

## Differential Refractometric Studies on the Charge Transfer Interaction of 4-Nitroquinoline-1-Oxide with Some $\pi$ - and $n$ -Donors

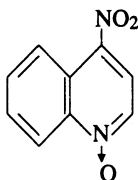
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4-Nitroquinoline-1-oxide (4-NQO) is a carcinogenic compound. In this paper the charge transfer interaction between acceptor 4-NQO and donors like benzene, toluene, *p*-xylene, aniline, N-N-dimethylaniline, triphenylphosphine, triphenylarsine and triphenylstilbene has been studied with the help of differential refractometric studies.

### INTRODUCTION

The carcinogenicity of 4-nitroquinoline 1-oxide (4-NQO) (I) is of great importance, because its potency to produce cancer is comparable to the most potent polycyclic aromatic hydrocarbon<sup>1</sup>.



(I)

The formation of charge transfer complexes between the carcinogens and protein or nucleic acid has been postulated by Mason<sup>2-4</sup> as a step in the chemical initiation of cancer. The quantum biological studies on 4-NQO have shown that it can act as a good electron acceptor<sup>5</sup>. However the experimental aspects of this work have remained unravelled.

Thus in order to investigate charge transfer complexation mechanism as a possible step in the chemical initiation of cancer on molecular level, the interaction of 4-NQO, a potent carcinogen, with benzene, toluene, *p*-xylene ( $\pi$ -donors) and aniline, N-N-dimethylaniline, pyridine and Ph<sub>3</sub>M (M = N, P, As, Sb) ( $n$ -donors) have been studied, in solutions using differential refractometric technique<sup>6-8</sup>.

These  $\pi$ -donors have been chosen because they are the basic units of polycyclic

hydrocarbons. Recently, Sahai *et al.*<sup>7,8</sup> have developed a more reliable and accurate model to calculate the equilibrium constant ( $K_1$ ) and extent of electronic polarization ( $\alpha$ ) using this technique. This model has been used to calculate charge transfer complexation parameters.

## EXPERIMENTAL

The donors (benzene, toluene, *p*-xylene, aniline, N-N-dimethylaniline, pyridine) were purified as reported in the literature<sup>10</sup>. Triphenylamine ( $\text{Ph}_3\text{N}$ ), triphenyl-phosphine ( $\text{Ph}_3\text{P}$ ), triphenylarsine ( $\text{Ph}_3\text{As}$ ) and triphenyl stilbene ( $\text{Ph}_3\text{Sb}$ ) (Fluka) were purified by recrystallisation; chloroform and carbon-tetrachloride (BDH, AR) were used after distilling thrice. 4-Nitroquinoline-1-oxide (4-NQO) was purchased from sigma and used as such.

Stock solutions of donors and acceptor were prepared by weighing on an analytical balance and then diluting to the required volume in volumetric flasks in appropriate solvents. These were further diluted with the same solvent to get the test samples.

The refractive indices were measured by Bausch and Lomb refractometer with an accuracy of  $\pm 0.0002$  at  $30^\circ\text{C}$ . These were measured for the following sets of solutions:

- (i) The refractive indices of donor solutions ( $n_D$ ),
- (ii) The refractive indices of acceptor solution ( $n_A$ ),
- (iii) The refractive indices of mixed solutions ( $n$ ) of donor and acceptor.

## RESULTS AND DISCUSSION

### Interaction of 4-NQO with $n$ -Donors

On mixing solutions of respective donors with a solution of the acceptor (4-NQO) in chloroform solvent, an appreciable increase in refractive indices was noticed. This appreciable increase in refractive indices has been interpreted to be taking place due to charge transfer from donor to acceptor and not due to the relative increase in donor concentration.

This was confirmed by a separate experiment. It was found that on mixing 1 mL of donor and 1 mL of acceptor solution, the refractive index increases appreciably more than that of separate component.

A change in electron cloud density in neutral atom or molecule would lead to a change in the polarizability. Since the complex is generally more polar than the components, the extent of electronic polarization or refractive index increases and the deviation depends upon the extent of interaction between donor and acceptor. Therefore, the stronger is the complex, larger is the deviation in the refractive index values. In the present case the deviation is positive and maximum as observed at 1 : 1 molar-ratio (Fig. 1).

The stoichiometry of the above charge transfer complexes has been determined using differential refractometric titration technique.

Through this technique, the change in the refractive index permittivity,  $\Delta\Omega_{\text{CDA}}$ , of a solution of one component (4-NQO) on the addition of successive

amount of the other component ( $\pi$ -donor) has been measured. Let us consider the addition of a donor to an acceptor producing a complex with a refractive index larger than the refractive index of separate component. The addition of a small amount of donor generates an equal amount of complex. The permittivity increases on successive additions of the donor and continues to increase until the equivalent quantities of the donor and acceptor are present. This situation is schematically shown by line XY of Fig. 1, which indicates the 1 : 1 stoichiometry of these complexes. Further addition of the donor increases the permittivity by an amount depending on the donor refractive index (line YZ in Fig. 1).

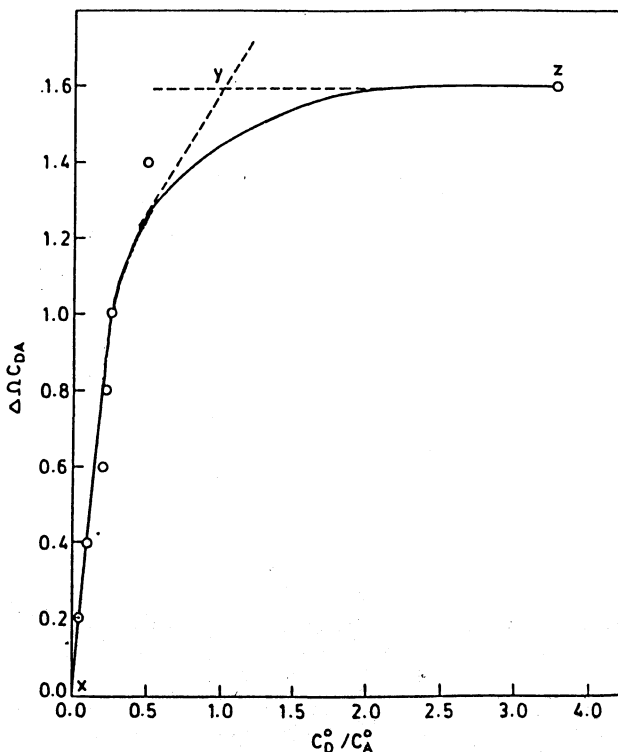


Fig. 1 Molar ratio plots for the molecular complexes of benzene with 4-NQO in chloroform

A break has been observed in the graph at the donor-acceptor ratio corresponding to the ratio existing in the complex.

Equilibrium constant data (Table-1) indicate the following complexing strength of the donors:



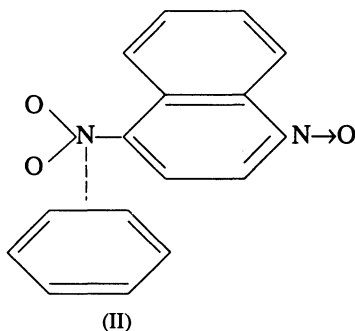
The presence of an electron withdrawing  $-\text{NO}_2$  group at  $C_4$  of the quinoline ring of 4-NQO makes it a  $\pi^*$ -electron acceptor and the aromatic hydrocarbons (*p*-xylene, toluene and benzene) work as a  $\pi$ -donor due to the presence of delocalized  $\pi$ -electrons in its ring.

TABLE-1  
EQUILIBRIUM CONSTANT ( $K_1$ ) AND EXTENT OF ELECTRONIC  
POLARIZATION ( $\alpha$ ) DATA FOR 1 : 1 MOLECULAR COMPLEXES OF 4-NQO WITH  
SOME  $\pi$ - AND  $n$ -DONORS IN DIFFERENT SOLVENTS AT 32°C

Donors	Solvent	Concentration range of donor*	$K_1$ ( $\text{dm}^3 \text{mol}^{-1}$ )	$\alpha \times 10^3$
Benzene	$\text{CHCl}_3$	0.50–6.40 M	$0.26 \pm 0.03$	1.16
Toluene	$\text{CHCl}_3$	0.26–1.30 M	$0.55 \pm 0.02$	2.30
<i>p</i> -Xylene	$\text{CHCl}_3$	0.50–2.40 M	$0.75 \pm 0.05$	3.10
N-N-Dimethylaniline	$\text{CHCl}_3$	0.087–3.333 M	$2.00 \pm 0.04$	5.90
Aniline	$\text{CHCl}_3$	0.033–1.270 M	$3.05 \pm 0.06$	7.40
Pyridine	$\text{CHCl}_3$	0.008–0.230 M	$17.00 \pm 1.00$	26.30
$\text{Ph}_3\text{N}$	$\text{CHCl}_3$	0.003–0.144 M	$60.00 \pm 4.02$	10.00
	$\text{CCl}_4$	0.002–0.072 M	$128.00 \pm 5.00$	
$\text{Ph}_3\text{P}$	$\text{CHCl}_3$	0.001–0.044 M	$150.15 \pm 5.00$	80.50
	$\text{CCl}_4$	0.0008–0.0290 M	$285.00 \pm 8.00$	
$\text{Ph}_3\text{As}$	$\text{CHCl}_3$	0.0009–0.060 M	$239.50 \pm 8.00$	125.00
	$\text{CCl}_4$	0.0003–0.0140 M	$520.00 \pm 10.00$	
$\text{Ph}_3\text{Sb}$	$\text{CHCl}_3$	0.0001–0.0020 M	$850.00 \pm 15.00$	220.50
	$\text{CCl}_4$	0.0006–0.0009 M	$1260.00 \pm 18.00$	

\*The concentration of acceptor (4-NQO) was kept constant at  $ca. 2 \times 10^{-4}$  M in each case.

These hydrocarbons transfer  $\pi$ -electron charge density to the  $\pi^*$ -orbital of nitrogen in the 4-nitro group of 4-NQO. From the equilibrium constant data (Table-1), it is evident that benzene, toluene and *p*-xylene form weak charge transfer complexes. This may be attributed to the weak  $\pi$ - $\pi^*$  interaction of these hydrocarbons with 4-NQO. A probable model for these interactions has been shown below.



### Interactions of 4-NQO with $n$ -donors (aniline, N-N-dimethylaniline and pyridine)

On mixing a solution of donors with a solution of acceptor (4-NQO) in the chloroform solvent, an appreciable increase in refractive index was noticed. This

appreciable increase in refractive index has been interpreted due to charge-transfer from donor to acceptor and not due to the relative increase in donor concentration. This was confirmed by a separate experiment.

It was found that on mixing 1 mL of donor and 1 mL of acceptor solutions, the refractive index increases appreciably more than that of the separate component. A change in electron cloud density in neutral atom or molecule will lead to a change in the polarizability. Since the complex is generally more polar than the components, the electronic polarizability or refractive index increases and the deviation depends upon the extent of interaction between the donor and acceptor. Therefore, the stronger is the complex larger is the deviation in the refractive index value. In the present case the deviation is positive and maximum is observed at 1 : 1 molar ratio in different refractometric titration curves (Fig. 2).

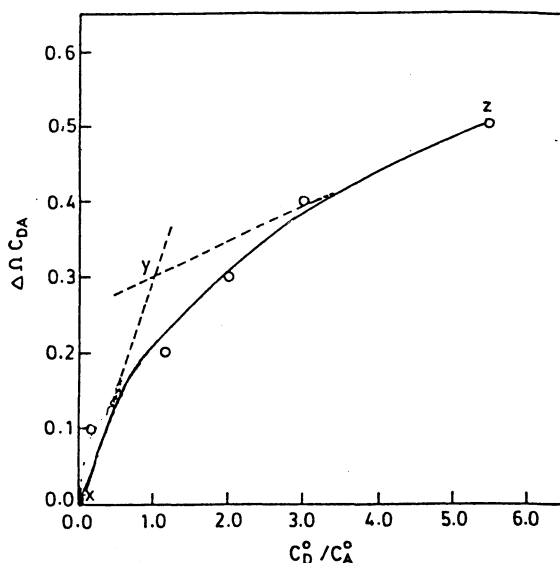


Fig. 2 Molar ratio plots for the molecular complexes of pyridine with 4-NQO in chloroform

The bases pyridine, aniline and N-N-dimethylaniline work as *n*-donor due to the presence of lone pair of electrons at N-atom, while 4-NQO acts as a  $\pi^*$  electron acceptor as explained earlier. Thus, the charge is transferred from the lone pair of respective bases to the  $\pi^*$  orbital of nitrogen in the 4-nitro group of 4-NQO. From Table-1, it is evident that  $K_1$  values observed for aniline-4-NQO, N-N-dimethyl-aniline-4NQO systems are less than those obtained for pyridine-4-NQO complex. The electron donating nature of aniline and N-N-dimethyl-aniline has been studied by Tsubmora<sup>11</sup>. The lone pair of electrons on nitrogen atom makes the  $NR_2$  or  $NH_2$  group an  $n \rightarrow \pi$  donor towards the  $C_6H_5$  group in intermolecular  $n\pi$ ,  $a\pi$  action. However, the intramolecular action of aniline and N-N-dimethylaniline is reduced by the nonplanarity of the molecules, but it still remains. The intramolecular charge transfer competes with the intermolecular

charge transfer and thus the base strength of aniline and *N,N*-dimethylaniline is reduced. The aniline-4-NQO complex is more stable than the *N,N*-dimethylaniline-4-NQO complex. This may be due to the presence of two methyl groups on nitrogen atom, creating steric hindrance. It was observed that the refractive index of  $n$ -donor-4-NQO complexes increases with time and the colour of the solution changes from light yellow to orange or purple. The increase in refractive index and colour change may be due to the increase in polarity of the complex resulting in the formation of ionic species as outlined below.

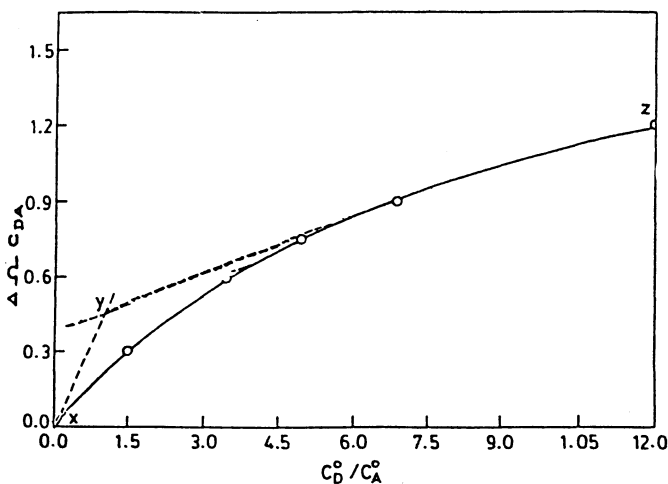
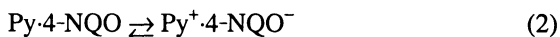
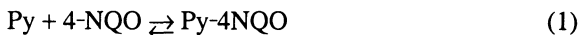


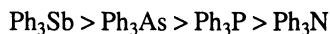
Fig. 3 Molar ratio plots for the molecular complexes of  $\text{Ph}_3\text{N}$  with 4-NQO in chloroform

### Interaction of 4-NQO with $\text{Ph}_3\text{M}$ ( $n$ -donors)

On mixing a solution of donor with a solution of acceptor (4-NQO) in chloroform or carbon tetrachloride solvent, an appreciable increase in refractive index was noticed. This appreciable increase in refractive index has been interpreted due to the charge transfer from donor to acceptor and not due to the relative increase in donor concentration. This was confirmed by a separate experiment. It was found that on mixing 1 mL of donor and 1 mL of acceptor solution, the refractive index increases appreciably more than that of separate components. A change in electron cloud density in neutral atom or molecule would lead to a change in polarizability. Since the complex is generally more polar than the components, the electronic polarizability or refractive index increases and the deviation depends upon the extent of interaction between donor and acceptor. Therefore, as explained earlier, the stronger is the complex, larger is the deviation in the refractive index value.

In the present case the deviation is positive and maximum is observed at 1 : 1 molar ratio of differential refractometric titration curves (Fig. 3).

The equilibrium constant data (Table-1) indicate the complexing strength of triphenyl compounds as noted below:



which are almost inversely related to ionization energy of donors. The formation constant studies of the complexes of 4-NQO with  $\text{Ph}_3\text{M}$  ( $\text{M} = \text{N}, \text{P}, \text{As}, \text{Sb}$ ) were performed in carbon tetrachloride and chloroform in order to investigate the dielectric effect of the solvent on the equilibrium constant. The  $K_1$  values observed for complexes are higher in carbon tetrachloride than those obtained in chloroform. The polarity of chloroform is more than that of carbon tetrachloride and the formation constant decreases with increase in polarity of the solvent.

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