CONDUCTOMETRIC STUDIES OF MOLECULAR COMPLEXES OF CHARGE TRANSFER TYPE FORMED BETWEEN AZA-AROMATICS AND HALOANILS

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Electrical conductivity technique has been employed to investigate the molecular interaction of aza-aromatics viz. pyridine, α-picoline, β-picoline and γ-picoline with haloanils, namely chloranil, bromanil and fluoranil. The stoichiometry of the charge transfer (CT) complexes has been established and molar conductivities of the complexes determined employing the method of Gutmann and Keyzer. A model has been proposed for determining the equilibrium constant (K) of 1 : 1 molecular complexes of CT type by conductometric measurements. The model involves the assumption: $1/\sigma = [(1 + K c_A^0)/\rho_d K c_A^0]\,(1/c_D^0) + (1/\rho_d c_A^0)$, where σ is the conductivity of the molecular complex, ρ_d is the extent of depolarization of the complex, c_A^0 and c_D^0 are the initial concentrations of the acceptors and donors, respectively. The values of K and ρ_d follows the expected trend of the conductometric parameters determined by the method of Gutmann and Keyzer as well as ionization potential of donors, thereby substantiating the validity of the model proposed. The observed and theoretical values of thermodynamic parameters for the aza-aromatic–chloranil systems that the interaction of aza-aromatics with haloanils is occurring through the lone pair of the nitrogen ring.

Although spectrophotometric method is probably the most common method used for determining the equilibrium constants and other thermodynamic functions of molecular complexes of charge transfer (CT) type, doubts have frequently been expressed as to the significance of the values of K and other thermodynamic parameters obtained by spectral method alone[1,2]. Hence, to attach any significance to the various parameters of interaction, obtained by spectral method alone, they should be studied by spectroscopic as well as by non-spectroscopic methods. Recently[3] we have reported the CT interactions between aromatic hydrocarbons and herbicides of triazine series by conductometric method of Gutmann and Keyzer[4–6]. As an extension to these studies, the interactions between four aza-aromatics, namely pyridine (P), α-picoline (α-P), β-picoline (β-P) and γ-picoline (γ-P) as donors (D) with three fungicides of benzoquinone series viz., chloranil (CA), bromanil (BA) and fluoranil (FA) as acceptors (A) have been investigated by the conductometric method. The biological active π-electron acceptors were selected in view of their practical utility.

The aim of our present study is to establish the conductometric parameters and stoichiometry of the CT complexes formed in aza-aromatic–fungicide systems by the methods of Gutmann and Keyzer[4 – 6], evolve a theoretical model based on Scott's model[7] to determine the equilibrium constant and other thermodynamic functions for 1 : 1 molecular complexes of CT type from conductometric method, compute the energy parameters from the available spectroscopic data, and correlate the conductometric and energy parameters estimated from spectroscopic data with those obtained from the model proposed and also with the nature of the electron donors and acceptors in order to substantiate the validity of model proposed.

THEORETICAL

The CT complex formed by the partial or complete transfer of an electron from D to A (refs[8,9]) tend to dissociate into D and A in a solvent of sufficiently high permittivity according to the scheme[10 – 12]:

$$\mathrm{D} + \mathrm{A} \overset{K}{\rightleftharpoons} \mathrm{DA} \rightleftharpoons \mathrm{D}^+ + \mathrm{A}^- \, .$$

The extent of dissociation depends on the nature of D and A and permittivity of the solvent media. The formation of CT complex can be followed by observing the variation of electrical conductivity σ of D on the addition of A or vice versa in a suitable solvent media. The plot of σ as a function of D or A generally results into a maxima which determines the stoichiometry of the CT complex[4 – 6]. The equilibrium constant K of 1 : 1 CT complex formed between D and A is given by the equation:

$$K = K_1 K_\gamma; \quad K_\gamma = \frac{\gamma_{\mathrm{DA}}}{\gamma_{\mathrm{A}} \gamma_{\mathrm{D}}} , \qquad (1)$$

where γ_i is the Raoult's activity coefficient of the species i. In general, K_1 and K_γ are not constant but functions of concentration of the reactants and products. Until recently, complexes had been studied almost entirely in solution. It generally has been assumed that K_γ is unity; so that calculations of equilibrium constant were based on the equation:

$$K = \frac{[\mathrm{DA}]}{[\mathrm{D}]\,[\mathrm{A}]} . \qquad (2)$$

The general procedure is to measure σ of the complex as a function of concentration of the donor i.e. [D]. Thus

$$\sigma = \rho_{\mathrm{d}}\,[\mathrm{DA}] , \qquad (3)$$

where ρ_d is the extent of depolarization of the complex.

If c_D^0 and c_A^0 are the initial concentrations of D and A, then Eq. (2) can be written as:

$$K = \frac{[DA]}{(c_D^0 - [DA])(c_A^0 - [DA])} . \qquad (4)$$

Equating [DA] from Eqs (3) and (4) (ref.[13]) and rearranging after neglecting the higher term* we get

$$\frac{1}{\sigma} = \frac{1 + K c_A^0}{\rho_d K c_A^0} \frac{1}{c_D^0} \frac{1}{\rho_d c_A^0} . \qquad (5)$$

Thus a plot between $1/\sigma$ and $1/c_D^0$ should give a straight line with slope $[(1 + K c_A^0)/\rho_d K c_A^0]$ and intercept $(1/\rho_d c_A^0)$. From the slope and intercept both ρ_d and K can be obtained.

EXPERIMENTAL

Chemicals and Apparatus

All the electron donors (A. R.) used were obtained commercially and purified by distillation after refluxing over KOH. Analytical grade haloanils were purified by vacuum resublimation. Acetonitrile (BDH) was purified by distillation over P_2O_5 (0.5 – 1.0 wt.%). The conductivity measurements were made on Elico conductivity bridge of type CM82T of cell constant (1.0 dm^{-1}) fitted with platinized platinum electrodes. The maximum uncertainty in the conductivity measurement was ±0.01 $\mu S\ dm^{-1}$. All measurements were made at 50 Hz in a thermostat in the range 293 to 313 K. The maximum uncertainty in the temperature measurement was ±0.01 K.

Procedure

Equimolar stock solutions ($5 \cdot 10^{-4}$ mol l^{-1}) of A and D were mixed in the conductivity cell in two ways while keeping the total volume constant. In one set of the experiment the concentration of D and A were varied simultaneously to scan the whole range of mole fractions in order to establish the composition of the complex by the method of Gutmann and Keyzer[4 - 6]. In the second set, the concentration of D was varied in order to determine K from the model proposed in the present article. The conductivity of the individual components at different levels of mole fractions has been determined by the base line method in order to get the same due to CT complex only.

There may be doubt that the relative increase in conductivity may be due to the concentration of D and not due to CT interactions. This problem has been solved by taking the conductivity of D and A separ-

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* $[DA]^2$ being a square term violates the linearity of the model and can be neglected under the condition: $c_D^0 > c_A^0 > [DA]$.

ately. On mixing equal amounts of D and A solutions, the conductivity increases appreciably more than that of the maximum value of the separate components.

The values of the measured electrical conductivity were plotted as a function of D or A and a representative plot of conductivity vs concentration for P-haloanils complexes is shown in Fig. 1. The molar conductivity coefficients σ_c were computed using the expression[4]:

$$\alpha\,\sigma_c = \frac{1}{c}\,\frac{\sigma_p - \sigma_0}{\sigma_0}\,, \tag{6}$$

where c is the concentration of D or A at the conductivity peak of the complex, σ_p is the conductivity at the conductivity peak, σ_0 is the linearly interpolated conductivity value read off from a base line joining the conductivities of the pure D and A solutions and α is the dissociation constant of the complex and is assumed to be unity in the present studies. The computed values of σ_c and σ_p along with the characteristic parameters of D and A are listed in Table I. The equilibirum constant K by electrical conductivity method was measured in each case employing Eq. (5). The observed values of K and ρ_d for various aza-aromatic–haloanil systems are recorded in Table I.

Enthalpies of CT complexation (ΔH) in aza-aromatic–CA systems were determined from the slope of the plot of $\ln K$ vs T^{-1}. The Gibb's free energy (ΔG) and entropy (ΔS) of complexation were calculated from K in the usual way and are recorded along with the values of ΔH in Table II.

The energy parameters namely weighting factors a and b in aza-aromatic–chloranil systems in $CHCl_3$ were calculated from spectroscopic data[14] employing the method of Sonnessa and Daisey[15]. The computed values of these parameters along with the predicted values of ΔH from the empirical formula[16], ($b^2/a^2 = -\Delta H_{\text{calc.}}/7.30\,h\,\nu_{CT}$) are also listed in Table II (ν_{CT} is the frequency of the CT band and h is the Planck constant).

RESULTS AND DISCUSSION

The appearance of a maxima in the plot (Fig. 1) is indicative of CT complexation in the D–A system[4 – 6]. The composition of CT complex formed between D and A was dedu-

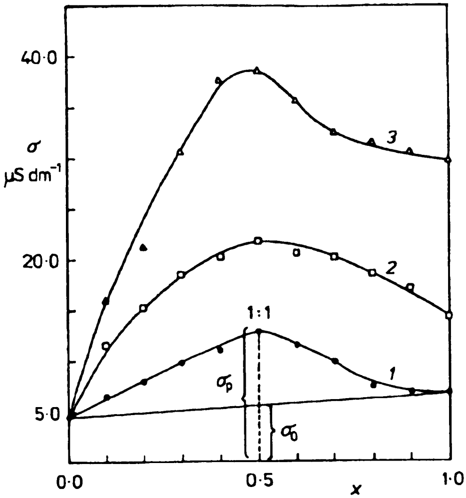

FIG. 1

A plot of conductivity σ vs mole fraction x of acceptor for P-haloanil systems at 293 K: *1* CA + P, *2* FA + P, *3* BA + P

TABLE I
Conductivity data and formation constants for 1 : 1 CT complexes formed between aza-aromatics and haloanils in acetonitrile at 293 K

System D + A	Ionization potential[a], eV		pK_a[b]	ln K	σ_p, μS dm^{-1}	σ_0, μS dm^{-1}	$\sigma_p - \sigma_0$ μS dm^{-1}	σ_c	K	ρ_d, μS dm^{2} mol^{-1}
	n–π*	π–π*								
P + CA				7.09	13.0	5.5	7.5	5 454	1 204	0.50
					(14.0, 14.8)[c]					
P + FA	9.76	9.271	5.25	6.95	21.8	9.3	12.5	5 376	1 046	0.66
P + BA				6.55	38.5	16.5	22.0	5 333	702	1.00
α-P + CA				7.47	19.0	5.6	13.4	9 571	1 764	0.33
					(20.0, 20.8)[c]					
α-P + FA	9.66	9.108	5.97	7.13	27.5	9.0	18.5	8 222	1 258	0.50
α-P + BA				6.87	45.5	16.4	29.1	7 097	972	0.66
β-P + CA				7.62	23.0	5.8	17.2	11 862	2 040	0.25
					(24.0, 24.8)[c]					
β-P + FA	9.71	9.111	5.68	7.47	30.5	9.5	21.0	8 842	1 764	0.33
β-P + BA				7.23	50.5	16.7	33.8	8 095	1 392	0.50
γ-P + CA				7.80	23.5	5.9	17.6	11 932	2 459	0.20
					(24.5, 25.3)[c]					
γ-P + FA	9.56	9.180	6.02	7.80	36.5	9.5	27.0	11 368	2 337	0.25
γ-P + BA				7.47	60.5	17.0	43.5	10 235	1 764	0.32

[a] Ref.[14]; [b] ref.[17]; [c] at 303 and 313 K.

ced from the stoichiometric maxima. The presence of a well developed maxima at a mole fraction of 0.5 in the conductivity concentration plots observed in all the systems studied are indicative of the fact that in the various aza-aromatic donors and fungicides of 2,4-benzoquinone series acceptors, CT complexes of 1 : 1 stoichiometry have been formed.

The numerical value of σ_p is a measure of the total number of ions carrying the current when D and A are mixed in stoichiometric proportions corresponding to the CT complex. When the solvent media, concentrations of D and A and the experimental parameters are kept the same for a fixed D, the value of σ_p reflect on the electron affinity of A and, for a fixed A, it reflects on the donicity of D provided all complexes dissociate to the same extent and the differences in configuration are not too great. The values of σ_p are expected to be high when the CT complexes between D and A are strong.

Since the conductivity of an ion depends upon its rate of movement, which is proportional to temperature, so we can write

$$\sigma_p = A \exp(-E^*/RT)\,, \tag{7}$$

where A is a constant which may be taken as being independent of temperature over a relatively small range and E^* is activation energy of the CT process which determines the rate of movement of ions, R is the gas constant and T is the absolute temperature. The value of E^* determined from Eq. (7) has been reported in Table II, follows the reverse trend of K as expected.

It is observed from Table I that the values of K, σ_p and σ_c (except ρ_d) for the CT complexes of aza-aromatic donors with different haloanil acceptors, increase with a decrease in the n–π^* ionization potentials (except α-P) of the donors[14] and follows the order: γ-P > β-P > α-P > P. However, no definite trend between the aforementioned parameters and π–π^* ionization potentials of the donors[14] have been noticed. On the other hand for a fixed A, the values of K, σ_c and ρ_d (except σ_p) increase with the decrease in the electron affinity of the acceptors[17,18], and the trend followed is: BA (1.37 eV) < FA (2.27 eV) < CA (2.40 eV). The values of $E_{1/2}$ of the acceptors[18] i.e. CA (0.01 V), BA (0.00 V) and FA (−0.04 V) bears no definite relationship with the aforesaid parameters.

If it is assumed that the complexation is at the lone pair of nitrogen of the ring, the values of ln K should follow the relative trend of pK_a values of the donors[17] i.e. γ-P > α-P > β-P > P. The trend which is actually observed on the basis of the values of ln K is γ-P > β-P > α-P > P. This is what would be expected if the complexation is occurring at the lone pair of ring-nitrogen. The anomalies between the expected and observed trend have been noticed in cases when $-CH_3$ group is in 2-position which results in hindering the approach of an acceptor to lone pair of nitrogen in the ring. The IR studies on hydrogen bonding between methanol and alkyl substituted pyridines indicate

TABLE II
Thermodynamic functions for 1 : 1 CT complexes formed between aza-aromatic–chloranil systems in acetonitrile at 293 K

System	K_{293}	K_{303}	K_{313}	$h\nu_{CT}$ [a] eV	*a*	*b*	$-\Delta H$, kJ mol^{-1}		$-\Delta G$ kJ mol^{-1}	$\Delta S \cdot 10^3$ kJ mol^{-1} K^{-1}	E^{*} kJ mol^{-1}
							obs.	calc.			
P + CA	1 204	1 111	990	2.67	0.90	0.40	7.72	7.09	17.28	32.62	5.06
	± 4.5	± 3.0	± 2.5				± 0.004		± 0.009	± 0.017	± 0.003
α-P + CA	1 764	1 562	1 403	2.64	0.90	0.41	8.67	7.42	18.21	32.55	3.48
	± 4.0	± 3.5	± 2.5				± 0.002		± 0.005	± 0.010	± 0.001
β-P + CA	2 040	1 820	1 645	2.64	0.90	0.41	9.03	7.42	18.56	32.52	3.08
	± 3.5	± 3.5	± 3.0				± 0.001		± 0.003	± 0.007	± 0.001
γ-P + CA	2 459	2 195	1 951	2.61	0.90	0.42	9.50	7.60	19.02	32.49	2.87
	± 4.0	± 3.0	± 2.5				± 0.001		± 0.004	± 0.010	± 0.001

[a] Ref.[14]; $\beta_0 = -1.00$ eV; $S_{01} = 0.01$.

that steric hinderance to hydrogen bonding also exists when bulky substituents are present in the 2-position[19].

There have been number of reports of linear correlation between ΔH and ΔS of complex formation[18,20,21]. There is also good overall correlation ($r = 0.9999$) betweeen ΔH and ΔS for the present class of donors. This is to be expected, for the donors are all structurally similar and interaction with CA in all the cases undoubtedly occurring through the lone pair of nitrogen ring.

A perusal of Table II reveals that there is also a good agreement between the experimental values of ΔH determined by conductometric method and the theoretically computed values of ΔH for n–π^* CT complexes formed in the aza-aromatic–chloranil systems (Table II). The uncertainty has been found to be of the order of ≤ 2 kJ mol^{-1}. This further lends support to the conclusion that complexation is through the lone pair of nitrogen of the ring.

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