

benzhydryl proton is not due to a solvent effect but due to molecular complex formation. The effect of donor on the resonance peaks of phenylic protons in DDT could not be studied due to their overlapping nature with the proton resonance of indoles. The range of donor concentration, the maximum observed chemical shifts and some equilibrium data are summarized in Table 1.

The utility of chemical shift in the study of π -complex formation has been demonstrated by various workers¹⁰⁻¹². Similar results have recently been reported by Ross and Biro¹³ on molecular complexes of DDT with aromatic donors,

Molecular orbital calculations¹⁴ on indoles and substituted indoles using the frontier-electron density principle¹⁵ support the suggestion of Szent-Gyorgyi *et al.*¹⁶ regarding somewhat localized π charge-transfer interaction involving C-2—C-3 atoms of indoles. Values of equilibrium constants in the present work are in good agreement with this hypothesis. The introduction of methyl group in the 2- or 3-position increases the value of K (Table 1). Highest value of equilibrium constant obtained in the case of 3-methylindole is indicative of the most effective increase in electron density and, hence, a formal negative charge, by methylation at the 3-position.

The interaction of a donor molecule with an acceptor molecule is probably, localized, in the respect that on complexation the perturbation of the electron density in the donor molecule is not uniformly distributed over the whole molecule. From the present work it is not possible to say, whether this affects the geometrical orientation of the donor and acceptor molecules relative to one another, although some degree of orientation towards such sites of high electron density might be expected. However, it should be recognized that with an acceptor such as DDT, which has a large molecular volume, a completely localized interaction at a particular region in the indole nucleus is not possible. Thus, it had to be supposed that the electron actually came from the π -electron pool of the whole indole molecule, while the actual transfer took place

at C-2 or C-3 atom or both, these atoms being conjugated to the rest of the molecule.

The formation of the above complexes is related with the mode of action of DDT and, further, it provides substantial support to Holan's theory⁸ of toxicity proposed recently in modification of Mullins theory¹⁷. Yet, the third probable site of interaction, i.e. trichloromethyl group in DDT, remains to be investigated.

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Reduction of Chloramine-T on Germanium Semiconductor/Electrolyte Interface

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Cathodic and anodic polarization behaviours of *n*- and *p*-Ge electrodes have been studied in 0.1N H₂SO₄ with and without chloramine-T. The process of reduction is found to involve injection of holes in the valence band electrons of the semiconductor.

TABLE 1—MAXIMUM OBSERVED SHIFTS (Δ_{\max}) AND EQUILIBRIUM DATA (K , Δ_0) FOR DDT COMPLEXES WITH INDOLES IN CARBON TETRACHLORIDE* AT 31°

Donor	Maximum donor conc.†	Δ_{\max} (Hz)	K (litre mole ⁻¹)	Δ_0 (Hz)
Indole	4.0M	34.0	0.308 ±0.010	64.6 ±3.3
2-Methylindole	3.0M	28.0	0.330 ±0.013	60.6 ±3.4
3-Methylindole	2.0M	23.5	0.468 ±0.024	52.8 ±3.8

*In recent years the use of carbon tetrachloride as "inert" solvent has been questioned. Unfortunately the volume magnetic susceptibility for this solvent which would be a rigorous index of its "inertness" is not available. Though it is reported that it interacts very weakly with aromatics¹ ($K \approx 0.01$ litre mole⁻¹), but still, it was the best choice in our study among available "inert" NMR solvents, due to several advantages specially the solubility of donor species.

†A concentrated solution ($\approx 4.0M$) of indole has an NMR spectrum similar to that of a more dilute (0.5M) solution in carbon tetrachloride⁸, thereby excluding any possibility of self-association.

THE rate of electrochemical reaction at a semiconductor electrode substantially depends on the electron structure of the semiconductor together with the phenomenon occurring in the solution or solution-semiconductor interface. The redox reactions, in particular, are specific in the sense that depending upon the redox potential of the system and biased potential both conduction band electron and valence band electrons may participate in the reaction. A number of redox reactions involving the change in the oxidation states of metal ions have been studied but the mechanism of redox reaction involving organic reagents has been scarcely investigated. In the present note the redox behaviour of chloramine-T at the surface of germanium single crystal has been investigated in acidic medium.

The results of cathodic and anodic polarization of germanium electrodes in acidic solutions of chloramine-T (GR, E. Merck) have been recorded galvanostatically in a stirred solution in dark, as described earlier¹.

The solution of sulphuric acid (BDH, Analar), used as supporting electrolyte, was pre-electrolysed before use. All the solutions were prepared in doubly distilled water. The solutions of chloramine-T were standardized iodometrically². The germanium single crystals were supplied by M/s Mullard Ltd, London. The type of conductivity, specific resistance and surface orientations were determined by usual procedures³.

The results obtained for the cathodic polarization of *p*-Ge electrode in 0.1*N* sulphuric acid show a well-developed saturation current density whereas on *n*-Ge the overpotential increases steadily with increasing current density. On the addition of chloramine-T to sulphuric acid both the electrodes behave in similar fashion towards cathodic polarization. Well-developed saturation current density is observed on both the cathodes, the magnitude of which decreases with concentration of the reductant, a behaviour similar to that observed for the reduction of ferricyanide ions⁴ and ceric ions⁴. In both the cases it has been found that valence band electrons participate in the reduction process. Therefore, it may be concluded that the reduction of chloramine-T at the surface of germanium electrode involves participation of valence band electrons.

The participation of valence bond electrons in the reduction process has been further confirmed from the comparison of anodic polarization behaviour of *n*- and *p*-Ge electrodes. The curves for *n*-Ge anode exhibit well developed saturation current density whereas no such saturation of anodic current on *p*-Ge is observed. In the case of *n*-Ge anode an increase in saturation current density on the addition of the reductant to sulphuric acid is observed. Gerischer and Beck^{5,6} have reported similar behaviour of anodic polarization curve for the reduction of ferricyanide ions on *n*-Ge electrode and concluded that during the reduction process valence band electrons were involved.

The anodic polarization curve in sulphuric acid represents the dissolution curve for germanium as a result of consumption of holes^{5,7}. The increase

in saturation current density indicates that there should exist some source of extra holes in the valence band. This can be explained if chloramine-T is assumed to be reduced by extracting electrons from valence band. Therefore, as chloramine-T is reduced, the number of holes in valence band increases which in turn increases the saturation current density. Thus, chloramine-T is reduced on the surface of germanium semiconductor with injection of holes in the valence band.

The solution of chloramine-T is photosensitive⁸, therefore, it had not been possible to study the effect of light illumination on the polarization curves, which could have given further support to our proposed mechanism.

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Heat of Formation of Cyclazines & Some Other Organic Compounds Containing Heteroatoms

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Heats of formation of some organic compounds containing nitrogen, oxygen, sulphur and halogens as heteroatoms have been calculated using a simplified version of IOC- ω -technique. The results are in agreement with the available experimental data.

KRISHNA and coworkers¹⁻⁴ have used the IOC- ω technique for calculating the heats of formation of some nitrogen containing heteromolecules and the results obtained are in fairly good agreement with the available experimental results. The heats of formation of some cyclazines calculated using IOC- ω technique are reported in this note.

The heat of formation of an organic compound is equal to the sum of the total π -bond and σ -bond energies (Eq. 1).

$$-\Delta H_f = E_{\pi b} + E_{\sigma b} \quad \dots(1)$$

The π -bond energy ($E_{\pi b}$) can be obtained using Eq. (2).

$$E_{\pi b} = -[\omega \sum_r q_r(1 - q_r) - \omega_s \sum_{j < r} q_r p_{rj} + 2\beta \sum_{r < s} p_{rs}] \quad \dots(2)$$