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On the Reliability of Equilibrium Data of the Charge-Transfer Complex Between 2,3-Dichloro-1,4-naphthoquinone and Hexamethylbenzene

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With 1 Figure

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In view of *Hammond*'s warning[6] about the "Conspiracy of errors", found in the case of low values of equilibrium constants of charge-transfer complexes a case is made out for redetermining the values for the system hexamethylbenzene—2,3-dichloro-1,4-naphthoquinone. Uncertainties in the parameters were estimated using the *Liptay*[8] matrix procedure. The solvent used was dichloromethane. The following data were obtained at 25 °C: $\bar{\nu}_{CT} = 22{,}220\ \mathrm{cm}^{-1}$; $E_A = 0.99$ eV; $K\,\varepsilon = 2599 \pm 57\ \mathrm{l}^2 \cdot \mathrm{cm}^{-1} \cdot \mathrm{mol}^{-2}$. $\varepsilon_{\max} = 1020 \pm 148\ \mathrm{cm}^{-1} \cdot \mathrm{mol}^{-1} \cdot \mathrm{l}$; $K = 2.55 \pm 0.37\ \mathrm{l} \cdot \mathrm{mol}^{-1}$; $-\Delta H = 2.7 \pm 0.3\ \mathrm{kcal} \cdot \mathrm{mol}^{-1}$.

Introduction

Substituted naphthoquinones are known to have quenching action on the fluorescence of pyrene and anthracene[1]. A relationship has been established between the quenching constants and the electron affinity of the quencher molecules indicating a charge-transfer interaction. It was therefore considered interesting to have the formation constant for the complexes with important donors determined as accurately as possible. However the available results of *Chatterjee*[2] on the hexamethylbenzene (*HMB*)—2,3-dichloro-1,4-naphthoquinone (*DCNQ*) system seem to be inconsistent with the data obtained on the chlorosubstituted benzoquinones by *Foster*[3]. Judged from the view point of the *K* values of 2.60 ± 0.25 for the *HMB* complex with 2,6-dichloro-p-benzoquinone (*DCBQ*) one would expect normally the formation constant for the naphthoquinones to be lower than that. *Peover*[4] has estimated the electron affinity of unsubstituted 1,4-naphthoquinone to be 0.20 eV lower than that of p-benzoquinone. Further the *DCNQ* complex shows a *CT* absorption maximum $\bar{\nu}_{CT}$ located about 1390 cm^{-1} higher than that of the 2,6-dichloro-p-benzoquinone complex. *Foster* and *Matheson*[5] have made a study of *HMB* complex at 19.45 °C with tetracyanoethylene (*TCNE*), a very strong electron acceptor and they report a value of only 20.48 for the formation constant. Therefore by all counts the *K* value of 6.27 $1 \cdot \mathrm{mol}^{-1}$ for the *HMB* complex with *DCNQ* observed by *Chatterjee* seems to be unusually high. A redetermination is called for in view of *Hammond*'s warning[6] and *Foster*'s observations[7] on the inseparability of *K* and ε values. The *Liptay* matrix procedure[8], a method highly recommended by *Mulliken*[9] is adopted for this purpose.

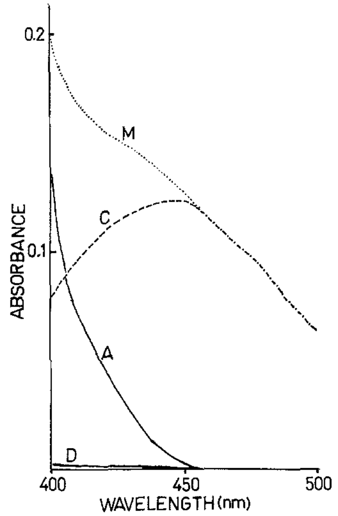

Fig. 1. D: *HMB* ($1.63 \times 10^{-1} M$); A: *DCNQ* ($6.45 \times 10^{-4} M$); M: Mixed solution having *HMB* ($1.63 \times 10^{-1} M$) and *DCNQ* ($6.45 \times 10^{-4} M$); C: Extra absorption due to C.T. Complex

Experimental

The experimental procedure and the method of calculation of uncertainties in the parameters are the same as adopted by *Liptay*[8]. Hilger Uvispek spectrophotometer was used for the determination of spectra. Laboratory grade hexamethylbenzene (Aldrich Chemical Co.) was recrystallised twice from ethanol; 2,3-dichloro-1,4- naphthoquinone was Fluka grade recrystallised from glacial acetic acid.

Results and Discussion

The *CT* absorption maximum at 450 nm (22,220 cm^{-1}) as given in Fig. 1, agrees with that of *Chatterjee*[2]. But the *K* value as now obtained is 2.55 ± 0.37 $l \cdot mol^{-1}$, whereas it is 6.27 $l \cdot mol^{-1}$ as obtained by *Chatterjee.* The molar absorbance $\varepsilon_{max.}$ of the complex is now found to be 1020 ± 148 $cm^{-1} \cdot mol^{-1} \cdot l$ which is about twice as that reported in the earlier work ($\varepsilon = 526$). As we have taken care to quantify the error limits of these values by the *Liptay* procedure, the values can be used to get other secondary data. Table 1 summarises all the results obtained on this system.

Table 1

HMB—DCNQ System at 25 °C in CH_2Cl_2	
$\bar{\nu}_{CT}$	22,220 cm^{-1}
E_A	0.99 e.v.
$K\,\varepsilon$	2599 ± 57 $l^2 \cdot cm^{-1} \cdot mol^{-2}$
ε_{max}	1020 ± 148 $cm^{-1} \cdot mol^{-1} \cdot l$
K	2.55 ± 0.37 $l \cdot mol^{-1}$
$-\Delta H$	2.7 ± 0.3 $kcal \cdot mol^{-1}$

The electron affinity value E_A was calculated by the *Batley* and *Lyons* method[10]. The enthalpy of formation was determined from a study of the variations of $K\,\varepsilon$ values with temperature. As the product $K\,\varepsilon$ values have much less relative errors than *K* values, the result obtained for ΔH this way has better reliability.

For the compounds p-benzoquinone, chloro p-benzoquinone, 2,6-dichloro-p-benzoquinone and tetrachloro-p-benzoquinone the electron affinity values E_A are in the following order[11]: 0.77, 0.97, 1.20, and 1.37 eV. *Foster*'s study on *HMB* complexes[3] with these acceptors shows that the *K* values at 18 °C tend to show a parallel correlation, their magnitudes being 0.58 ± 0.02, 1.37 ± 0.08, 2.60 ± 0.25, and 10.29 ± 0.35 respectively. The weaker the acceptor the smaller is the formation constant. As the electron affinity value of 0.99 of *DCNQ* lies between 0.97 of chloro-p-benzoquinone and 1.20 for 2,6-dichloro-p-benzoquinone, the present observation that the *HMB—DCNQ* complex has its *K* value as 2.55 ± 0.37 $l \cdot mol^{-1}$ seems to be quite reasonable.

This study highlights the importance of including a rigorous error analysis while working on spectrophotometric methods to get the properties of weak electron donor acceptor complexes. *Briegleb* and *Liptay*'s matrix procedure[12] has been singularly helpful here in clearing an anomalous situation in the reporting and interpretation of charge-transfer spectral data.

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