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IISc THESES ABSTRACTS

Thesis Abstract (Ph.D.)

Effect of di(2-ethylhexyl) phthalate on mitochondrial turn over and cholesterol metabolism by Nandini Nair.

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Department: Biochemistry

1. Introduction

The industrial plasticizer diethylhexyl phthalate (DEHP, fig. 1) is used widely in the manufacture of flexible tubing and medical devices like disposable syringes, transfusion bags, heart valves, catheters, dialyzing units, vascular grafting materials and intrauterine devices. In the plastic the concentration of DEHP could be as high as 60%. Since it is not covalently bound, the plasticizer can easily leach out from plastic containers. Thus DEHP has been detected in stored blood as well as in tissues of patients receiving blood transfusion. Because of this and its occurrence ubiquitously in the soil, plant and stored food, the toxic potential of DEHP has been widely investigated.

Administration of DEHP to experimental animals has been reported to proliferate mitochondria in the liver and to depress cholesterol in circulation. The results of a detailed investigation on these two aspects are presented and their implications discussed in this thesis.

2. Materials and Methods

Male albine rats (140–150 g) of the Institute-inbred strain were fed with DEHP (2% w/w) in the diet for 3–4 weeks. Animals were killed by cervical dislocation, and hepatic mitochondria isolated[1]. Polarographic determination of oxygen uptake was made in a Gilson K-ICT-C oxygraph[2] The cytochrome content of mitochondria and sonic submitochondrial particles was calculated from difference (reduced-oxidized) spectra.

Incorporation of amino acids into mitochondria *in vitro* was carried out in the presence of ATP generating system. For the determination of half-life of mitochondria[^{14}C] bicarbo was used

Cholesterol in the serum and liver was determined after saponification and extraction into petrol[3] The content of ubiquinone in liver and subcellular fractions was determined by spectrophotometry[4]. Microsomal HMGCoA reductase was assayed according to Shapiro *et al*[5], and 7α-hydroxylase according to Carlson and Goldfarb[6].

3. Results and conclusions

Administration of DEHP (2% w/w) in the diet decreased the weight gain of animals by 10–20%, increased the size of liver by 40–50% and depressed serum cholesterol by 4% and doubled the

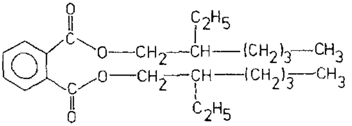

FIG 1 Structure of diethylhexyl phthalate (DEHP)

mitochondrial protein content (fig. 2) The number of mitochondria per liver cell was doubled on DEHP administration. These mitochondria showed decreased respiratory activity (50%) The content of cytochrome oxidase also decreased by half The specific incorporation of aminoacids into the proteins of whole liver and into mitochondria was not enhanced The half-lives of whole liver proteins and of mitochondria were increased in the plasticizer administered animals. The half-life of cytochrome oxidase was, however, unaffected by the treatment

Microsomes isolated from the livers of DEHP-fed animals showed lowered specific activity of HMGCoA reductase activity (50%) The incorporation of acetate but not of mevalonate into hepatic cholesterol was decreased (52%) in these animals The release of bile acids was increased by 100% and the activity of 7α-hydroxylase was stimulated 70% on DEHP

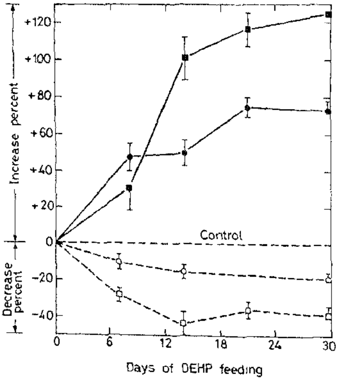

FIG 2 Effects of administration of DEHP Rats were fed with DEHP (2% w/w) in the diet for the period indicated The values represent the increase or decrease of body weight (○), serum cholesterol (□), liver weight/100 mg body weight (●) and liver mitochondria (■) taking the corresponding control as 100 Some typical values of standard deviation are also shown

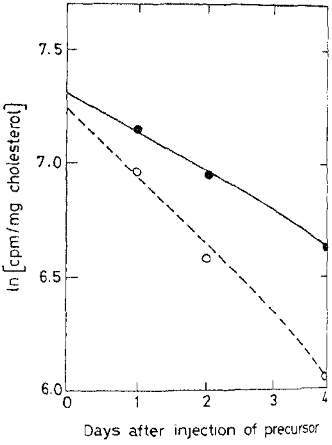

FIG. 3 Effect of administration of DEHP on the concentration of ubiquinone in rat liver The concentration of ubiquinone (nmoles/g liver) in control (O) and DEHP-fed (2% w/w) animals (●) are given Some typical values of standard deviation are indicated

administration Even though the capacity of mitochondria to oxidize the side chain of cholesterol was not enhanced in DEHP-fed animals, the half-life of cholesterol in liver had decreased by 50% in treated animals

The administration of DEHP caused a three-fold increase in the content of ubiquinone in liver (fig 3) The concentration of the quinone/mg of mitochondrial protein doubled The increase in ubiquinone concentration is caused by a stimulation of synthesis and not by a change in the rate of degradation.

Neither the administration of the antithyroid agent propylthiouracil nor thyroidectomy affected the hypocholesterolaemic action of DEHP Mitochondrial proliferation was also not affected The induction of carnitine acetyl transferase was not affected by thyroxine deficiency. In contrast, DEHP-induced increase in α-glycerophosphate dehydrogenase activity of hepatic mitochondria had significantly diminished on thyrosine depletion There was no decrease in the circulating levels of thyroxine in animals fed with DEHP These results indicated that thyroxine may not mediate the action of DEHP except in the induction of α-glycerophosphate dehydrogenase.

The potential of DEHP as a antihypercholesterolemic drug should be explored.

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Thesis Abstract (Ph.D.)

Blue-emitting ac electroluminescence (EL) in $Zn_{1-x}Mg_xS$:Cu,Br powder phosphors by R. Revathi.

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Department: Inorganic and Physical Chemistry.

1. Introduction

The recent advances in information-processing techniques have stimulated investigations on many kinds of display devices The large area LED display panels, based on pn-junction light emission is presently at cross roads between monolithic and discrete assembly The former is limited by the high-power dissipation and the latter, due to difficulties in fabrication and high costs. In comparison, ac-powder EL phosphors are easy to manufacture and can therefore be used for large area displays. These powders emit visible light when excited by ac voltage of audio frequencies. Among the ACPEL phosphors, green-emitting electroluminescent (EL) ZnS:Cu,Br powder phosphors have been well characterised but blue EL emitters are difficult to prepare[1,2]. Efforts to prepare blue emitters through the fabrication of p-n junctions have only met with partial success. In this context, it has been found that the $Zn_{1-x}Mg_xS$:Cu,Br phosphors emit in the blue for a wide [Cu]/[Br] and hence can serve as potential candidates for display applications.

2. Experimental techniques

The $Zn_{1-x}Mg_xS$:Cu,Br powders have been prepared by firing appropriate amounts of ZnS and $Mg(OH)_2 \cdot MgCO_3$ in H_2S at 900°C. Cu and Br are added in the form of copper acetate and ammonium bromide, respectively. Phosphor is washed with KCN to remove excess Cu from the surface. The Cu and Br contents in the resultant phosphor are estimated. The $Zn_{1-x}Mg_xS$ powders are prepared for various values of x and the phase contents are determined. Lattice parameters are calculated for both hexagonal and cubic phases. Optical absorption and luminescence spectra are taken for the solid solutions. The band gap E_g is determined as a function of x using diffuse-reflectance technique.

The luminescence properties are studied in the photo- and electroluminescence mode. EL panels are prepared from $Zn_{0.82}Mg_{0.18}S$:0.3mole%Cu,0.3mole%Br. The dependence of EL brightness on voltage and frequency is determined. Photoluminescence spectra are taken at 300 and 80K for different values of x as well as for varying [Cu]/[Br] ratios.

During the investigation on the deterioration of EL phosphors it is found that the life time of the phosphor is influenced by impurities present natively. The effect of Mn has been studied using the EPR technique. The intensity of the Mn^{2+} signal is monitored for phosphors with varying Cu, and measured before and after its deterioration. The brightness is measured for Mn varying from 10^{-6} to 10^{-4} mole%.

One of the techniques used by workers of the past for the improvement of the life time of EL phosphor is to anneal the phosphor in static air after the initial firing[3]. The ZnS:Cu,Br and $Zn_{1-x}Mg_xS$:Cu,Br phosphors with varying [Cu]/[Br] are annealed in atmospheres of varying p_{O_2}. The luminescence, EPR spectra and the deterioration characteristics of these phosphors have been studied.

3. Results and discussion

The preparation of $Zn_{1-x}Mg_xS$ powder is complicated by the unreactive nature of MgO, if formed, during the reaction. Heating $MgCO_3 \cdot Mg(OH)_2$ with ZnS can lead to $Zn_{1-x}Mg_xS$ without MgO if care is taken to avoid moisture in the starting material. The solubility limit for MgS in ZnS is 24 mole% at 900°C. The formation of the solid solution is accompanied by a transformation of the crystal structure from 3C to 2H as the x values are increased. Lattice expansion also takes place along with. However, the x values vary somewhat with conditions of preparation and the temperature of firing. Knowing the stability regions of 2H and 3C, a pseudobinary phase diagram is drawn. It is found that the band gap E_g increases with x values. The Vegard's law is not obeyed for the $Zn_{1-x}Mg_xS$ solid solution.

The photoluminescence (PL) spectra of $Zn_{1-x}Mg_xS$ show an intense blue emission ($\lambda_{max} = 468$nm). The intensity of the emission is two orders of magnitude greater than the corresponding emission for pure ZnS. The intensity reduces if x is increased beyond 0.025[4].

AC EL panels prepared from $Zn_{0.85}Mg_{0.15}S$:0.3Cu,0.3Br emit in the blue unaccompanied by any other side band. The brightness increases with increasing operating voltages and saturates 300cd/m^2. The emission maxima remain unchanged with frequency of operation. The temperature shift of λ_{max} and half-band width are similar to those observed for Cu blue emission in ZnS:Cu,Br. For ZnS under the same conditions of operation the λ_{max} is 520nm. The PL spectra are similar in character to EL spectra. For $Zn_{0.85}Mg_{0.15}S$:Cu,Br the emission maxima vary with [Cu]. If [Cu] is 10^{-4} mole%, the emission spectrum shows both the blue and the green bands. If [Cu] is increased to 0.5mole%, only the blue band is observable.

The EPR spectra of ZnS:Cu,Br phosphors indicate the presence of Mn present as native impurity. The intensity of Mn^{2+} EPR signal increases with Cu. The intensity enhancement is more perceptible for lower concentrations of Mn. Mn plays an important role in the deterioration of EL phosphor. This is checked by measuring the EPR intensity before and after the deterioration of the phosphor. The Mn^{2+} signal intensity decreases during deterioration and regains when the phosphor is reheated at 200°C to recover the brightness.

On annealing the phosphors in air, the intensity of emission is enhanced and there is a shift in λ_{max} to higher values. Simultaneously, the half-life of the phosphor is increased. For the $Zn_{1-x}Mg_xS$ powder, annealing in the presence of oxygen reduces the solubility limit to 11 mole%. For $Zn_{1-x}Mg_xS$:Cu,Br, the solubility limit is further lowered with increasing Cu on annealing in the presence of oxygen.

The above observations indicate that substitution of MgS in ZnS gives rise to blue emission whereas, the green band cannot be minimised in ZnS:Cu,Br. The preparation of $Zn_{1-x}Mg_xS$:Cu,Br is complicated by the limited solubility of MgS in ZnS. The expansion of the lattice due to Mg substitution is explained as due to the ionicity differences between the Zn-S and Mg-S bonds. The variation of phase content with conditions of preparation indicates that the system may have thermodynamic metastability. Vegard's law is not obeyed indicating that the solid solutions are not ideal.

The presence of 0.5mole% of Mg in ZnS increases the intensity of the SA (self-activated) luminescence by two orders of magnitude. The enhancement is due to the modification of the $[V_{Zn}-D]'$ centre (V_{Zn} is a zinc vacancy and D is a donor) by Mg which acts as an isoelectronic acceptor in ZnS. Mg effectively screens the electron repulsive character of $[V_{Zn}-D]'$ and increases its electron-capture cross section. Hence the intensity is enhanced.

The luminescence spectra indicate that Mg can bring about a change in the nature of the luminescent centres in ZnS due to the change in the nature of the chemical bonding. In $Zn_{1-x}Mg_xS$, increasing the concentration of Mg modifies the lattice so that more Cu-blue centres are formed in preference to the Cu-green. This is probably due to the expansion of the lattice on Mg substitution resulting in a higher concentration of the interstitial Cu impurities. The blue emission in ZnS is explained to be arising from a centre of the kind $[Cu_{Zn}^{-}-Cu_i^{+}]$[4].

The variation of the Mn^{2+} signal during EL deterioration indicates that hole attractive centres such as Mn^{2+} play important roles in the deterioration of the EL phosphor. This phenomenon is explained on the basis of the model for the EL in ZnS proposed by Fischer[5]. According to this model, Cu forms conducting precipitates which decorate the dislocations in ZnS. These help to concentrate the electric field at the charged dislocations in the insulating phosphor. In the presence of Mn^{2+}, Cu is distributed as Cu^{1+} and Cu^{2+} (preferentially at the dislocations) which increases the conductivity of these precipitates. During the EL process, MN^{2+} can trap holes which results in the conversion of an equivalent amount of Cu^{2+} to Cu^{1+}. The reduction in the concentration of Cu^{2+} is identified to be the cause of the deterioration. The hole trapping by Mn^{2+} is kinetically controlled and can take place slowly in time during extended periods of operations. With this model as the back ground, the longer life time of phosphorus annealed in the presence of oxygen is explained. Oxygen forms an isoelectronic centre when doped in ZnS. Due to its higher electronegativity (when compared to S^{2-}), oxygen can act as a hole trap. Thus, in the presence of O, the hole trapping by Mn^{2+} is inhibited. The $[Cu^{2+}]/[Cu^{1+}]$[5] is maintained for a longer period of time thus slowing down the deterioration process[6].

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Thesis Abstract (Ph.D.)

Contributions to the chemistry of phosphorus-fluorine compounds and a few complex fluorides by H. P. Sampath Kumar

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Department: Fluorine Laboratories, Inorganic and Physical Chemistry

1. Introduction

The thesis deals with the contributions made to the chemistry of phosphorus-fluorine compounds, complex metal fluorides of transition elements and to the reactive chemistry of sulphur trioxide, iodic acid, periodic acid, sodium nitrite, potassium nitrite, nitryl chloride, iodine monochloride and pyridinium poly (hydrogen fluoride). The chemistry of phosphorus and fluorine compounds continues to pose exciting and challenging problems to the chemical community[1]. Phosphorus with its expandable valence shell can incorporate electrons from heteroatoms and form a variety of ring, chain and ionic compounds. Fluorine with its small size and highest electronegativity enforces the maximum oxidation state and coordination number for the element with which it combines. This in turn leads to several ionic complexes involving fluorine. Thus, phosphorus-fluorine compounds undergo a variety of reactions — such as oxidation, substitution and adduct formation. The P–F bond is stronger than P-Cl bond as is evident from the ease of hydrolysis of PCl_3 when compared to PF_3.

From the reported reactions one can gauge the versatility of phosphorus atom to form several types of linkages[2]. Phosphorus in phosphorus trifluoride can thus undergo oxidation or substituion or adduct formation It was of interest to study this with respect to· a) well-known oxidising eagents which had different elements for coordination or substitution, namely, sulphur trioxide, leum, iodine monochloride, nitryl chloride, sodium nitrite, potassium nitrate, iodic acid and periodic icid; b) The room temperature cleavage studies of some stable complex fluorides with sulphur rioxide Another study is that an elegant synthetic procedure has been evolved for the com- ounds, $C_5H_5NHVF_6$ $(C_5H_5NH)_3CrF_6$, $(C_5H_5NH)_3FeF_6$ and $(C_5H_5NH)_4$ CoF_6, based on the reacti- ity of pyridinium poly (hydrogen fluoride)[3].

. Experimental, results and discussion

1 *Oxidation studies of phosphorus trichloride/thiophosphoryl chloride*

with sulphur trioxide/oleum

iown amounts of phosphorus trifluoride and sulphur trioxide $PF_3 \cdot \begin{matrix} \text{(Moles)} & (4\ 068) \\ \text{(mg)} & (358\ 0) \end{matrix}$; SO_3: $\begin{matrix} 068) & \text{(Moles)} \\ 25\ 4) & \text{(mg)} \end{matrix}$ were condensed (liquid N_2 coolant) into a glass reaction vessel fitted with icuum stopcocks and G G. joints. The contents were allowed to attain room temperature (25°C) er a period of 10 minutes. The infrared spectrum of a sample of the gaseous products was corded on a Perkin Elmer-599 spectrophotometer. The spectrum indicated the presence of $)F_3$ and SO_2 and also the absence of PF_3, indicating completion of reaction in ten minutes. Ana- sis of sulphur dioxide formed (calc. 4.069 moles, obtd: 4.048 moles) indicates a percentage idation of PF_3 as 99 50%. In a similar manner, oleum (1.12 ml) was treated with PF_3 [4.434 oles (384–3 mg)]. The reaction was sluggish at room temperature. However, on warming to 0°C for 30 min, the reaction proceeded to completion giving rise to 4.421 moles or 283 0 mg lphur dioxide. This amounts to an yield of 99.71%. The overall reaction mode can be repre- nted as

$$PF_3 + SO_3/\text{oleum} \xrightarrow[100°C]{rt} POF_3 + SO_2.$$

the case of thiophosphoryl fluoride, the products were elemental sulphur, phosphoryl fluoride d sulphur dioxide. The precipitated sulphur undergoes further reaction with excess sulphur tri- de to form sulphur dioxide The reaction in each case goes to completion, the overall mode ng.

$$2PSF_3 + 2SO_3 \rightarrow 2\ SO_2 + 2S + 2\ POF_3$$

$$S + 2\ SO_3 \rightarrow 3\ SO_2.$$

Oxidation with iodine monochloride (ICl)

:ess ICl, 4 615 moles (750.0 mg) was taken in a reaction vessel, frozen with a liquid N_2 lant, uncondensable gases pumped away and a known amount of PF_3 [1 852 moles 3.0 mg)] was condensed over it and the contents thawed to room temperature (over a period ialf an hour). Violet crystals of iodine were deposited on the walls of the reaction vessel The duct gas was analysed by IR spectroscopy Phosphorus trifluoride undergoes complete oxidation by this interhalogen compound iodine monochloride to form PF_3Cl_2 with a concomitant amount of iodine thrown out The overall reaction could be represented as .

$$PF_3 + 2\ ICl \rightarrow PF_3Cl_2 + I_2$$

Reaction conducted in a similar fashion with thiophosphoryl chloride and iodine monochloride resulted in the formation of quantitative amounts of iodine in terms of the equation·

$$PSF_3 + 2\ ICl \rightarrow PF_3Cl_2 + S + I_2$$

The sulphur formed reacts further with the oxidant to form sulphur monochloride resulting in an overall reaction of

$$2\ PSF_3 + 6\ ICl \rightarrow 2PF_3Cl_2 + S_2Cl_2 + 3\ I_2$$

c) *Oxidation studies with nitryl chloride*

1 793 moles of PF_3 are condensed over 2 654 moles of nitryl chloride and thawed to room temperature At the end of 2 hours, phosphorus trifluoride is oxidised to phosphoryl fluoride and nitrosyl chloride is formed, according to the equation

$$PF_3 + NO_2Cl \rightarrow POF_3 + NOCl$$

It is interesting to note that the reaction of PSF_3 with NO_2Cl, does not take place at room temperature or below 100°C though thermodynamically it is a favoured reaction ($\Delta G° = -41$ K Cal, mol^{-1}) It does not occur perhaps due to a high energy of activation needed for the reaction.

The results of these investigations highlight the pathway of oxidation of PF_3/PSF_3 with three different oxidising reagents, SO_3, ICl, NO_2Cl and indicate the high stability of the P–F bond and the easy formation of the P = O bond resulting in the formation of phosphoryl fluoride and no other P–F compounds

2 2 *Reaction of some stable complex fluorides with sulphur trioxide*

Known weights of hexafluorophosphates ($NaPF_6$, KPF_6 and NH_4PF_6), when treated with sulphur trioxide, undergo abstraction of metal fluoride and release the parent Lewis acid, phosphorus pentafluoride according to the equation

$$MPF_6 + SO_3 \rightarrow \underset{\displaystyle M\,SO_3F}{\underset{\downarrow}{(MF + SO_3)}} + PF_5$$

$(M = Na,\ K,\ or\ NH_4)$

The salt, MSO_3F, has been identified by X-ray powder diffraction data and ^{19}F NMR signal and the gas, PF_5, by IR spectral analysis A similar type of cleavage is noted with the pyridinium salts of hexafluorophosphates, tetrafluoroborates and hexafluoro silicates on reaction with sulphur trioxide The abstracted pyridinium fluoride gets complexed with SO_3, to form pyridinium fluorosulphate. The released Lewis acid gases, PF_5, BF_3, and SiF_4 have been isolated and characterised by infrared spectral analysis The overall reaction can be represented as:

$$C_5H_5\ NHPF_6 + SO_3 \rightarrow C_5H_5\ NHSO_3F + PF_5$$

$$C_5H_5\ NHBF_4 + SO_3 \rightarrow C_5H_5\ NHSO_3F + BF_3$$

$$(C_5H_5NH)_2\ SiF_6 + SO_3 \rightarrow 2C_5H_5NHSO_3F + SiF_4\,.$$

The importance of these reactions has been the release of the Lewis acid gases at room temperature and stabilization of the unstable pyridinium fluoride as pyridinium fluorosulphate

2.3. The next investigation has established that the versatile fluorinating reagent, pyridinium poly (hydrogen fluoride), can be elegantly employed for the synthesis of transition metal fluorides This one step procedure at room temperature has several advantages over the presently reported methods which need high temperatures, or report low yields, or need further work-up procedures to obtain pure salts Another advantage of this method is that the oxidation state of the metal is retained and the attached chlorine or oxygen gets displaced completely by fluorine. For example, pyridinium hexafluroroyanadate ($C_5H_5NHVF_6$) is prepared by reacting vanadium (V) oxide (5.23 g) in portions with 50 ml of pyridinium poly (hydrogen fluoride), PPHF, at room temperature in a polythene vessel under a cover of nitrogen After 1 h, 100 ml portions of chloroform are added which dissolve away the displaced pyridine and the white solid that separates out is filtered, washed with chloroform and dried. Analysis and spectral data identify it as $C_5H_5NHVF_6$ Similarly, the salts $(C_5H_5NH)_3$ CoF_6, $(C_5H_5NH)_3$ FeF_6, and $(C_5H_5NH)_4$ CoF_6 have been prepared in yields varying around 80–90% All the salts have been characterised by IR spectral analysis, ^{19}F NMR spectrum and chemical analysis. The salts have been found to be very pure

2.4 The supplementary chapter has the results of the investigations of the reactions of PF_3 with iodic and periodic acid. The highlight of this work is that no iodination occurs and it is noted that they function only as oxygenating salts based on the formation of phosphoryl fluoride as the product of reaction.

The next part enumerates the studies of the bifunctional (oxidant and reductant) compounds, sodium nitrite and potassium nitrite with phosphorus trifluoride This reaction occurs only at elevated temperatures (100–200°C). The nitrites function as oxidating species and the product is phosphoryl fluoride which further reacts to form metal fluorophosphate. The nitrite undergoes reduction to nitric oxide. The overall reaction would be represented as

$$2PF_3 + 4MNO_2 \rightarrow 2MF + 4NO + M_2PO_3F + POF_3.$$

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