

the normal shape of erythrocytes, even though the plasma cholesterol is elevated. This shows that the presence of onion extract helps to maintain the normal membrane lipid levels and thus in the maintenance of the shape of erythrocytes.

The altered appearance of erythrocytes and increased level of fibrinogen may be partly responsible for the increased aggregation tendency of erythrocytes of Group III. The absence of aggregation in Group IV indicates that the presence of some additional factors in the medium from onion extract which counterbalances the deleterious effect of cholesterol and fibrinogen on erythrocytes. The onion which is known for its fibrinolytic activity<sup>17</sup> may also explain the absence of aggregation in this group.

A comparison between Groups I and II shows that onion alone has no deleterious effect on the erythrocytes and the fibrinogen level in these groups remain unaltered.

The presence of some additional factors of onion extract in Group IV plasma is well established by *in vitro* studies. When erythrocytes from Group III rabbits were incubated with the plasma from Groups II or IV, they regained their normal shape<sup>1</sup>. Identification of such factors in onion is in progress.

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## CONDUCTOMETRIC AND SPECTROSCOPIC STUDIES ON THE INTERACTION OF IMIDAZOLE WITH IODINE

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### ABSTRACT

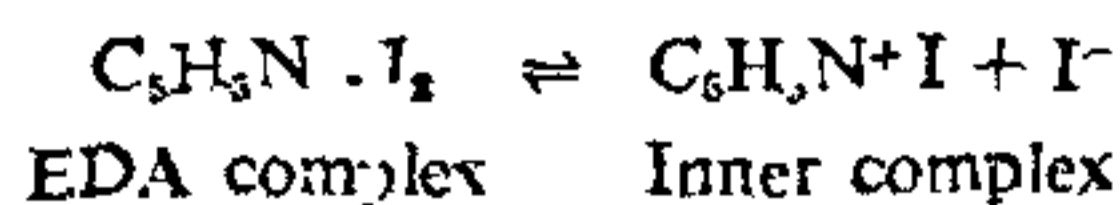
Interaction of imidazole with iodine has been examined by employing conductometric and spectroscopic techniques. Conductometric measurements indicate the formation of a 1 : 1 electron donor-acceptor (EDA) complex between imidazole and iodine. The  $\sigma_M$  and  $\sigma_P$  values for the complex are reported and the effect of solvent and temperature on  $\sigma_P$  has been studied. Spectral investigations show evidence for the transformation of the initially formed EDA complex into the inner complex thereby giving rise to the triiodide ion. Kinetics of the transformation reaction has been examined.

### INTRODUCTION

MULLIKEN<sup>1</sup> pointed out that the interaction between an electron donor (D) and an electron acceptor (A) can give either the associative outer (EDA) complex or the dissociative inner complex depending on the distance of approach between D and A and the

relative magnitude of the no-bond and dative wave functions. In many donor-acceptor systems with halogen acceptors<sup>2-3</sup>, the formation of trihalide ion is often noticed which can only result through the formation of inner complexes from the initial EDA complexes. Electrical conductance of iodine in pyridine solution was one of the early evidences for

the transformation of EDA complexes to the inner complexes. An explanation for the conductance was provided by Mulliken and Reid<sup>4</sup> on the basis of the following equilibrium:



We have presently examined the interaction between imidazole and iodine by employing conductometric and spectroscopic techniques. The kinetics of transformation of the EDA complex to the inner complex has been investigated by measuring the time dependence of the triiodide ion band.

#### EXPERIMENTAL

The solvents were dried and distilled before use. Imidazole was obtained commercially and purified by recrystallisation. Analytical grade iodine was used after resublimation.

The conductance measurements were made on a WTW conductivity bridge using a conductivity cell of the fixed cell constant and fitted with platinized platinum electrodes. Equimolar stock solutions of electron donors and acceptors were thermostated to a constant temperature. These solutions were mixed in the conductivity cell by keeping the total volume constant and varying the volumes of the donor and the acceptor. The solutions were stirred and a constant time interval was permitted to elapse between the addition and the bridge adjustment. The molar conductivity coefficient,  $\sigma_M$ , was calculated by using the expression<sup>5,6</sup>

$$a\sigma_M = \frac{1}{M} \cdot \frac{\sigma_p - \sigma_0}{\sigma_0}$$

where  $M$  is the molar concentration of the donor or acceptor at the conductivity peak of the complex,  $\sigma_p$  is the conductivity at the conductivity peak,  $\sigma_0$  is the linearly interpolated conductivity value read off from a base line joining the conductivities of the pure donor and acceptor and  $a$  is the dissociation constant of the complex.

The spectral measurements were made on a Beckman DU spectrophotometer fitted with a variable temperature cell compartment using matched silica cells of 1 cm path length. First-order rate constants,  $k$ , for the transformation of the EDA complex to the inner complex were evaluated graphically by employing the equation

$$k = \frac{2.303}{t} \log \frac{D^\infty - D_0}{D_\infty - D_t}$$

at the  $\lambda_{\text{max}}$  of the triiodide ion. Here  $D_0$ ,  $D_t$  and  $D_\infty$  are the absorbances at time 0,  $t$  and at the end of the reaction respectively. Freshly prepared stock solutions were used in these measurements.

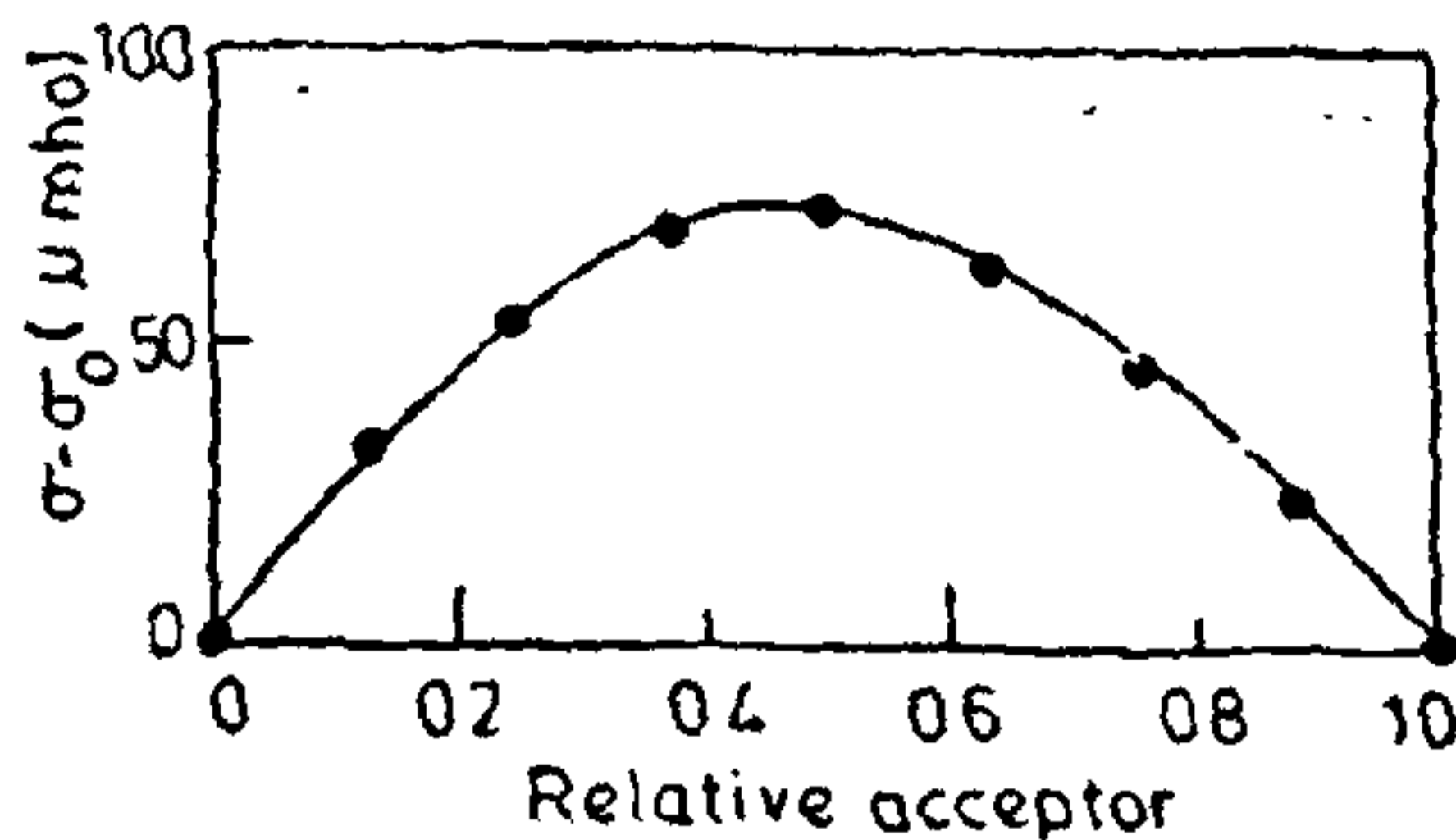


Fig. 1

FIG. 1. Typical plot of  $\sigma - \sigma_0$  versus relative acceptor for the imidazole +  $\text{I}_2$  complex in acetonitrile solution at  $33^\circ\text{C}$ .

#### RESULTS AND DISCUSSION

##### Conductance Data

The appearance of a peak in the conductance versus concentration (cf  $D$  or  $A$ ) plot is a sure indication of complex formation between  $D$  and  $A^{5-8}$ . This relation is linear in the absence of complex formation. The imidazole +  $\text{I}_2$  system yields an ill-defined conductivity peak in the conductance versus relative acceptor plot. This is due to the serious mismatch of the initial conductivities of the pure donor and acceptor solutions. The stoichiometry of this complex has been determined by correcting for the background conductivity obtained by linear interpolation procedure<sup>6</sup>. The  $\sigma - \sigma_0$  values, thus obtained, exhibited a well-developed maximum when plotted against relative acceptor (see Fig. 1). The observed stoichiometry,  $\sigma_p$  and  $\sigma_M$  values for the complex are listed in Table I. Like Gutmann and Keyzer<sup>5,6</sup>,  $a$  has been assumed to be unity for the evaluation of  $\sigma_M$ . The value of  $\sigma_p$  for the EDA complex increases with an increase in the dielectric constant of the solvent. A similar variation of  $\sigma_p$  with the dielectric constant of the solvent has been reported earlier<sup>7,9</sup>. The  $\sigma_p$  values (in  $\mu\text{mho}$ ) for the imidazole +  $\text{I}_2$  at  $33^\circ\text{C}$  and  $43^\circ\text{C}$  are 170 and 185 respectively, indicating that the  $\sigma_p$  values increase with an increase in temperature. These observations on  $\sigma_p$  values reveal that the EDA complexes ionise to a greater extent in the solvents of higher dielectric constant as well as at higher temperatures. These results are in harmony with our recent findings<sup>10</sup> where it has been shown that the rate of electron transfer in EDA complexes is enhanced by increase in solvent polarity as well as temperature.

##### Spectral Data

The electronic absorption spectra of the imidazole +  $\text{I}_2$  system exhibit neither the charge-transfer nor the blue-shifted iodine bands. Instead, absorption bands

TABLE I  
Conductance data<sup>(a)</sup> on the EDA complex of imidazole with iodine at 33° C

Solvent	Dielectric constant of the solvent	Stoichiometry	Conductance <sup>(b)</sup> ( $\mu$ mho)			
			$\sigma_p$	$\sigma_o$	$\sigma_p - \sigma_o$	$\sigma_M$
CH <sub>3</sub> CN - CCl <sub>4</sub> (1 : 1)	19.8	1 : 1	92	42	50	476
CH <sub>3</sub> CN	37.5	1 : 1	170	82	88	429

(a) Stock solutions of D and A were  $5.0 \times 10^{-3}$  M each.

(b) Conductance values are to be multiplied by the cell constant (0.5639) to obtain the conductivities.

TABLE II  
Rate data<sup>(a)</sup> on the transformation of the EDA complex to the inner complex for the imidazole + I<sub>2</sub> system

Solvent	Dielectric constant	$k^{(b)}$ , min <sup>-1</sup> ( $\times 10^3$ )	Ea, k cal mole <sup>-1</sup>	$\Delta S^\ddagger$ , eu
Chloroform	4.5	0.43	~2	-77.6
Chloroform + dichloromethane (1 : 1)	6.6	0.44	~2	-77.5
Dichloromethane	9.1	0.45	~2	-77.5

(a) Donor concentration  $20.0 \times 10^{-4}$  M; I<sub>2</sub> concentration  $1.1 \times 10^{-4}$  M.

(b) Temperature 35° C.

characteristic of I<sub>3</sub><sup>-</sup> (at 295 nm and 365 nm) appear immediately after mixing even in chloroform solution. Progressive intensification of the I<sub>3</sub><sup>-</sup> absorption is noticed, indicating that the initially formed EDA complex transforms into the inner complex (which gives rise to I<sub>3</sub><sup>-</sup>) in a relatively slow step. The kinetics of transformation of the EDA complex to the inner complex is of the first order and the rate data are summarised in Table II. The large negative entropy of activation is consistent with a transition state which is more polar than the initial state (which is likely to be the neutral EDA complex). Similar large negative entropies of activation are reported by Rao and coworkers<sup>3</sup> for such transformations. The energy of activation is small even in chloroform solution. The solvent dependence of the rate constant is very small. The transformation is very fast and I<sub>3</sub><sup>-</sup> appears almost immediately after mixing in all the solvents studied. However, the choice of the solvents was very limited because in carbon tetrachloride, the yellow colour of I<sub>3</sub><sup>-</sup> fades with time (possibly due to the interaction of I<sup>-</sup> with CCl<sub>4</sub><sup>11</sup>) and in polar solvents like acetonitrile, I<sub>2</sub> alone yields I<sub>3</sub><sup>-</sup>.

Rao and coworkers<sup>3</sup> applied the Kirkwood equation<sup>12</sup> to the transition state theory<sup>13</sup> for the reaction :

Outer complex (0)  $\rightleftharpoons$  activation complex (\*) and obtained the relation,

$$\ln k = \ln k_0 - \frac{N}{RT} \left( \frac{D-1}{2D+1} \right) \left( \frac{\mu_0^2}{r_0^3} - \frac{\mu_*^2}{r_*^3} \right)$$

Here,  $k_0$  stands for the rate constant in a condensed medium of unit dielectric constant,  $\mu$  for the dipole moment of the species,  $D$  for the dielectric constant of the medium and  $r$  for the radius. According to this relation, a plot of  $\log k$  versus  $(D-1)/(2D+1)$  should be linear. Such linear relationships have indeed been observed by Rao and coworkers<sup>3</sup>. Our kinetic data in Table II for the imidazole + I<sub>2</sub> system also show a fairly good linear relationship of  $\log k$  with  $(D-1)/(2D+1)$ .

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