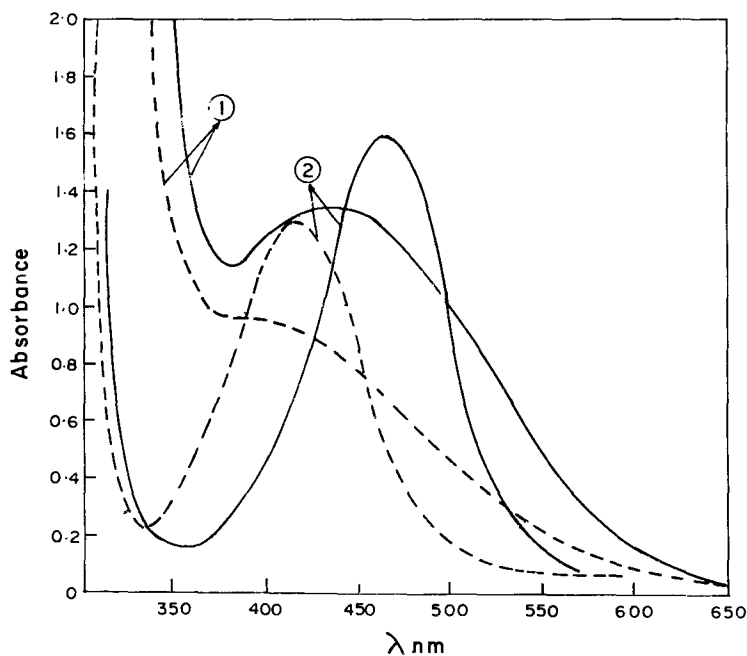


Figure 1. Charge transfer spectra of (1) aniline-PQ and (2) N-methyl aniline-PQ complexes in methanol (—) and aqueous methanol (---).

method and are reported in table 1, together with the ΔG at 25°C. The ΔH values, however, were also determined from the variation of $\log K\varepsilon$ with temperature as this is supposed to yield more accurate values of ΔH over those obtained from variation of $\log K$ with temperature in which the correct separation of K and ε is doubtful. The values of ΔH obtained from the two methods differed by ± 0.02 kcal mole⁻¹. The linearity of Benesi–Hildebrand plots indicated the formation of 1:1 complex which was also verified by Job's continuous variation method (figure 2).

3. Results and discussion

Colourless solutions of paraquat and aniline turned reddish brown immediately after mixing. Substituted anilines also produced characteristic colours with paraquat indicating the formation of charge-transfer complexes. All the complexes are stable for several hours unlike the complexes of anilines with TCNE (Isaacs 1966) or with 2,4-dinitrochlorobenzene (Ross *et al* 1954) which decomposed soon into products. The complex of aniline PQ exhibited a new band at 440 nm in methanol (400 nm in aqueous methanol, figure 1) where neither the donor nor acceptor have any absorption. The substituted anilines also exhibited well resolved absorption bands in the region 400–600 nm (table 1). The positions of the CT bands are at longer wavelengths in methanol as compared to those in aqueous methanol.

3.1 Effect of substituents on the CT bands

The CT band of the PQ-aniline complex (440 nm) is significantly affected by both ring and N-substituents. The band is shifted to longer wavelengths by electron-releasing ring substituents viz. *p*-NH₂, *p*-OCH₃, *p*-CH₃, *m*-CH₃ and N-substituents viz. N-methyl and N,N-dimethyl. The electron-attracting *p*-Cl causes a little hypsochromic shift. The shifts are in the order: *p*-NH₂ > N,N-dimethyl > *p*-OCH₃ > *p*-CH₃ > N-CH₃ > *m*-CH₃ > *p*-H > *p*-Cl (table 1).

The shifts in the CT bands are explicable in terms of mesomeric and inductive interactions of the substituents. The +M effect of *p*-NH₂, *p*-OCH₃ and the +I effect of *p*-CH₃, *m*-CH₃, N-methyl and N,N-dimethyl boost up the energy of the HOMO of the donor and bring it closer to the LUMO of the PQ, lower the energy gap between the two orbitals and therefore shift the CT band to longer wavelengths. The -I effect of chloro substituent stabilises the donor level and produces a small hypsochromic shift.

3.2 Correlation between the energies of CT bands and the ionization potentials of the donors

The E_{CT} values obtained from the CT bands of the present study are plotted against the ionization potentials (I_D) of the donor calculated from the CT band positions of the aniline–TCNE (Isaacs 1966) and the aniline–I₂ complexes (Chandra and Mukherjee 1964). A linear relationship is obtained between the E_{CT} and I_D of donors obtained from the CT bands of aniline–TCNE complexes while those obtained from the anilines–I₂ exhibited a scatter. This indicates that the donation of the electron occurs from the ψ_1 donor level rather than from the ψ_1^* level (Tsubomura 1960) and complexation involves π – π interaction. This view is also substantiated by existence of a linear relationship between the ν_{CT} of PQ complexes and ν_{CT} of TCNE complexes with the same set of donors (White 1969).

Table 1. Charge transfer bands and stabilities of the complexes.

Substituent	Methanol			Aq. Methanol			Methanol		
	$\pi-I_D$	λ_{nm}	K ($l\text{mol}^{-1}$)	ϵ ($l\text{mol}^{-1}\text{cm}^{-1}$)	λ_{nm}	K ($l\text{mol}^{-1}$)	$-\Delta H$ (kcal. mol^{-1})	$-\Delta S$ (cal. deg^{-1} mol^{-1})	$-\Delta G$ (kcal. mol^{-1})
<i>p</i> -NH ₂	7.18	555	15.4	640	460	9.8	7.46	19.0	1.80
<i>N,N</i> -dimethyl	7.45	500	10.8	540	*	*	6.84	17.7	1.56
<i>p</i> -OCH ₃	7.46	495	4.46	510	425	3.0	5.12	14.2	0.89
<i>p</i> -CH ₃	7.61	469	3.16	480	413	2.1	4.15	12.3	0.48
<i>N</i> -CH ₃	7.65	460	2.70	420	410	1.61	3.97	12.0	0.40
<i>m</i> -CH ₃	7.75	446	2.34	420	403	1.5	3.90	11.8	0.38
<i>p</i> -H	7.78	440	1.90	400	400	1.17	3.74	11.5	0.313
<i>p</i> -Cl	7.91	429	0.91	360	398	0.61	3.62	11.2	0.28

*Insoluble

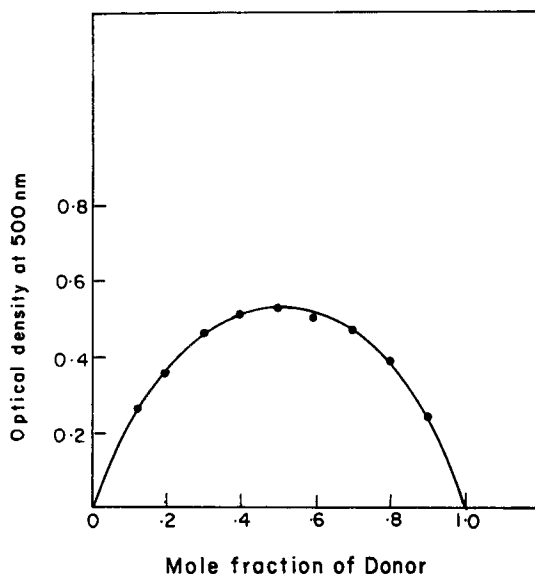


Figure 2. Job's continuous variation plot of PQ and N,N-dimethyl aniline (0.05 M each).

3.3 Formation constants and thermodynamic parameters of the complexes

The formation constants of the complexes were determined by the Benesi-Hildebrand method employing the condition $[D_o] \gg [A_o]$ and are reported with an accuracy of ± 0.1 litres mole⁻¹ (table 1). The formation constants of the complexes and molar extinction coefficients increase with electron-releasing ability of the substituents present in the benzene ring or on the nitrogen and are in the order: $p\text{-NH}_2 > \text{N,N-dimethyl} > p\text{-OCH}_3 > p\text{-CH}_3 > \text{N-CH}_3 > m\text{-CH}_3 > p\text{-H} > p\text{-Cl}$. The logarithmic functions of the formation constants are linearly related to the Hammett σ constants. The stabilities of the complexes are greater in methanol than in aqueous methanol.

The thermodynamic parameters viz. ΔH and ΔS were determined from the slope and intercept of the plot of $\log K$ vs $1/T$. The ΔG values were calculated using the relation $\Delta G = \Delta H - T\Delta S$. The enthalpies of formation are below 10 kcal mole⁻¹, a characteristic feature of weak CT complexes. The ΔH , ΔS and ΔG values increase with increase in electron-releasing ability of the substituents. A linear relationship is obtained between ΔH and ΔS for all the complexes. It is interesting to note that the N-methyl and N,N-dimethyl anilines, too, fit into the linear relation showing that complex formation is not sterically hindered (Foster 1969). If the complex formation is due to n -donation, a steric hindrance by N-methyl groups to the approach of acceptor towards the N atom is reasonably expected. Sterically unhindered complex formation too, indicates that the interaction is of the π - π type.

4. Conclusion

Anilines form molecular complexes with paraquat and exhibit CT bands. The linear relationship between the energies of the CT bands and the π -ionization potentials of the

donors indicates a π - π interaction between the donor and the acceptor. The positions of the CT bands and the stabilities of the complexes depend both on the ring and N-substituents.

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