

IISc. THESES ABSTRACTS

Thesis Abstract (Ph.D.)

Synthesis, thermal rearrangement and silylation reactions of (alkoxy)-(aryloxy) cyclotriphosphazenes by S. Karthikeyan.

Research supervisors: S.S. Krishnamurthy and A.R. Vasudeva Murthy.

Department: Inorganic and Physical Chemistry.

The objective of the work is (i) to synthesize chloro-(aryloxy) and (alkoxy) (aryloxy) cyclotriphosphazenes and to unravel the mechanistic features involved in their formation, (ii) to investigate the effect of aryloxy substituents on the thermal rearrangement of (alkoxy) cyclophosphazenes and (iii) to study the silylation reaction of (alkoxy) (aryloxy) cyclotriphosphazenes with a view to prepare silyloxy-substituted cyclophosphazenes which would serve as model systems for incorporating phosphazene units into silicone polymers^{1,2}

Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) reacts with sodium *p*-cresoxide or sodium phenoxide in THF to give a series of chloro (aryloxy) cyclotriphosphazenes, $N_3P_3Cl_{6-n}(OAr)_n$ ($n = 1-6$; $Ar = C_6H_5$, $C_6H_4CH_3-p$). Products with different degrees of chlorine replacement (n) have been isolated by column chromatography. The isomeric compositions of the positional isomers have been determined from the 1H NMR spectra of the dimethylamino and alkoxy derivatives, $N_3P_3(OAr)_{6-n}(R)_n$ ($n = 1-5$; $R = NMe_2$, OMe , OEt , OCH_2CF_3 , OCH_2Ph ; $Ar = C_6H_5$, $C_6H_4CH_3-p$). The ^{31}P NMR spectra for the chloro precursors also yield valuable structural information. The chlorine replacement pattern is predominantly nongeminal and at the *bis* stage, the *cis* and *trans* isomers are formed in comparable amounts. A 'through-space' interaction involving $2p$ and $3d$ orbitals of the oxygen and phosphorus atoms respectively has been invoked to account for this result. Isomeric compositions observed at other stages of substitution can be explained on the basis of statistical considerations³.

Attempts to separate the geometrical isomers of chloro and dimethylamino (*p*-cresoxy) cyclotriphosphazenes have been unsuccessful; however, chromatographic techniques have been successfully employed for the isolation of geometrical isomers of the methoxy derivatives. All these compounds have been characterised by 1H , ^{13}C and ^{31}P NMR spectroscopy. The salient features of the spectroscopic data are discussed in detail.

Thermal rearrangement reactions of various (alkoxy) (*p*-cresoxy)-cyclotriphosphazenes, $N_3P_3(OR)_{6-n}(OC_6H_4CH_3-p)_n$ ($n = 1-6$; $R = Me$, Et , CH_2Ph) have been carried out. The mono (*p*-cresoxy) compound, $N_3P_3(OC_6H_4CH_3-p)(OMe)_5$ thermally rearranges to give an isomeric pair of oxocyclotriphosphazanes, $N_3Me_3P_3O_3(OC_6H_4CH_3-p)(OMe)_2$. In contrast, all other (alkoxy) (*p*-cresoxy) cyclotriphosphazenes undergo thermal rearrangement stereospecifically, resulting in the formation of a single oxocyclophosphazane. Thus *cis*- $N_3P_3(OC_6H_4CH_3-p)_2(OMe)_4$ rearranges to yield an oxocyclotriphosphazane, which is the geometrical isomer of the oxocyclotriphosphazane, $N_3Me_3P_3O_3(OC_6H_4CH_3-p)_2(OMe)_4$ obtained in the thermal rearrangement reaction of *trans*- $N_3P_3(OC_6H_4CH_3-p)_2(OMe)_4$. Similarly, the geometrical isomers of $N_3P_3(OC_6H_4CH_3-p)_3(OMe)_3$, $N_3P_3(OC_6H_4CH_3-p)_3(OEt)_3$, $N_3P_3(OC_6H_4CH_3-p)_3(OCH_2Ph)_3$ and $N_3P_3(OC_6H_4CH_3-p)_4(OMe)_2$ give the respective isomeric oxocyclo-

phosphazenes. An increase in the number of aryloxy group necessitates a corresponding increase in the rearrangement temperature (160 to 205°C). Also, an increase in the length of the alkyl chain requires an increase in the rearrangement temperature [$N_3P_3(OC_6H_4CH_3-p)_3(OMe)_3$ - 185°C; $N_3P_3(OC_6H_4CH_3-p)_3(OEt)_3$ - 285°C]. The 1H , ^{13}C and ^{31}P NMR spectroscopy have been used to monitor the course of these reactions and to characterize the products.

The crystal structure of the oxocyclotriphosphazene, $N_3Me_3P_3O_3(OC_6H_4CH_3-p)_3$, obtained from the thermal rearrangement of *trans*- $N_3P_3(OC_6H_4CH_3-p)_3(OMe)_3$ has been determined. The crystal is triclinic with the space group *PT*. The structure has been solved by direct methods (final R factor = 0.060). The *trans* geometry of the aryloxy groups in the starting material is retained in the product. The cyclotriphosphazene ring adopts a twist-boat conformation. The ring conformation and the molecular parameters are compared with the data available for other oxocyclotriphosphazenes. The crystallographic data provide a basis for interpreting the NMR spectroscopic data for $N_3Me_3P_3O_3(OC_6H_4CH_3-p)_3$ and other oxocyclophosphazenes obtained in the present study.

The reactions of (alkoxy) cyclophosphazenes with the chlorosilanes $ClSiMe_3$, Cl_2SiPh_2 and $ClSiPh_3$, require forcing conditions. But in the presence of anhydrous sodium iodide in methyl cyanide medium, these reactions proceed rapidly and almost quantitatively. However, the resultant siloxy products are extremely moisture sensitive; consequently hydrolysed products are invariably obtained. Even the introduction of bulky phenyl substituents on silicon and incorporation of the P-O-Si linkages in a polymeric chain do not improve the hydrolytic stability of the (siloxy)—phosphazenes. Although silylation has failed to yield hydrolytically stable (siloxy) cyclophosphazenes or phosphazene polymers, it affords a simple and versatile method for the controlled hydrolysis of (alkoxy) cyclophosphazenes. This method has thus proved useful for the synthesis of several (hydroxy) cyclophosphazenes which are otherwise difficult to obtain. All the (hydroxy) cyclotriphosphazenes exist in the oxophosphazadiene tautomeric form.

References

1. KRISHNAMURTHY, S.S., *Adv. Inorg. Radiochem.*, 1978, **21**, 41.
SAU, A.C. AND WOODS, M.
2. ALLCOCK, H.R. *Phosphorus-nitrogen compounds*, Academic Press, New York, 1972.
3. KARTHIKEYAN, S. AND KRISHNAMURTHY, S.S. *Z. Anorg. Allg. Chem.* 1984, **513**, 231.

Thesis Abstract (Ph.D.)

Ontogeny of muscarinic cholinergic and dopaminergic receptors in human foetal brains by B.V. Ravi Kumar.

Research supervisor: P.S. Sastry.

Department: Biochemistry.

Understanding the function of the brain especially the human brain is perhaps the most challenging task that confronts contemporary scientific endeavour. While a great deal is known about the structure and biochemistry of the brain as yet very little is known about the basis of its higher functions. Brain is unique among all organs in its ability to establish intercellular communication through its network of

synaptic connections and this property most likely is the key for higher mental functions and complex behaviour. It is now well established that the transmission of a nerve impulse across this synapse involves 'neurotransmitters' which in turn bind to specific molecules on the post-synaptic membranes, 'the receptors' and thus mediate intercellular communication. Thus the existence of a number of 'neurotransmitter receptors' in brain is now recognised and a wealth of information now available on their properties is constantly leading to closer understanding of the basis of brain function¹. It is reasonable to expect that during brain development temporal relationship exists between the ontogeny of specific synapses and acquisition of some behavioral traits. This in effect means an investigation of synaptogenesis in developing brain and correlating it with the appearance of sensory, motor and other functions. At the present time due to the availability of specific neurotransmitter agonists and antagonists which are radiolabelled, synaptogenesis can be best studied by following the ontogeny of specific neurotransmitter receptors. There is already some information available on the ontogeny of a few receptors in the brain of rats and other lower animal species². However, human brain with its higher level of function is a particularly important tissue which has not been studied adequately so far.

This investigation envisages a study of the ontogeny of muscarinic cholinergic and dopaminergic receptors in human brain, during foetal development and also as far as possible in postnatal life. With this objective a number of human foetal brains from medically-terminated pregnancies spanning the gestational period from 14 weeks till birth (40 weeks), a few postnatal and adult brains were collected as fresh as possible and stored at -70°C . It was established that storage at -70°C did not alter receptor characteristics.

The specific binding of [^3H]-quinuclidinyl benzilate, a muscarinic antagonist was monitored using a rapid filtration technique. The binding sites in human foetal brains were shown to be specific muscarinic receptors by their subcellular localization, saturability and by their pharmacology. In frontal cortex muscarinic receptors appear by 16th week and from then on they increase in number without any change in affinity. This increase shows a phase of slow formation between 16 and 20 weeks, a lag phase between 20 and 24 weeks and a phase of rapid receptor increase in the third trimester. Both NaCl and GTP reduced agonist affinity and for GTP, this effect was more pronounced at birth than at 16 weeks³.

In corpus striatum and brainstem there is a phase of slow formation between 16 and 24 weeks and a rapid increase in the third trimester. In cerebellum the receptors maintained a constant level throughout the foetal life. In all the regions the receptor concentration maintained well into paediatric life but showed a decrease with age⁴.

To study the ontogeny of the dopaminergic receptors [^3H]-spiroperidol binding was monitored. Under the conditions used for assay in foetal brains, [^3H]-spiroperidol binds to D_2 -type receptors. The results show that receptor numbers were unaltered during foetal life. But at 16, 20 and 24 weeks the binding data indicated a heterogeneity with two different receptors, one with high affinity and the other with low affinity. The high affinity receptor was D_2 type and persisted in later life. Low affinity receptors disappeared during the third trimester. D_2 receptor number increased postnatally. GTP decreased the agonist binding of D_2 receptors at all ages⁵.

From these studies, it is concluded that the ontogeny of muscarinic cholinergic and dopaminergic receptors show definite patterns of development which are specific for each case. The third trimester of pregnancy appears to be the most crucial for their ontogeny and there is evidence suggesting synapse elimination with respect to both receptors in adult life.

References

1. SNYDER, S.H. *Science*, 1984, **224**, 22.
2. MEISAMI, E. AND TIMIRAS, P.S. *Biochemical development of the foetus and neonate* (ed. Jones, C.T.) Elsevier Amsterdam, 1982, p. 759.
3. RAVI KUMAR, B.V. AND SASTRY, P.S. *J. Neurochem.*, 1985, **44**, 240.
4. RAVI KUMAR, B.V. AND SASTRY, P.S. *J. Neurochem.*, 1985, **45**, 1948.
5. RAVI KUMAR, B.V. AND SASTRY, P.S. International symposium on molecular aspects of neurobiology, Florence, Italy, June 9-12, 1985, Abstr. No. 9, p. 31.

Thesis Abstract (Ph.D.)

Further crystallographic studies on lysozyme by B. Veerapandian.

Research supervisor: M. Vijayan.

Department: Molecular Biophysics Unit.

Introduction

Lysozyme is perhaps the most thoroughly studied enzyme and the results of these studies are extensive. A substantial part of the result pertains to hen egg white (HEW) lysozyme. The tertiary structure of the protein and the geometrical basis of its activity in terms of the binding of NAG-NAM copolymer to the cleft of the molecule, were established through pioneering studies on the tetragonal form¹. Several other crystal forms of HEW lysozyme, one triclinic, another monoclinic and two orthorhombic, have also been subsequently examined. Other chicken-type lysozymes which have been studied crystallographically include those from humans, tortoise and turkey. Studies on chicken-type lysozymes have resulted in contributions not only to molecular enzymology but also to the understanding of the mobility and the hydration of proteins^{2,3}. Lysozymes from *streptomyces erythraeus*, bacteriophage T4 and goose egg white, which were studied by X-ray methods, are not homologous to chicken-type lysozyme. However, interesting structural and evolutionary relationships have been established among chicken-type, T4 and goose lysozymes⁴.

Interaction of lysozyme with BPR and BPB. Solution studies

The explanation of the lytic activity derived from X-ray results has been entirely based on the binding of the polysaccharide component of the peptidoglycan to the hexasaccharide cleft in the enzyme molecule. It is, however, known that the peptidoglycan is a better substrate of lysozyme than the NAG-NAM copolymer suggesting that the conventional explanation of lysozyme activity is perhaps inadequate. Recently it has been shown that the enzyme when bound to dyes such as bromophenol red (BPR) and bromophenol blue (BPB), is still active against the polysaccharide, but not against the bacterial cell wall^{5,6}. It was therefore of interest to characterize the binding site of these dyes in the enzyme by X-ray diffraction methods. Spectroscopic and inhibition studies were carried out as a prelude to the X-ray work. These studies were carried out at pH 4.6, the pH at which tetragonal lysozyme is crystallized. The studies showed that BPR exists predominantly in the neutral form at pH 4.6 whereas both the forms of BPB have substantial concentrations. Both the dyes bind to lysozyme at this pH without any appreciable change in their ionization state. They also inhibit competitively the lytic activity of the enzyme at pH 4.6.

Structure of the dyes

Attempts were made to crystallize BPR and BPB, but good crystals of the latter only could be obtained. X-ray structure analysis of these crystals was carried out⁷. The BPB molecules in the crystals exist in the closed neutral form. The molecule consists essentially of three planar groupings, namely, the sulfonphthalein ring system and two dibromophenol rings attached to the tetrahedral carbon atom of the five-membered ring of the sulfonphthalein system. The dibromophenol rings are inclined with respect to each other at 73° whereas they make angles of 85° and 68° with respect to the sulfonphthalein system. There is no steric or electronic reason why the structure of the closed form of BPR should be substantially different from that of BPB. Therefore, the X-ray analysis provides a description of the closed forms of both the molecules.

An X-ray study of the lysozyme-BPR complex. Characterization of an additional binding site

Attempts were made to prepare lysozyme-dye complexes by soaking tetragonal lysozyme crystals in BPR and BPB solutions. Reproducible positive results were obtained only in experiments involving BPR. The X-ray analysis at 5.5Å resolution of the lysozyme-BPR complex thus obtained was performed⁸. Data were collected diffractometrically from the native as well as the complex crystals. The native data and the phase angles kindly made available by Prof. D.C. Phillips were also made use of in the analysis. Several difference Fourier maps were computed. All of them contained a predominant common feature which could be explained in terms of the closed form of BPR with a geometry similar to that of BPB in its crystal structure. The residues in the immediate neighbourhood of the dye are Arg5, Lys33, Ala22, Trp123 and Arg125. Other neighbours include Phe34 and Phe38. The residues in the binding site are largely invariant or conserved. The composition of the binding site is consistent with the available results of the solution studies. The dye binding site, outside the cleft close to the subsite F, is presumably involved in interactions with the peptide component of the peptidoglycan in the action of lysozyme against bacterial cell wall.

Water-mediated transformations in lysozyme crystals

Hydration of lysozyme and the structural changes caused by it have received considerable attention. Such studies have so far been carried out in non-crystalline state. Work of this nature was carried out on single crystals of lysozyme^{9,10}. Different crystal forms of lysozyme were examined under controlled environmental humidity in the relative humidity (r.h.) range of 100 to 75%. Tetragonal, orthorhombic and monoclinic lysozyme undergo reversible structural transformation at r.h.'s around 90%, as evidenced by discontinuous changes in the diffraction pattern, the unit cell dimensions and the solvent content. Triclinic lysozyme does not transform in the 100 to 75% r.h. range. The r.h. at which tetragonal lysozyme transforms decreases when it is presoaked in 2-methylpentan-2,4-diol (MPD). The transformations appear to involve changes in crystal packing as well as conformational transitions in protein molecules. They appear to provide a useful handle to explore conformational transitions in and the hydration of protein molecule.

References

1. IMOTO, T., JOHNSON, L.N., NORTH, A.C.T., PHILLIPS, D.C. AND RUPLEY, J.A. In *The enzymes* (ed. P.D. Boyer), Vol. 7, pp. 665-868, Academic Press, New York, 1972.

2. ARTYMIUK, P.J., BLAKE, C.C.F., GRACE, D.E.P., OATLEY, S.J., PHILLIPS, D.C. AND STERNBERG, M.J.E. *Nature (Lond.)*, 1979, **280**, 563-568.
3. BLAKE, C.C.F., PULFORD, W.C.A., AND ARTYMIUK, P.J. *J. Mol. Biol.*, 1983, **167**, 693-723.
4. GRUTTER, M.G., WEAVER, L.H. AND MATTHEW, B.W. *Nature (Lond.)*, 1983, **303**, 828-831.
5. KRISHNAMOORTHY, G., PRABHANANDA, B.S. AND GURNANI, S. *Biopolymers*, 1979, **18**, 1937-1963.
6. KRISHNAMOORTHY, G. AND PRABHANANDA, B.S. *Biochim. Biophys. Acta*, 1984, **709**, 234-246.
7. VEERAPANDIAN, B., SALUNKE, D.M. AND VIJAYAN, M. *Acta Cryst.*, 1984, **40**, 500-502.
8. VEERAPANDIAN, B., SALUNKE, D.M. AND VIJAYAN, M. *FEBS Lett.*, 1985, **186**, 163-167.
9. SALUNKE, D.M., VEERAPANDIAN, B. AND VIJAYAN, M. *Curr. Sci.*, 1984, **53**, 231-235.
10. SALUNKE, D.M., VEERAPANDIAN, B., KODANDAPANI, R. AND VIJAYAN, M. *Acta Cryst.*, 1985 (In press).

Thesis Abstract (Ph.D.)

Understanding of electrical trees in PMMA with partial discharge and thermally-stimulated discharges by B. Prathap.

Research Supervisor: V. Prabhashanker.

Department: High Voltage Engineering.

Introduction

Treeing is an important ageing process which leads to electric breakdown in solid dielectrics under electrical stress. The process is complex. It also depends on the ambient conditions whether electrical, water or electro-chemical trees are formed. This thesis is concerned with a study of electrical treeing.

A study of literature¹⁻¹³ indicates that the problem of treeing in electrical insulation is yet to be understood completely. Experience shows that the trees are not initiated and propagated in a

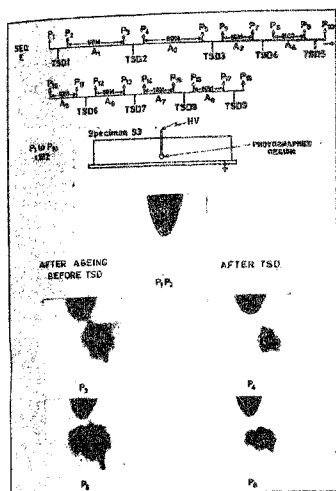
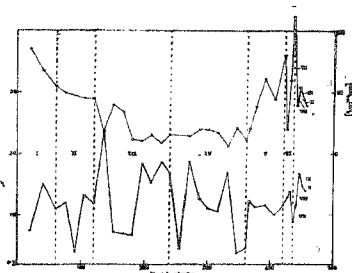


FIG. 1. A partial discharge ageing sequence.

FIG. 2. Variation of η and $[q(\eta_0) = q(\delta_3)]$ with time.

foreseeable manner. The shape and the growth rate varies widely even under identical experimental conditions. A feeling^{5,7,11-13} has grown over the years that trapped charges have a significant role to play in the initiation and propagation of tree channels. If so, removal or altering internal charges in the material should affect the growth of the trees and the partial discharges observed during the growth of the trees. If these discharges are affected by the trapped charge, changes in the trapped charges should alter the nature of the partial discharges.

In this thesis, an attempt is made to check whether this contention is justified. More specifically, experiments have been conducted to study whether partial discharges can be used to characterize tree growth. Also whether modifying the nature of the trapped charges by subjecting the samples aged by partial discharges, to thermally-stimulated cycle under electrical stress (thermally-stimulated discharges-TSD)⁶⁻⁸ would affect the characterization.

The study of electrical treeing was conducted on PMMA (polymethyl methacrylate) as it is transparent and microscopic study and photographing of treeing are possible. Further, good quality perspex sheet was also available readily in the market.

Experimental procedure

Perspex samples with imbedded gramophone needles were prepared. The samples were placed on a ground plate giving rise to a 3 mm point/plane gap in perspex. These samples were aged at 50 Hz at a

voltage level which allowed the tree or bush to grow at a reasonable speed. The samples were tested under oil in a generally used PD discharge ageing set-up. Using a 454 Textronic, 140 MHz oscilloscope and an ECL 1024 channel PHA (rise time .1 to .5 μ s, fall time .1 to 10 μ s), 256 channels were used for the amplitude analysis. The measuring impedance was an LRC circuit which resonates at 500 kHz.

One experimental sequence is shown in fig. 1. 'P' indicates that the specimen has been removed for photographing the tree growth. 'A' indicates the time interval over which the specimen has been subject to partial discharge ageing. 'TSD' indicates that the specimen has been subjected to a temperature cycle (25 to 95°C) with a 1 kV dc polarizing stress.

Experimental results

In the above experiments, treeing is characterized by partial discharges. These discharges have been defined in all cases by Weibull distributions. The parameters of Weibull distributions are affected by the removal of charges with thermally-stimulated discharges (TSD). In all, about 60 Weibull plots and 30 TSD curves along with a number of microphotographs have been obtained and studied.

The parameters σ and η of the Weibull distributions are correlated to one another. The variation of η and $[q_{90} - q_{63}]$ where q_{90} and q_{63} are 90% and 63% quantiles with time for one sequence is shown in fig. 2. A study of the correlations indicates that the difference between the largest and the most probable pulse magnitudes increases as the most probable pulse magnitude increases. However, the probability of finding the 10% quantiles tends to remain within the 10 to 20 lowest levels. Apparently as the (bush/tree) growth increases, the most probable pulse magnitude increases, the probability of finding large pulses increases but small pulses also continue to occur.

The introduction of TSD into the cycle affects the ageing process significantly but the nature of the distribution continues to be Weibull with correlation between the parameters (the Fisher regression co-efficients in all cases were between 0.37 and 0.77).

Conclusions

The experiments indicate that the removal of trapped charges affects the tree growth substantially including the partial discharge pattern. Intermittent partial discharges on the a.c. peaks, characterize the 'branch' type of trees. Continuous partial discharges throughout the a.c. cycle characterizes the 'bush'-type tree. In both the cases partial discharges follow a Weibull-type magnitude distribution. The Weibull parameters are correlated with each other and vary with ageing time. The removal of charges with TSD does not affect the smaller pulses but affects the most probable pulse magnitude. The magnitude of the maximum pulse tends to increase whenever the magnitude of the most probable pulse increases. The total number of pulses increases with increasing time of ageing.

A tentative ageing model can be thought of as an extension of an earlier model¹³. In this model, it is proposed that a critical area is involved in each unit discharge and that a critical stress has to be exceeded over a critical distance. Though a qualitative explanation is possible there is need to collect more experimental data.

References

1. McMAHON, E.J. A tutorial on treeing, *IEEE Trans. Electr. Insulation*, 1978, EI-13(4), 277-288.
2. EICHORN, R.M. Treeing in solid extruded electrical insulation, *IEEE Trans. Electr. Insulation*, 1977, EI-12(1), 2-18.
3. MASON, J.H. Dielectric breakdown in solid insulation, Chapter I of *Progress in dielectrics*, Vol. I, Heywood, London, 1959.

- BAHDER, G.,
DAKIN, T.W.,
AND LAWSON, J.H.
Analysis of treeing type breakdown, *International conference on large HV electric systems*, Vol. I 25th Session, CIGRE, 1974.
- DENSLEY, R.J.
An investigation into the growth of electrical trees in XLPE cable insulation, *IEEE Trans. Electr Insulation*, 1979, **EI-14**(3), 148-158.
- TANAKA, T. AND
GREENWOOD, A.
Effects of charge injection and extraction on tree initiation in polyethylene, *IEEE Trans. Pwr. Apparatus Systems*, 1978, **PAS-97**(5), 1749-1759.
- DORLANNE, O.,
SAPIEHA, S.,
WERTHEIMER, M.R. AND
YELON, A.
Thermally stimulated discharges of polyethylene following AC stressing, *IEEE Trans. Electr Insulation*, 1982, **EI-17**(3), 199-202.
- WATSON, D.B., AND
MORRIN, P.C.
Initial tree growth in PMMA, *IEEE Trans. Electr Insulation*, 1980, **EI-15**(5), 394-397.
- OLSHAUSEN, R.
Factors influencing the growth of partial discharge channels in polymers, *Conf. Partial discharges in Electrical Insulation*, April 1974, Bangalore, India.
- LAURENT, C.,
MAYOUX, C. AND
SERGENT, A.
Electrical breakdown due to discharges in different types of insulation, *IEEE Trans. Electr Insulation*, 1981, **EI-16**(1), 52-58.
- BORISHADE, A.B.
The development of electrical discharges in simulated tree channels, *IEEE Trans. Electr Insulation*, 1977, **EI-12**(5), 348-354.
- LAURENT, C.,
MAYOUX, C.,
NOEL, S. AND
SINISUKA, N.I.
A study of emission lines from electrical trees, *IEEE Trans. Electr Insulation*, 1983, **EI-18**(2), 125-130.
- INDRANEEL SEN,
NARAYANACHAR, M.N.
AND PRABHASHANKER, V.
Partial discharge pulse magnitude distribution, *J. Indian Inst. Sci.*, 1977, **59**(9), 315-322.