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Charge-Transfer Interaction Between 1-Piperidinethiocarboxanilide With Trinitrobenzene and Trinitrotoluene

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With 1 Figure

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In view of the biological importance of substituted thioureas as electron donors, the charge-transfer interaction of 1-piperidinethiocarboxanilide with 1, 3, 5-trinitrobenzene and 2, 4, 6-trinitrotoluene was studied. From the electronic spectra in carbon tetrachloride, values have been obtained for the formation constant of the 1 : 1 complexes and data for the changes in enthalpy, free energy and entropy are presented.

The importance of thioureas in promoting cell division and regeneration has been recently recognised and *Szent-Györgyi* has indicated that charge-transfer interaction might hold a clue to their functioning[1]. Some of the substituted thioureas show pronounced antithyroid and antitubercular activity[2].

In this communication the results obtained by us on the spectral study of 1-piperidinethiocarboxanilide (*PTCA*) as donor and 1,3,5-trinitrobenzene (*TNB*) and 2,4,6-trinitrotoluene (*TNT*) as acceptors are reported.

Absorption spectra were determined in carbon tetrachloride. A set of 6 solutions with constant acceptor and varying excess donor concentrations were used keeping in view *Person*'s criterion for choice of concentration[3]. There is pronounced general increase in absorption beyond the wavelength longer than 400 nm. However there is no sharp charge-transfer maximum observable perhaps because of the overlap of the strong donor absorption with the charge-transfer band suggesting mixing of the dative state of the complex with the donor excited states. It is noteworthy to mention that in such cases it is possible to determine the equilibrium constant for the complex formation from measurements on the general increase in absorption[4, 5]. Fig. 1 illustrates the excess absorption in the case of *PTCA—TNB* system. Similar increase was observed in the case of *PTCA—TNT* system as well. The solutions were stable and there were no changes in absorption with time.

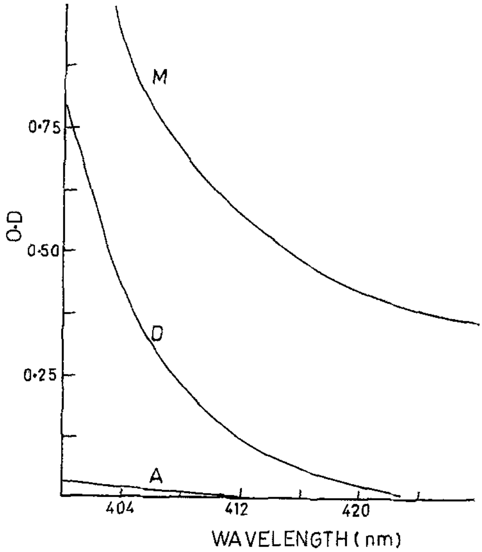

Fig. 1. D Spectrum of *PTCA* (6.663 · 10^{-2} mole · l^{-1}). A Spectrum of *TNB* (1.2134 · 10^{-3} mole · l^{-1}). M Spectrum of *PTCA* (6.663 · 10^{-2} mole · · l^{-1}) + *TNB* (1.213 · 10^{-3} mole · l^{-1})

Table 1. *Thermodynamic Properties of the Charge-Transfer Complexes of PTCA with TNB and TNT at 35 °C in* CCl_4

System	K_c l · mol^{-1}	— Δ H^0 kcal · mol^{-1}	— Δ F^0 cal · mol^{-1}	— Δ S^0 e. U.
PTCA—TNB	2.23 ± 0.11	2.3 ± 0.2	491 ± 30	5.9 ± 0.7
PTCA—TNT	4.19 ± 0.42	2.5 ± 0.2	878 ± 62	5.3 ± 0.7

The values of the free energy change and the negative enthalpy of formation are of the right order of magnitude within the range of a reversible biological process.

Very good linearity for the *Benesi—Hildebrand* plots[6] was obtained showing the presence of a *1 : 1* complex. There is no wavelength dependance of *K* over the range. The 1 : 1 nature of the interaction and the absence of higher order complexes were confirmed by the *Foster—Hammick—Wardley* plots[7]. As we found that the uncertainties for the product $K\,\varepsilon$ values are much smaller than those for K and ε individually, the negative enthalpy of formation $-\Delta H^0$ was found by plotting $\log K\,\varepsilon$ rather than the $\log K$ values against $1/T$.

The thermodynamic values obtained for the two complexes are given in Table 1.

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