

Electron Donor-Acceptor Complexes of Anilines with 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone

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Interaction of aniline, *o*-, *m*- and *p*-toluidines, diphenylamine and *N,N*-dimethylaniline as electron donors, with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone as electron acceptor has been studied by conductometric technique. The results indicate formation of 1:1 electron donor-acceptor complexes. The conductance σ_p and the molar conductance coefficient σ_M of the complexes are found to increase with increase in donor strength. Solvent and temperature effects on the σ_p values have been also investigated.

Gore and Wheals¹ and Mukherjee and Chandra² have independently investigated the electron donor-acceptor (EDA) interaction of chloranil with aniline and its methyl derivatives by the aid of electronic absorption spectroscopy. Nagakura and coworkers³ have reported the formation of π - π type EDA complex between aniline and chloranil at temperatures below 200 K in the mixed solvent of ether-isopropyl alcohol (3:1). With increasing temperature, the reaction proceeds further yielding 2,5-dichloro-3,6-dianilino-*p*-benzoquinone as product. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) is similar to chloranil in structure and possesses greater electron affinity than chloranil⁴. In spite of this, relatively little attention has been focused on the interaction of DDQ with electron donors⁴⁻⁶. As a part of an extended programme on the study of the EDA complexes of DDQ, we undertook the investigation of the interaction of DDQ with aniline and substituted anilines. Electronic spectroscopy is one of the best techniques to study such complexes. However, the charge-transfer bands characteristic of EDA complexes are not observed in these systems. In this study, we have investigated the formation of EDA complexes in these systems by employing a conductometric technique⁷⁻¹⁰. The importance of conductometric studies of EDA complexes is increasing rapidly on account of their use as semiconductors.

Materials and Methods

All the anilines were obtained commercially and purified by standard methods. Acetonitrile (BDH) was purified by treatment with calcium hydride followed by distillation over P_2O_5 (0.5-1%, w/v). Carbon tetrachloride (BDH, AR) was dried and distilled before use. DDQ was purified by recrystallization from chloroform.

Conductance measurements were made on a WTW conductivity bridge using a conductivity cell fitted with platinized platinum electrodes. Equimolar stock solutions of electron donors (D) and electron acceptor (A) were prepared in acetonitrile and thermostated to a constant temperature. These solutions were mixed in the conductivity cell, keeping the total volume constant and varying the volumes of D and A. The solutions were stirred after each addition. A constant time interval was permitted to elapse between the addition and the bridge adjustment. The expression (1)

$$\alpha \sigma_M = \frac{1}{M} \cdot \frac{\sigma_p - \sigma_o}{\sigma_o} \quad \dots (1)$$

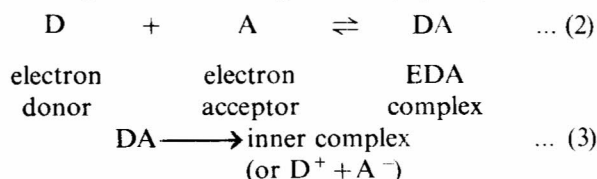
was used to calculate the molar conductivity coefficient (σ_M). Here, M is the molar concentration of D or A at the conductivity peak of the complex, σ_p is the conductivity at the conductivity peak, σ_o is the linearly interpolated conductivity value at the concentration ratio of the peak read off from a base line joining the conductivities of pure D and A solutions, and α is the dissociation ratio of the complex.

Results and Discussion

Anilines, on mixing with DDQ, yield a blue solution which instantaneously changes into green (λ_{max} , 540 nm) and finally becomes yellow (λ_{max} , 350 nm) in all the solvents studied. As the blue solution turned green before spectral measurements, its absorption could not be measured. This blue colour may be attributed to the EDA complex (or the outer complex in Mulliken's scheme) formed between anilines and DDQ. The intensity of the 540 nm band decreases with time whereas the intensity of the 350 nm band continues to increase until the end of the reaction. This shows that the 350 nm band is due to the final reaction product. From an analogy with the

reaction of aniline with chloranil³ (which is similar to DDQ in structure), we may expect the final product to be 2-chloro-5-cyano-3,6-dianilino-*p*-benzoquinone (a disubstituted product). The elemental analyses agree well with the calculated values. The 540 nm band may be assigned to a monosubstituted product (either 2,3-dichloro-5-cyano-6-anilino-*p*-benzoquinone or 2-chloro-5,6-dicyano-3-anilino-*p*-benzoquinone). However, we did not proceed further to identify these products as we were interested only in establishing the formation of an EDA complex in these systems. Although, the inner complex may be expected to exist as a reaction intermediate in these systems, it will be too unstable to give any absorption, as suggested by Nagakura and coworkers³ for similar systems. The possibility of the participation of the inner complex as a transition state in the overall reaction of anilines with DDQ may be explored by the procedure adopted by Basu and coworkers¹¹⁻¹³.

The anilines + DDQ solutions in acetonitrile exhibit appreciable conductivities, which may be explained if we presume the formation of an EDA complex between anilines and DDQ. The EDA complex changes over to inner complex (or the radical ions) according to the following scheme (Eqs 2,3).



The radical ions (or the inner complex) thus produced do not show any absorption and undergo

further reaction yielding the monosubstituted product having absorption at 540 nm which finally changes into a disubstituted product (λ_{max} , 350 nm). The conductivities of the solutions do not vary with time indicating that the formation of the inner complex (or the radical ions) and its conversion into the monosubstituted product proceed at the same rate.

The formation of EDA complexes can be followed by measuring changes in the electrical conductivity of a solution of D in an inert solvent of sufficiently high dielectric constant on adding a solution of A in the same solvent, or vice versa. The plot of conductivity (σ) versus composition of D and A yields a peak which determines the stoichiometry of the EDA complex^{7-10,14-16}. All the electron donors exhibit non-linear conductivity-concentration plots indicating formation of an EDA complex. However, a well-developed conductivity maximum is not obtained except in the case of *o*-toluidine + DDQ and N,N-dimethylaniline + DDQ systems. This is due to a steeply sloping base line caused by a serious mismatch of the initial conductivities of pure D and A solutions. The stoichiometries of the EDA complexes in these cases have been determined by correcting for the background conductivity obtained by linear interpolation. The $\sigma - \sigma_0$ values, thus obtained, were plotted against relative concentration of A. A typical plot is shown in Fig. 1 for the aniline + DDQ system.

The observed stoichiometries of the EDA complexes studied are listed in Table I along with their σ_p and σ_M values. While α is not known, a comparison of the σ_M , $\sigma_p - \sigma_0$ and σ_p values should give some information, at least on the relative magnitudes of the dissociation

Table I—Conductance Data^(a) for EDA Complexes at 30°C

Electron donor	Ionization potential (eV)	Solvent	Dielectric constant of solvent	Stoichiometry	Conductance (μ mho)			σ_M
					σ_p	σ_0	$\sigma_p - \sigma_0$	
Aniline	7.70	CH ₃ CN + CCl ₄ (1:1)	19.8	1:1	20	—	—	—
		CH ₃ CN	37.5	1:1	60	29	31	427.6
<i>m</i> -Toluidine	7.66	CH ₃ CN + CCl ₄ (1:1)	19.8	1:1	28	—	—	—
		CH ₃ CN	37.5	1:1	72	30	42	560.0
<i>o</i> -Toluidine	7.62	CH ₃ CN + CCl ₄ (1:1)	19.8	1:1	39	—	—	—
		CH ₃ CN	37.5	1:1	84	26	58	892.3
<i>p</i> -Toluidine	7.48	CH ₃ CN + CCl ₄ (1:1)	19.8	1:1	45	—	—	—
		CH ₃ CN	37.5	1:1	98	24	74	1233.3
Diphenylamine	—	CH ₃ CN + CCl ₄ (1:1)	19.8	1:1	15	—	—	—
		CH ₃ CN	37.5	1:1	36	23	13	226.08
N,N-Dimethylaniline	7.20	CH ₃ CN + CCl ₄ (1:1)	19.8	1:1	57	—	—	—
		CH ₃ CN	37.5	1:1	110	26	84	1292.4

^(a)Stock solutions of D and A were 5×10^{-3} M each.

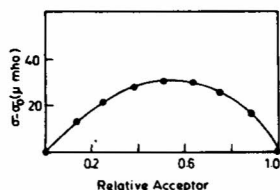


Fig. 1— $\sigma - \sigma_0$ versus concentration plot for aniline + DDQ system in acetonitrile solution at 30°C.

constants of the EDA complexes. Like Gutmann and Keyzer^{7,8}, we have assumed α to be unity in all the cases for the evaluation of σ_M . It can be seen from the data in Table 1 that the σ_p , $\sigma_p - \sigma_0$ and σ_M values increase with increase in donor strengths (decrease in ionization potential) of electron donors. This trend of σ_M values is to be expected because the anilines may be assumed to have similar α values. These results are in accordance with the observations of Gutmann and Keyzer⁹ on the chlorpromazine + benzene derivative acceptor systems as well as those of Dwivedi and coworkers¹⁷ on the *n*-alkylamine + substituted quinone systems. The σ_0 values are the conductivities which would be obtained in the absence of any interaction from merely mixing D and A solutions and are, therefore, meaningless for the interaction. σ_p is a measure of the total number of ions carrying current at the stoichiometry of the complex. Therefore, for a fixed acceptor, if the solvent, the concentration and the experimental conditions are maintained the same, σ_p should reflect the donor strengths of electron donors provided that their geometrical differences are not too great and that all the complexes dissociate to the same extent. This is indeed observed in Table 1. Based on the σ_p data, diphenylamine appears to be the weakest electron donor among all.

Dwivedi and Rao¹⁸ have shown that the rate of electron transfer in EDA complexes is enhanced by increase in solvent polarity and temperature. The σ_p values (which provide a measure of the total number of ions) are therefore expected to increase with increase in solvent polarity and temperature. To verify this fact, we have examined the effect of solvent and temperature on σ_p values. The σ_p values were measured in two solvents and at different temperatures in the range 30°–50°C. The results are shown in Tables 1 and

Table 2—Effect of Temperature on the σ_p Values of EDA Complexes in CH_3CN Solution^(a)

Electron donor	σ_p (μ mho)	
	30 C	40 C
Aniline	60	74
<i>m</i> -Toluidine	72	96
<i>o</i> -Toluidine	84	110
<i>p</i> -Toluidine	98	130
Diphenylamine	36	45
N,N-Dimethylaniline	110	160

^(a)The data are given at two temperatures only for the sake of brevity.

2. It is indeed gratifying to note that these σ_p values show an increase with increase in solvent polarity and temperature, as expected. Similar variation of σ_p with solvent and temperature has been observed earlier in many instances^{14–17,19}.

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