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IISc. THESES ABSTRACTS

Thesis Abstract (Ph.D.)

Studies in opium alkaloids: (i) Synthetic utility of amine quaternization (ii) Microbial transformations of morphine by Samuel T. Manoharan.

Research supervisor: K.M. Madyastha.
Department: Bio-organic Section, Organic Chemistry.

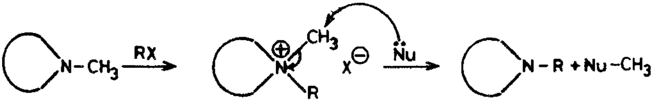
Introduction

A large number of compounds have been prepared by structural modifications of opium alkaloids. One of the common modifications has been the replacement of the N-methyl group of these alkaloids with various other alkyl groups. The methods reported in literature for effecting this change have involved the N-demethylation followed by realkylation by desired alkyl groups[1,2]. However, the conditions employed for demethylation are in many instances rather stringent resulting in low yields and some of the reagents used are either toxic or expensive, placing a limitation on their utility.

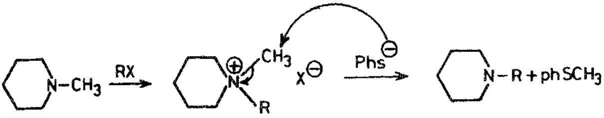
We have developed a simple method for the replacement of the tertiary N-methyl by other alkyl groups in two simple steps: (i) quaternization of the tertiary N-methyl compound with appropriate alkyl halide and (ii) preferential removal of the methyl group by a nucleophile (Scheme 1)[3,4] Thiophenoxide, which has been shown to remove methyl group preferentially[5] seemed suitable for our purpose.

This simple method has been initially applied for the replacement of N-methyl of 1-methylpiperidine, 4-methylmorpholine, 2-methyl-1,2,3,4-tetrahydroisoquinoline and tropine by *n*-propyl, *n*-butyl and isopropyl groups, in high yields[3,4] (Scheme 2). It has been established that demethylation is strongly favoured over the removal of *n*-propyl, and *n*-butyl groups, whereas deisopropylation occurs to some extent. Surprisingly, in the case of tropine, the quaternary salt prepared by treating it with isopropyliodide, upon reacting with thiophenoxide resulted in the predominance of deisopropylation.

This simple method for the replacement of tertiary N-methyl by other alkyl groups has been applied to morphine, codeine and thebaine. The replacement of N-methyl of morphine by *n*-propyl and *n*-butyl groups that of codeine and thebaine by *n*-propyl, *n*-butyl and isopropyl groups has been achieved in good yields[3,4]. N-3-Hydroxypropyl northebaine has also been prepared. The rapid



Scheme-1



1. $R = -CH_2-CH_2-CH_3 ; X = Br$
2. $R = -CH_2-CH_2-CH_2-CH_3 ; X = I$
3. $R = -CH_2-CH_2-CH_3$
4. $R = -CH_2-CH_2-CH_2-CH_3$

Scheme-2

quaternization of thebaine has been assigned to the absence of H-14 in this alkaloid. The fact that the quaternary salts of thebaine, which are susceptible to aromatization of the nucleus by extrusion of the ethanamine chain, are smoothly demethylated to N-alkylnorthebaines in good yields indicates that demethylation, a bimolecular nucleophilic displacement, competes very successfully with elimination reaction.

Thebaine reacts with excess epichlorohydrin in refluxing chloroform to give the 2,3-epoxypropyl ether of thebaol[6]. The same product is also obtained when the quaternary salt from thebaine and propyliodide is treated in the same way. This seems to be the first case where an ether of thebaol is formed through action of an alkyl halide upon thebaine. This reaction is quite analogous to the reaction of thebaine with acid chlorides or anhydrides producing esters of thebaol. A possible mechanism has been proposed. Benzenethiolate anion, being a nucleophile can open up epoxide ring and replace easily leaving groups like halides. Deallylation of the quaternary salts competes well over demethylation with sodium benzenethiolate. Quaternization of narcotine with 1-iodopropane followed by reaction with sodiumbenzenethiolate, yielded mono and bis o-demethylated derivatives of N-propylnornarceine.

Stereoselectivity in quaternization of thebaine

The high resolution PMR (270 MHz) studies in detail on the quaternization of thebaine with *n*-propyl iodide and the comparatively bulkier isopropyl iodide have revealed that the major diastereomer is formed to the extent of ~ 75% of the mixture by axial attack of the alkyl halide. The stereoselectivity in quaternization has been further proved by the technique of reverse quaternization. The diastereomers have been separated by column chromatography and fully characterized.

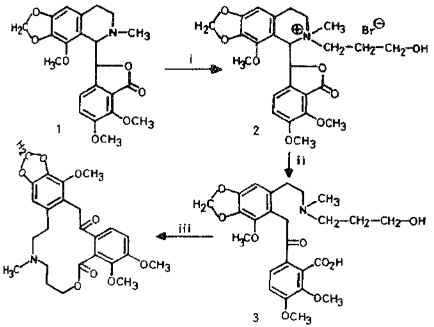
Conversion of narcotine into a macrolide

Narcotine which belongs to phthalideisoquinoline group is invariably obtained as a by-product when opium is processed for large-scale isolation of morphine. The conversion of alkaloid, narcotine into a 14-membered macrolide (Scheme 3) has been accomplished for the first time[7]. This has been achieved by a simple three-step process using cheap reagents. Narcotine was quaternized with 3-bromopropanol; the resulting quarternary salt was treated with aq. potassium hydroxide to give N-(3-hydroxypropyl) nornarceine which on lactonization with TsCl and TEA (triethylamine) in chloroform, yielded the 14-membered macrolide. It is quite possible that this compound may be biologically more active than the parent compound.

The reaction of cyanuric chloride with TEA has been utilized to convert TEA into diethylamine for the first time.

Microbial transformations of morphine

A gram-positive bacterial strain isolated from soil utilizes morphine as the sole source of carbon and



Scheme 3: (i) Br-CH$_2$-CH$_2$-CH$_2$-OH; (ii) aq. KOH; (iii) TsCl and TEA.

energy. Fermentation of morphine by this strain resulted in the formation of codeine, 14-hydroxymorphinone, 9,14-dihydroxymorphine N-oxide and a conjugate of 14-hydroxydihydromorphinone. The 9,14-dihydroxymorphine N-oxide is a new metabolite of morphine hitherto unknown. The finding of 14-hydroxylation of morphine during bacterial transformations parallels results previously obtained with fungal systems. One of the peculiarities of the bacterial system is its ability to carry out N-oxidation in a stereospecific manner producing only one diastereomer contrary to what has been observed in the case of higher plant systems.

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Thesis Abstract (Ph.D.)

Contributions to the chemistry of the complex fluorides of phosphorus, boron, silicon and titanium by K. Syed Mohamed.

Research supervisors: D.K. Padma and A.R. Vasudeva Murthy.
Department: Fluorine Laboratories, Inorganic and Physical Chemistry.

Introduction

The thesis deals with the contributions made to the chemistry of the complex fluorides of phosphorus, boron, silicon and titanium.

Complex fluoro salts exhibit interesting chemistry and are widely studied for their fundamental chemistry and have found several industrial applications. The structural features of these compounds pose challenging problems. For such studies highly pure salts are essential. The methods of preparation so far reported have limitations, such as, tedious procedures and low yields of pure products. The procedure, evolved and standardized in the present investigation is convenient, one pot reaction and occurs at room temperature. The salts are isolated in good yields and high purity. The salts have been characterized by elemental analysis, infra-red, NMR spectroscopy and X-ray powder diffraction. In addition, a few physico-chemical investigations such as thermal decomposition and flame-retardant studies have been made.

Procedure

The general procedure consists of treating the appropriate compound $PCl_5/B_2O_3/SiCl_4/TiCl_4$ with pyridinium poly (hydrogen fluoride) directly or in the presence of a solvent (ether) under stirring at room temperature. Extracting out the liberated pyridine with chloroform and concentrating the other phase when crystals of the desired pyridinium compound (PyH^+PF_6, PyH^+BF_4, $(PyH^+)_2SiF_6$, $(PyH^+)_2TiF_6^-$) are thrown out. The compounds are filtered, washed and dried in a vacuum dessicator. Mpt, chemical analysis and physical studies are done. Table I reports the physicochemical data on pyridinium hexafluorophosphate. Such data have been obtained for PF_6^-, BF_6^-, $SiF_6^=$ and $TiF_6^=$ (IV) salts also.

Thermal decomposition of hydrazinium hexafluorophosphate

Hydrazinium hexafluorophosphate has been prepared for the first time. This simple method of treating pyridinium hexafluorophosphate with hydrazine hydrate gives rise to the salt of high purity as indicated by chemical analysis and infrared spectroscopy. The thermal decomposition of this compound has been studied using thermal analytical techniques (DTA and TG).

The DTA shows an endotherm at 111° C which corresponds to the melting point of the compound and an exotherm at 248° C followed by a large endotherm with the peak temperature at 342° C. The sharp exotherm at 248° C is attributed to the decomposition of $N_2H_5PF_6$ to the corresponding ammonium salt which decomposes immediately to ammonia, hydrogen fluoride and phosphorus pentafluoride which is shown by the large endotherm. The mode of decomposition could be represented as:

Table I
Physico-chemical data on pyridinium hexafluorophosphate

Compound	**Reagents**	**Medium**	**Yield**	**Mpt**	**Estimation**	
$PyH^+PF_6^-$	PPHF and $PCl_5/POCl_5$	PPHF	90%	170-175°C 208°C (dec)	PF_6^- Cal./found 64.44/63.88	Pyridine Cal./found 35.11/34.93

IR

$$\underbrace{\text{3330 vs}\quad\text{3210 s}\quad\text{3150 s}\quad\text{3120 s}}_{\nu(\text{N-H}) \text{ and } \nu\text{ (C-H) vibrations}}\qquad\underbrace{\text{1640 s}\quad\text{1610 vs}\quad\text{1540 vs}\quad\text{1490 vs}}_{\text{ring vibrations}}\qquad\underbrace{\text{1335 m}\quad\text{1252 m}\quad\text{1208 m}\quad\text{1175 m}\quad\text{1056 m}\quad\text{1002 m}}_{\text{inplane hydrogen deformation vibrations}}$$

830 vs 730 s 670 s

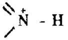
ν_3 (F_{1u} ν_{P-F} ring vibrations

558 s

ν_4 (F_{1u}) δ_{P-F}

s = strong; vs = very strong

^{1}H NMR*

Pyridine	Pyridine salt	
8.0 δ	8.45 δ	13.15 δ

^{19}F NMR: Solvent CH_3CN ($CFCl_3$ Internal Standard)
doublet (equal intensity)
PF_6^- 71.6 ppm upfield w.r.t. $CFCl_3$
Coupling constant J_{P-F} 702 Hz.

^{13}C NMR * Chemical shifts (ppm)

		α	β	γ
Pyridine	Obs.	149.7	123.94	136.14
	Reported	150.2	123.9	135.95
$C_5H_5N^+H$ (Cation)		142.45	128.95	148.35
$C_5H_5N^+$ HPF_6^- (Salt)		141.97	127.25	146.43

* Solvent, DMSO-d_6; TMS Internal Standard

$$3N_2H_5PF_6 \xrightarrow{248^\circ C} 3NH_4PF_6 + NH_3 + N_2$$

$$NH_4PF_6 \xrightarrow{342^\circ C} NH_3 + HF + PF_5.$$

Flame retardant characteristics of ammonium hexafluorophosphate on cellulose

Phosphorus-containing compounds are the most widely used flame retardants for cellulosic materials, especially ammonium phosphates: $NH_4H_2PO_4$, $(NH_4)_2HPO_4$. The presence of nitrogen in the ammonium salts is believed to involve the formation of heat stable P-N bonds during combustion which facilitates phosphorylation. It was of interest to see if NH_4PF_6 would also be an effective retardant. The dried strips of cellulose were subjected to pyrolysis experiments in air, making use of simultaneous DTA/TG/DTG analyses. The rate of heating was maintained at 20°C/minute and the experiments were carried out in the range 25°-650°C. The untreated cellulose was also subjected to pyrolysis under the same conditions.

The untreated cellulose decomposes in air exhibiting two exothermic peaks at 370°C and 528°C. The peak 370°C is assigned to oxidative degradation of cellulose and the second at 528°C to the flameless glowing of char. The NH_4PF_6-treated cellulose decomposes at lower temperatures. The first occurs at 335°C (2% NH_4PF_6), 325°C and 320°C (5 and 10% NH_4PF_6) and can be attributed to the sensitization by the flame-retardant additive, favouring the dehydration pathway of cellulose pyrolysis, thus resulting in increased char formation. The char then undergoes flameless combustion with increase in temperature as shown by continuous weight loss in the TG curve. This is similar to that shown by $NH_4H_2PO_4$, a well-known flame retardant thus indicating that NH_4PF_6 is equally efficient for similar weights of retardant. However, it should be pointed that NH_4PF_6 contains 19.01% phosphorus while MHP contains 26.95% phosphorus indicative of a better performance by NH_4PF_6. This is attributed to the presence of fluoride which may have the synergistic effect on phosphorus on its flame retardant ability.

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Thesis Abstract (Ph.D.)

Structural, kinetic and mechanistic aspects of the carboxylic ionophore-mediated transmembrane cation transport by B.P. Shastri.
Research supervisor: K.R.K. Easwaran.
Department: Molecular Biophysics Unit.

Introduction

One of the mechanisms by which cations are transported across membranes is the carrier mechanism in which the carrier ionophore complexes with the cation at one membrane interface to form a lipid-soluble complex which then diffuses through the hydrophobic core of the membrane interior, releases the cation at the other interface and travels back[1,2]. However, the chemical structures of the carrier ionophores being wide and varied, the cation binding selectivities, the rates of complexation/decomplexation and diffusion would vary from one carrier ionophore to another. Such details have not yet been worked out for the carboxylic ionophores. The structural, kinetic and mechanistic aspects of the carboxylic ionophore (in particular, lasalocid and A23187)-mediated transmembrane cation transport have been discussed here.

Experimental

Lasalocid, A23187, L-α-dimyristoylphosphotidylcholine (DMPC) and L-α-dipalmitoylphosphotidylcholine (DPPC) were obtained from Sigma Chemical Co., and the deuterated solvents (D_2O, CD_3CN and CD_3OD) were from Stohler Isotopes. All the perchlorate salts and lanthanide oxides were from Alfa Inorganics. The overall conformational changes of the ionophore lasalocid on complexation with cations have been followed by circular dichroism (CD) and the titration data have been used to determine the stoichiometries and stability constants of the complexes[3,4]. In the case of lanthanides, fluorescence studies have also been performed to determine the stoichiometries of the complexes in methanol. The changes in the chemical shifts and coupling constants observed in ^1H and ^{13}C NMR experiments of the lasalocid-cation complexation have been used to arrive at the final conformations of the complexes. The interaction of carrier ionophores with DMPC and DPPC liposomes has been studied by differential scanning calorimetry (DSC), ^1H and ^{31}P NMR methods. The transport kinetics of three lanthanide ions (*viz.*, Pr^{3+}, Nd^{3+} and Eu^{3+}) mediated by A23187 and the sodium salt of lasalocid across DMPC and DPPC vesicles has been studied by ^1H NMR.

Results and discussion

The interaction of three alkali metal (Li^+, Na^+ and K^+) chlorides and perchlorates with lasalocid in methanol and acetonitrile have been studied by CD, ^1H and ^{13}C NMR techniques. It has been found that while $LiClO_4$ forms complexes of both 1:1 and 2:1 (ionophore-cation) stoichiometries with lasalocid in acetonitrile of appreciable stability, the other two cations form only equimolar 1:1 complexes. The coordination to the cation is mainly provided by the oxygens of the carbonyl, the tetrahydrofuran, the tetrahydropyran and the two hydroxyl groups of the ionophore whereas the salicylic acid part of the molecule does not seem to participate in coordination[5]. The conformations of lasalocid-$LiClO_4$ complexes in acetonitrile are significantly different from those in methanol, whereas there seem to be no differences between the conformations of sodium and potassium complexes of lasalocid in methanol and acetonitrile. In acetonitrile, there are certain differences in the conformations of lasalocid−$LiClO_4$ and lasalocid−LiCl complexes manifested in their ^1H NMR spectra indicating that the counter-ion (*i.e.* the anion) might also play a role in the conformations of lasalocid-cation complexes).

From the results of CD, ^1H and ^{13}C NMR studies on the interaction of alkaline earth cations (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) with lasalocid in methanol and acetonitrile it has been found that in acetonitrile, while the perchlorates of Mg^{2+} and Ca^{2+} form complexes of both 1 : 1 and 2 : 1 stoichiometries, the other two perchlorates (Sr^{2+} and Ba^{2+}) form predominantly equimolar complexes. Once again, the conformations of lasalocid-$CaClO_4$ complexes are distinctly different from the other three cation complexes in acetonitrile and different from the lasalocid-$CaClO_4$ complex in methanol. The observed differences in the stoichiometries and the conformations of lasalocid-alkaline earth cation complexes can be attributed to the differences in the size of the cation, the counter-ion and the solvent polarity.

The results of the CD and fluorescence studies on the interaction of the lanthanide ions with lasalocid in methanol and acetonitrile have shown that they form both 1 : 1 and 2 : 1 complexes in the two solvents, the complexes being more stable in acetonitrile than in methanol. It has been found from the CD data analyses that while the larger lanthanide ions prefer to form equimolar complexes, the smaller ions favour the formation of non-equimolar 2 : 1 complexes and this feature is also reflected in their stability constants. From the fluorescence studies in methanol, it had been possible to deduce that in the 2 : 1 complexes the salicylic acid part of the molecule does not participate in coordination to the cation.

The interaction of four carrier ionophores (*viz.*, valinomycin, nonactin, A23187 and lasalocid) with DMPC and DPPC liposomes (both unilamellar and multilamellar vesicles) have been investigated by DSC, ^1H and ^{31}P NMR techniques. The DSC studies have indicated the interaction of the carrier ionophores with polar head groups of the lipids alone. From the ^1H NMR line width measurements, it is deduced that all the ionophores under consideration penetrate the hydrophobic core of the vesicles in both DMPC and DPPC systems with the exception of valinomycin in DPPC vesicles where it possibly adsorbs on the membrane surface[6]. The ^{31}P NMR studies on the DMPC and DPPC multilamellar vesicles incorporated with the ionophores indicated the formation of 'lipidic particles' in the case of nonactin, A23187 and lasalocid whereas valinomycin reduced the observed chemical shift anisotropy parameter ($\Delta\sigma$) indicating the interaction with the lipid head groups. The observation of lipidic particles in the case of nonactin, A23187 and lasalocid is possibly due to their relatively flexible chemical structures which allow their functional groups to interact with the phospholipid head groups.

The transport kinetic data of lasalocid and A23187-mediated translocation of lanthanide ions across DMPC and DPPC vesicles have been analyzed to obtain the rate constants and the stoichiometry of the transporting species[7,8]. It has been found that in the case of both A23187 and lasalocid it is the non-equimolar 2 : 1 complex that is responsible for the transport of lanthanide ions across the membrane in accordance with the earlier complexation and transport sequence studies with divalent cations[9]. It has also been found that the 'presence' or 'absence' of intravesicular isomorphous La^{3+} ions has a profound effect on the observed rate constants.

Conclusions

The following salient features have evolved as a result of these investigations: (1) The observation of non-equimolar complexes for the carrier ionophore-cation complexes can now be considered to be a rule rather than an exception. (2) Unlike the conformations of the neutral carrier ionophore-cation complexes (*e.g.*, valinomycin-K^+ complex), the conformations of the carboxylic ionophore-cation complexes are governed by various factors like the size, charge and coordination number of the cation, the counter-ion, the solvent polarity and the state of the ionizable carboxyl group, (3). The stoichiometry of the transporting species for the carboxylic ionophore-mediated transmembrane cation transport has been established to be the 2 : 1 non-equimolar complex. (4) From the results of the solution studies on the lasalocid–cation complexes and the ionophore-phosholipid liposome interaction studies, a plausible mechanism by which the carboxylic ionophores induce the transmembrane cation transport can be proposed. First of all, the cation binds to the ionized carboxyl group of the ionophore. Then, it is handed over to the rest of the molecule which is buried in the membrane where the cation is completely encapsulated by the ionophore to form a lipid soluble 2:1 complex. The complex then diffuses through the membrane interior and releases the cation at the other end.

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Thesis Abstract (Ph.D.)

Ecology of the Asian elephant (*Elephas maximus*) and its interaction with man in South India by R. Sukumar.

Research supervisor: Madhav Gadgil.

Departments: Microbiology and Cell Biology Laboratory and Centre for Ecological Sciences.

The Asian elephant which once roamed over a substantial portion of the Indian sub-continent is now reduced to a number of discrete populations totalling 17,000-20,000 individuals[1]. Of these, about 6,000-7,000 elephants occur in two major populations in South India. Inevitably, elephant and man have been in constant conflict with the elephant destroying man's crops and occasionally killing him, while man has considerably reduced and modified the elephant's habitat and also captured them for domestication or hunted the males for ivory.

In the present study, the process of elephant-man conflict is viewed within the overall life-history strategy of the elephant under natural conditions. In particular, the strategy of seasonal movement and feeding in the natural habitat is correlated with the crop raiding pattern.

Field work was carried out between June 1980 and July 1983. The study area comprised 1130 km^2 of forest in the Chamarajanagar and Satyamangalam Forest Divisions at altitudes from 250 to 1800 m above msl. About 16,000 people inhabit the 70 km^2 area of cultivated enclaves within the forest. There exists a mosaic of vegetation types including thorn forest (250-400 m), deciduous forest (400-1500 m) and evergreen shola-grassland (1500-1800 m). Based on topography, location and floristics, the area was divided into 19 zones, each representing a fairly homogeneous habitat type. Annual rainfall varies from 60 to 200 cm along an altitudinal gradient. Three broad seasons were defined, a dry period (Jan-Apr), first wet season (May-Aug) and second wet season (Sep-Dec).

The number of elephants in an area of 928 km^2 was estimated by various methods including a registration of identified individuals, density in different zones by ground transects and a total count organized by the forest department. The average number was between 475 and 500 elephants, giving a crude density of just over 0.5 elephant/km^2. Mean group size was higher during Jan-Apr (8.2) and Sep-Dec (8.8) compared to May-Aug (5.8). This was due to a dispersal from the high density dry season range into a wider area after the first rains and a regrouping after heavy rains to move into lower elevation zones.

An identification file was built on family units and lone bulls. Elephants were aged by determining their shoulder heights by a photographic method and relating these to a mean age-height growth curve[2]. Age structures for 1981, 1982 and 1983 were constructed. Adult (> 15 years) males formed 7% while adult females formed 36% of the total population. In females the mean age of first calving was about 17 years and reproduction continued until 60 years. Mean calving interval calculated from the age difference between the last two calves of a female and also from the proportion of mature females giving birth in a year was 4.7 years. Post-mortem reports of 396 elephants from the States of Karnataka and Tamilnadu during 1975-1983 were used to determine mortality rates and causes of death. Males showed a much higher mortality rate than females due to both natural causes and killing by man. The minimum annual mortality rate based on the numbers found dead in the study area during 1981-82 was 2% for females and 12% for males above 5 years.

A simulation of population trends by the Leslie matrix method was carried out[3]. Using the current age structure and fertility rate, the age-specific mortality rates of both sexes were varied. Even at very low mortality rates the rate of population growth was only 1.5% per annum. At current levels of mortality the growth rate was close to zero. However, a significant reduction in adult males could act as a negative feedback mechanism in reducing the rate of conception and hence recruitment into the population.

Elephant occupancy indices/densities were calculated for the various zones at two-month intervals. The overall movement patterns and strategy of habitat utilization are interpreted from the seasonal distribution. Minimum home range sizes for a few identified bulls and family units were determined. Home range areas for both bulls and family units with numerous resightings were approximately between 150 and 300 km^2. Based on dry season distribution about 5 different elephant 'clans' are thought to utilize the study area. These clans have overlapping home ranges.

Although the elephant is a generalist feeder, consuming over 100 plant species in the wild, over 80% of the diet consisted of under 25 species from four botanical taxa - the order Malvales and the families Leguminosae, Palmae and Poaceae. Feeding strategy may vary from one clan to another. In general, browse is important during the dry season (Jan-Apr) with the freshly growing tall grasses being preferred mainly during the first rainy season (May-Aug). When the tall grasses become relatively unpalatable during the second rains (Sep-Dec) elephants again switch over to a higher proportion of browse. Such a foraging strategy is clearly related to the changing crude protein content of grasses. By analyzing stable carbon isotopic ratios ($^{13}C/^{12}C$) in bone collagen the average proportion of C_3 plants (browse) and C_4 plants (grass) in the diet was found to be equal[4]. However, individual elephants showed preferences for either browse or grass, consuming up to 80% of one plant type.

Preliminary investigations on the carrying capacity of the habitat were undertaken[5,6]. Elephant damage to four tree species (*Acacia leucophloea, A. suma, Kydia calycina* and *Grewia tiliaefolia*) was quantified. Except for *A. suma* woodland, regeneration in other species can adequately replace dead and damaged trees. While the potential net primary production of grasses was adequate for the requirement of the elephant population, the major consumer of grass was domestic livestock. Domestic and wild mammalian herbivores together consumed between 6 and 50% of the net grass production in different zones during 1982, a year of less than half the normal rainfall.

Crop damage by elephants was investigated in 10 enclaves of cultivation within the forest and two villages adjoining the forest boundary. By far, the major crop eaten was finger millet or ragi (*Eleusine coracana*), while damage to jowar or cholam (*Sorghum vulgare*), maize (*Zea mays*), paddy (*Oryza sativa*), coconut, banana and sugarcane also occurred. Adult male elephants were more habitual raiders than family herds. Male-male association during raiding at night was significantly higher than the normal daytime association in the forest. The mean quantity of food eaten in crop fields by one elephant per day of raiding was 40 kg (dry weight) by adult males and 18 kg by family herds. Of their total annual food requirement, adult males derived about 9% and family units about 2% from cultivated land. This was over 20% of the diet for certain notorious raiding bulls.

Crop raiding, which was sporadic during the dry season, gradually increased with more area being cultivated with the onset of rains. Raiding frequency reached a peak during Oct-Dec when ragi millet was grown by most farmers. At this time some villages were visited by elephants almost every night. The monthly frequency of raiding by herds in the villages was clearly related to their seasonal movement pattern. Preference for cultivated crops can be explained by their higher palatability and nutritive value, especially protein, calcium and sodium, compared to the analogous wild plants. The economic loss to crops in the study villages was Rs. 189,600 in 1981, this amount being around 10% of the total potential yield. On the average an adult bull was responsible for a loss of Rs. 6720 and an elephant in family herds for Rs. 320 worth of crops.

Contact between elephant and man in cultivated land may result in aggressive interactions. Elephants kill over 30 people every year in South India. Of these, 44% occurred in cultivation and the rest in the forest. Manslaughter can be largely attributed to a few aggressive adult bulls.

Man also kills a substantial number of elephants in defence of crops (22% of female and 6% of male elephant deaths) or poaching for ivory (60% of male deaths). Over 100 male elephants were poached annually during 1980-83 in South India. With a mean tusk weight of 9.5 kg this contributed close to 2 tons of raw ivory to the the illegal trade which is significant considering the low imports of African ivory in recent years.

The elephant's habitat has also undergone considerable manipulation by man. Man's impact in terms of reduction in area due to agricultural expansion, shifting cultivation, timber and fuel wood extraction, competition for the elephant's food plants, livestock grazing, fires, raising of monoculture plantations and creation of water reservoirs are all discussed.

Recommendations for the conservation of the elephant population and protection of agricultural land from elephants have been made.

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Thesis Abstract (Ph.D.)

A study of residual electric strength of polypropylene film in short-term surface discharge ageing under sub-atmospheric conditions by H.P. Inamdar.

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Introduction

Apart from the phenomenon of direct flashover and dielectric breakdown at higher stresses, it has been recognized that in the presence of localized discharges within the insulation, the electric strength of solid insulation decreases with time[1]. These localized discharges which do not completely bridge the inter-electrode insulation are called partial discharges[2,3]. The energy of individual partial discharges is quite small and the discharges do not cause an immediate failure of the insulation system. Continued exposure of the insulation to these discharges, however, leads to a progressive deterioration and ultimately to a complete electrical breakdown of the system.

Experimental programme

The present work is related to polypropylene film insulation used in capacitors. Capacitors contain air inclusions between the layers of the film with a range of sizes, because of variation in tightness of windings and occluded air bubbles trapped within the windings. The air inclusions in the capacitor insulation system can be at different sub-atmospheric pressures. The experiments conducted consisted of (1) short-term ageing of polypropylene film with a pre-determined initial maximum discharge magnitude, (2) micro-photographs of the surface affected by the discharges and (3) measurement of dielectric strength over the aged area.

Main results and conclusions

Observations on discharge inception and extinction voltage in a typical air gap of 0.5 mm between metal and polypropylene film at various pressures between 10 and 685 torr are presented in this work. By using discharge breakdown criteria in gases, an empirical equation for inception voltage has been developed. A procedure to determine critical 'pressure x air spacing' (P.t') from this equation is also described to give minimum inception voltage. It is later established that the observed values closely agree with the values calculated from the proposed equation.

Ageing tests (duration 3 to 15 hours) have been carried out for a typical air spacing of 0.5 mm at pressures of 685, 252 and 13 torr at average stress of about 50 V/μm (equal to the design stress in polypropylene film capacitors) under various values of pre-determined initial maximum discharge magnitudes. Important partial discharge quantities, such as inception and extinction voltage, number of pulses per second, maximum discharge magnitude have been recoded at pre-determined intervals of time during ageing. Total and average discharge magnitude and pulse distribution are obtained from this data. Exponential and linear regression methods are attempted for determining relationship between the various discharge quantities and the ageing time.

Every aged specimen has been found to have a very uniform surface discharge ageing. Short-time electric strength of the aged area is determined by measuring breakdown voltage at twenty sites, using a rod-plane electrode system in an oil-cell. Statistical representative value (median, mean and scale parameter from Weibull distribution) of these observations gives Residual Electric Strength (RES), Relative Residual Electric Strength (RRES) is obtained by expressing RES as a ratio of strength of fresh specimen. The RRES values for specimens aged under the same initial maximum discharge magnitude (q_m) for various durations (ageing time) are plotted to give RRES-t characteristic representing rate and relative amount of degradation of the specimens. By extrapolation of these RRES-t characteristic, an extrapolated life-time under that discharge ageing condition is obtained. These values are further used to provide an empirical relationship between life and q_m. It has been concluded that the electric strength of the film reduces systematically in comparison to its original value, the reduction being dependent on the initial maximum discharge magnitude, ageing time and pressure.

The microphotographs of the aged surface reveal the extent of progressive degradation of the polypropylene film surface due to surface discharges. The diameter of the pits increases with discharge magnitude, ageing time, voltage stress and amount of overvoltage (V_a / V_i). For specimens having largest diameter of pits, a significant reduction in residual electric strength is observed suggesting that a dependence exists between the dimensions of the pits and residual electric strength.

Some conclusions have been drawn from the studies reported in the thesis. These are as follows: The discharge inception voltage V_i between metal-polypropylene film can be calculated by using the relationship

$$V_i = \frac{BP}{ln\,(pt') + K}\,[t' + \frac{t}{\epsilon_r}]\,\text{Volts (peak)}$$

where $B = 365$ volts/torr-cm

$$K = [(pt')/M]^N$$

for $0.5 < pt' < 1.25$ torr-cm, $M = 0.9831$, $N = 0.2729$ and for $1.25 \leq pt' \leq 35$ torr-cm, $M = 1.5692$, $N = 0.2776$, P in torr-cm.

Out of the various mathematical models attempted for RRES-t characteristic such as modified ageing law by Dakin and Mamlow [*i.e.*, $l - p^{(B+1)} = (B+1)\,K.t$], Simoni's equation for voltage ageing [$l - g^{n+1} = g^n\,(t/t_{F_0})\,(n+1)$], exponential function [$t = ae^{b.p}$]; the representation by the exponential function seems to be the best fit. Further, a relationship between predicted life (L) and initial maximum discharge magnitude (q_m) has been found by using the equation $L = Aq_m^{\text{[illegible]}}$.

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