

Notes

Estimation of Coulomb Integral Variation Parameter of Sulphur Atom & Electron Affinity of Iodine from Charge Transfer Spectra of Complexes of Several Thioureas with Iodine

B K SEAL*, B BANERJEE & D C MUKHERJEE†

Department of Chemistry, University of Burdwan,
Burdwan 713 104

Received 11 February 1986; revised and accepted 21 April 1986

From the linear correlation between charge transfer (CT) transition energies ($h\nu_{CT}$) of the complexes of several thioureas with iodine and the square of the orbital coefficients (C_{rj}^2) on the sulphur atom of the donors, the coulomb integral variation parameter, h_s , for the sulphur atom and the electron affinity of iodine [$E_A(I_2)$] have been determined. The results agree well with literature data.

The charge transfer (CT) transition energy ($h\nu_{CT}$) of a CT complex formed between an electron donor (D) and an electron acceptor (A) is given by the relation^{1,2},

$$h\nu_{CT} = I_D - E_A - \Delta \quad \dots (1)$$

where ν_{CT} is the wavenumber (cm^{-1}) of the CT transition, I_D the vertical ionisation potential of the donor, E_A the electron affinity of the acceptor and Δ the stabilisation energy of the complex. For complexes formed by a series of structurally similar donors with a fixed acceptor in a common solvent both E_A and Δ may be taken as constants so that $h\nu_{CT}$ may be correlated with I_D which can, in turn, be linearly correlated with the Hückel energy of the highest molecular orbital (HOMO) of the donor.

With molecular iodine thioureas form n -donor- σ -acceptor type 1:1 complexes of high thermodynamic stability³. Recently Mottaleb *et al.*⁴, emphasised the role of $C=S$ π -electrons of thioureas in studying their donor properties towards iodine. These authors calculated the π -ionisation potentials, eigenvectors and charge densities of several thioureas by HMO technique assuming a planar geometry of the donors. They showed that $h\nu_{CT}$ values of thiourea-iodine complexes decrease with increase in the value of the eigenvector on the sulphur atom. The object of the present communication is to calculate the coulomb integral variation parameter for the sulphur atom and the electron affinity of iodine from a linear correlation

between the values of $h\nu_{CT}$ of several thiourea-iodine complexes and the square of the orbital coefficients on the sulphur atom of these donors.

Iodine complexes of the following thioureas were studied: (i) *s*-diphenylthiourea (SDPTU), (ii) phenylthiourea (PTU), (iii) thiourea (TU), (iv) benzylthiourea (BTU), (v) dibenzylthiourea (DBTU) and (vi) tetramethylthiourea (TMTU). Data for the eigenvectors on the sulphur atom of these donors, their ionisation potentials and $h\nu_{CT}$ of their complexes with iodine were taken from the literature⁴. For complexes of SDPTU and PTU $h\nu_{CT}$ values were taken from our own work (unpublished). Data are recorded in Table 1.

According to Coulson-Longuet-Higgins⁵ perturbation theory, the change in coulomb integral of carbon atom replaced by another atom or group, alters the energy of the j th Hückel molecular orbital by an amount

$$\Delta E = E_j - E_j^0 = \frac{\partial E_j}{\partial \alpha_r} \delta \alpha_r = \delta \alpha_r C_{rj}^2 = h_s \beta_0 C_{rj}^2 \quad \dots (2)$$

where $\partial \alpha_r$ is the change in the coulomb integral of the r th atom from the standard value of the coulomb integral of carbon atom in ethylene; C_{rj} the atomic orbital coefficient of the r th atom in the j th MO in the unperturbed system; E_j^0 the energy of the j th MO in the unperturbed system, i.e. ethylene; h_s the coulomb integral variation parameter for the sulphur atom; β_0 the resonance integral for $C=C$ in ethylene; and E_j equals the ionisation potential of the donor and is given by Eq. (2)

$$E_j = I_D = E_j^0 + \delta \alpha_r C_{rj}^2 \quad \dots (3)$$

Combining Eq. (3) with the Eq. (1) yields

$$h\nu_{CT} = E_j^0 + \delta \alpha_r C_{rj}^2 - (E_A + \Delta) \quad \dots (4)$$

Table 1—Charge Transfer Transition Energies ($h\nu_{CT}$), Ionisation Potentials (I_D) and Atomic Orbital Coefficient of r th Atom (C_{rj}^2)

Donor	$h\nu_{CT}$ (eV)	I_D (eV)	C_{rj}^2
SDPTU	3.97*	8.36	0.467
PTU	4.10*	8.46	0.495
TU	4.16	8.58	0.594
BTU	4.08	8.45	0.562
DBTU	3.94	8.36	0.555
TMTU	3.71	7.62	0.453

*Taken from our own work (unpublished).

†Department of Pure Chemistry, Science College, Calcutta 700009.

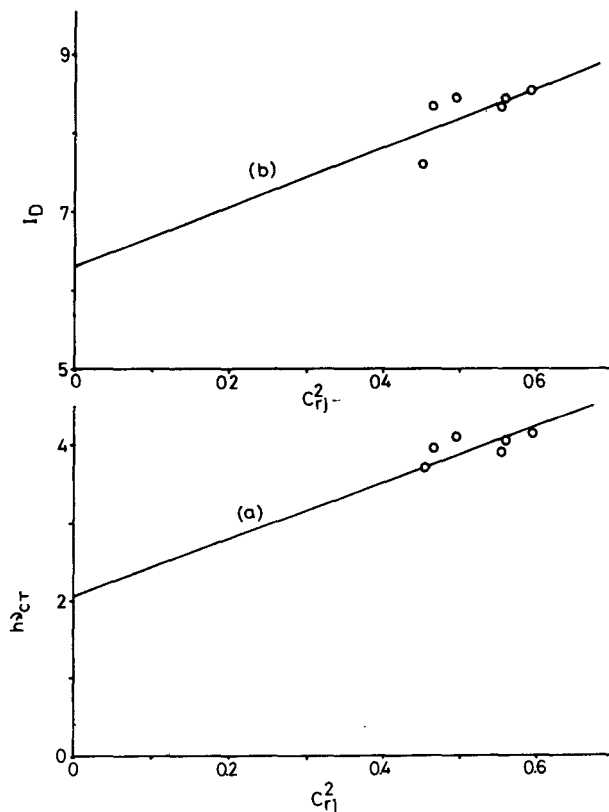


Fig. 1(a)—Plot of CT transition energies ($h\nu_{CT}$) of some thiourea-iodine complexes against square of the orbital coefficient (C_{rj}^2) on sulphur atom of donors

Fig. 1(b)—Plot of the ionisation potentials (I_D) of donors against square of the orbital coefficient (C_{rj}^2) on sulphur atom of donors

The plot of $h\nu_{CT}$ versus C_{rj}^2 , according to Eq. (4), should be linear, with slope $= \delta\alpha_r$, and the intercept $= E_j^\circ - E_A - \Delta$ from which the electron affinity of I_2 can be determined provided E_j° and Δ are known. E_j° is obtained from the linear plot of I_D versus C_{rj}^2 . The stabilisation energy, Δ , is given by the relation^{6,7}.

$$\Delta = W_1 - W_0 \quad \dots (5)$$

where W_0 and W_1 refer to the energies of the no bond and dative states of the CT complex respectively.

The stabilisation energies (Δ) of several thiourea-iodine complexes were calculated by us in an earlier paper⁸. An average value, 2.55 eV, of Δ has been used in the present investigation. The plots of $h\nu_{CT}$ versus C_{rj}^2 and I_D versus C_{rj}^2 are fairly linear (Fig. 1; curves a and b). The curve a is more linear than curve b. Both the plots have nearly the same slope, an average $\delta\alpha_r$ is equal to 3.7125 eV ($\delta\alpha_r = 3.625$ eV from Eq. 4 and 3.80 eV from Eq. 3). From the average slope and using β_0 equal to 2.48 eV, h_s is found to be 1.497 eV which compares well with the value 1.5 eV reported by Streitwieser⁹ for sulphur atom when the core potential is taken into consideration. The intercept of the plot according to the Eq. (4) is 2.05 eV. E_j° obtained from the plot of I_D versus C_{rj}^2 is 6.3 eV. From these data and using Δ equal to 2.55 eV the electron affinity of iodine i.e. $E_A(I_2)$ comes out to be 1.7 eV which agrees very well with the value 1.7 eV as reported by Person¹⁰.

References

- 1 McConnell H, Ham J & Platt J, *J chem Phys*, **21** (1953) 66.
- 2 Mulliken R S & Person W B, *Ann rev phys Chem*, **13** (1961) 107.
- 3 Bhaskar K R, Gosavi R K & Rao C N R, *Trans Faraday Soc*, **62** (1966) 29.
- 4 Abdel-Mottaleb M S A, El-Arrash A M & Abu-All M M, *Z phys chem*, **259** (1978) 6, S. 1083.
- 5 Coulson C A & Longuet-Higgins H C, *Proc Roy Soc (London)*, **A191** (1947) 39.
- 6 Chan R K & Liao S C, *Can J Chem*, **48** (1970) 299.
- 7 Sonnessa A J & Daisey J M, *Spectrochim Acta*, **32A** (1976) 465.
- 8 Seal B K, Banerjee B & Mukherjee D C, *J Indian chem Soc*, **62** (1985).
- 9 Streitwieser A (Jr), *Molecular orbital theory for organic chemists* (John Wiley, New York), 1961.
- 10 Person W B, *J chem Phys*, **38** (1963) 109.