Miscellaneous

Prof. U. N. Singh

Vice-chancellor.

Univ of Allahabad

Misc

Living systems maintain their structures by entropy and energy exchange with the environment. A dead structure has its form regardless of the interactions with the environment.

Prigogine.

National Symposium on Facets of Indian Chemistry in 2000 A.D.

ALLAHABAD, OCTOBER 19-21, 1982

Under the UGC Special Assistance Programme

CHAIRMAN :

Professor Arun K. Dey

Head of the Department

Department of Chemistry
University of Allahabad
Allahabad - 211 002

~~Allahabad Office~~ Seniority - ~~Division~~

9

Dr. Om Chandra Saxena Memorial Research Scholarship :-

As the students who have obtain first class are ~~[illegible]~~ sure to get recei UGC or CSIR fellowships or have greater chances of being absorbed in schemes of higher ~~studies~~ ~~Miss Poonam~~ the senior most student has been recommended for the award of this scholarships

→ ~~Among~~ the ~~applications~~ ~~[illegible]~~ the senior most student is Miss Poonam Srivastava so I recommended that she be awarded this scholarship.

[illegible]

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SYMPOSIUM COMMITTEE

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Dr. O. Prakash Jr.

Departmental Scholarship

To encourage higher educatio
in girls, it is appropriate to
award the departmental scholarship
~~to the~~ the meritorious M Sc Student of 1982
from own university with a
good career.

So I hereby recommend the
award of the departmental scholarship
to Miss Rajini Srivastava.

Fig. 1 :- Splitting of water in sunlight and fixation of nitrogen as indicated by decrease in pressure in Warburg's flask by complete Jeevanu, HM (Modi) J (Ac) 60, the blue rod (BR) formed by treating the molybdenum Jeevanu and the yellow residue obtained by treating the filtrate after removing the BR.

Fig. 1. Graph showing gas exchanges as indicated by increase or decrease in the pressure in cm. of mercury in the Warburg's flask on exposing aqueous mixture Jeevanu (J), HM (Modi) J (Ac) 60, blue rod (BR) and acid precipitated Yellow residue (YR) during exposure to sunlight and when the mixture stood in shade.

Please type it on a separate sheet.

Fig. 1 :- Graph showing gas exchanges as indicated by increase or decrease in the pressure in cm. of mercury in the Warburg's flasks on exposing aqueous mixture of the molybdenum Jeevanu, HM (Modi) J (Ac) 60; blue rods (BR) and acid precipitated fraction (YR) during exposure to sunlight and when the mixture stood in shade.

Fig 2 :- Graph showing gas exchanges as indicated by increase or decrease in the pressure in cm. of mercury in the Warburg's flasks on exposing aqueous mixture of the Si-Mo Jeevanu, 1:2:1:1:1:1 J (Ac) 24, blue rods (BR) and acid precipitated fraction (YR) during exposure to sunlight and when the mixture stood in shade on the first day.

Fig. 3 : ---- the second day
Fig 4 ..... the third day.

Fig - 5 Efficiency of the Si-Mo Jeevanu, their BR and the YR as indicated by the limit of fluctuation in the pressure in the Warburg's flask in cm. of mercury in one complete cycle of light and shade in one day.

APPENDIX TO THE RESEARCH PROPOSAL
Complete this form and submit with your Research Proposal.

NOTE: The prospective sponsoring Laboratory or Center must be advised *at the time of application* of any special requirements essential to a proposed research program. Consultation with the prospective adviser is not required, but may be helpful, before listing these requirements.

Statement of Anticipated Program Needs

(l) Any program activities related to the acquisition or collection of data, such as balloon launches, field activities, research voyages, observatory use, etc.

(2) Computational Resources

(3) Specialized Equipment (Example: Items that are not available at the laboratory as may be determined in consultation with the prospective research adviser.)

(4) Other

Signature _____ Date _____

Fig. 1 :- Graph showing gas exchanges as indicated by increase of decrease in pressure in cm. of mercury in the Warburg's flasks on exposing aqueous mixture of the molybdenum Jeewanu, HM (Modi) J (Ac)60, blue rods BR and acid precipitated fraction YR during exposure to sunlight and when the mixture stood in shade.

Fig. 2 :- Graph showing gas exchanges as indicated by increase or decrease in pressure in cm. of mercury in the Warburg's flasks on exposing the aqueous mixture of the Si-Mo Jeewanu, 1:2:1:1:1:1 J(Ac)24, the BR and acid precipitated fraction YR during exposure to sunlight and when the mixture stood in shade on the first day.

Fig. 3 :- Graph showing gas exchanges as indicated by increase or decrease in pressure in cm. of mercury in the Warburg's flasks on exposing aqueous mixture of the Si-Mo Jeewanu, 1:2:1:1:1:1 J(Ac)24, the BR and acid precipitated fraction YR during exposure to sunlight and when the mixture stood in shade on the sacond day.

Fig. 4 :- Graph showing gas exchanges as indicated by increase or decrease in pressure in cm. of mercury in the Warburg's flasks on exposing aqueous mixture of the Si-Mo Jeewanu, 1:2:1:1:1:1 J(Ac)24, the BR and acid precipitated fraction YR during exposure to sunlight and when the mixture stood in shade on the third day.

Fig. 5 :- Efficiency of the Si-Mo Jeewanu, their BR and the YR as indicated by the limit of fluctuation in the pressure in the Warburg's flask in cm. of mercury in one complete cycle of light and shade in one hour on one day.

Dear D. D. Singh.

~~Expert No.~~ With reference to your letter No. Proj - 8/4/83 dated 18/6/83
My reply to experts observation is as follows: -

~~Expert No. 1~~ 1. The Chloroplast - ferredoxin - hydrogenase system of algae which split water to hydrogen and oxygen are deactivated with in 15 min. to one hour irreversibly. The photoredox system of organo-molybdenum microstructure remain active for a few weeks. Then the costly chemicals used in their preparation which is molybdenum can be recycled. Other chemicals as diammonium hydrogen phosphate and biological materials are cheap. More over very little of them are needed. This is about the final deactivation of the particles.

However there is temporary deactivation of the particles after the day's exposure. However this is recovered during the dark phase gap of the night. So the deactivated particles after the days exposure are fresh again next morning after standing in dark in night.

2. Literature review ~~is also~~ has not been given in detail to reduce the bulk of the material to be cyclostyled into 20 copies. A detail uptodate review of the work on photolytic splitting of water has already been "given by us (1.) ~~was presented by us in Goa Discussion on Recent Development in~~ .... I am here with sending a photocopy of the paper.

Technical details and methodology to be used has been described in each of D.Phil Thesis ~~quoted as follows~~ (1, 2, 3, 4, 5, 6, 7, 8 and 9) ~~and so they were omitted in the text of the project.~~ [illegible]

Bhatnagar,
Prasad,
Mukerji,
Prasad,
Rakesh,
Vijaya,
Srivastava,
Rathore,
Shekhar.

Thesis

These were not included in the report to keep the size of the report short.

3. The organo molybdenum microsomes have three systems

(1) which causes photochemical splitting of water in sunlight. ~~It~~ ~~produces~~ ~~molecular~~ O_2 ~~as~~ by-product.

(2) ~~extract~~ Particles have nitrogenase-like material also and it fixes the ~~nitrogen~~ hydrogen set free. In presence of the particles it is ionic reaction and ~~(3)~~ it takes place both in light and will continue ~~of H_2~~ even in dark if the hydrogen formed during light is available.

(3) ~~Nitrogen loss~~ Particles also have a nitrogen loosing system. It ~~is~~ decomposes NH=NH diimide formed to N_2 and H_2 and this is also ionic reaction and follows after rapid fixation of nitrogen.

~~I~~ We are trying to solve this problem of nitrogen fixation by the ~~proc~~ method.

~~I~~ We are preparing such particles which have good water splitting ability in light ~~we~~ have poor nitrogen fixing property.

~~II~~ II We are also study the various physico-chemical factors which may hinder nitrogen fixation.

~~III~~ III We are ~~of~~ also ~~fractionally~~ fractionating different constituents of the organo-molybdenum ~~microsome~~ or microsomes with a view to ~~to~~ have water splitting constituent ~~separated~~ separated from nitrogen fixing constituents. It is here where ~~I~~ We will need ultra centrifuge. Here I agree that high speed refrigerated Centrifuge giving 20,000 rpm (approx. 38000 xg) will be ~~only~~ equally good I hope.

Abst recommendation:

(1) I suggest ISRS and 4 JFE be continued.

We have already abt 12 research students on some aspect or the other of this problem. Adding 3 will ~~not~~ be ~~very much help~~. ~~Plant Genetics~~ a insignificant.

(2) (i) I have requested for Rs 50,000 per year as Repair and working cost of Perkin's Elmer Model 990 Gas Chromatograph. I request that this may be granted.

(ii) Glass apparatus may be cut down to 20,000 per year. Chemicals are getting costly every month. This may be kept as Rs 40,000 per year, I request that otherwise it must be kept as Rs 2,000 per year.

Travel Expenses:

I request it should not be curtailed because we may need to call some foreign scientists for discussion.

※ ~~Rao, K.K., Morris, P. and Hall, D.O. (1978)~~

1. Sri Rao, K.K.,
2. Folson
3. T.I.C.S.

O this expert did not see them so he wrote 'mystic and Scientific,"

Expert No. 2

On me the university give to me & Dr Dhiya that I only need to write a project

1. ~~The term 'mystic & Scientific' has been used perhaps I could not~~ and I need not include the photocopies of the papers in my file ~~what the~~ ex Expert will have access to them ~~give enough of data and information in the project assuming that you~~ So I just write the project ~~this~~ the expert knows the cards & the photocopies are in my file! If agrees ① Please ~~will~~ send the photocopies of the scientific papers ~~quoted~~ to the ~~expert~~ B.T. also. ~~XX~~ I am sending the photocopies of some of our papers recently presented in: . . . . . and

(1)

(2)

(3)

Please send photocopies of these together with photocopies of our earlier papers to him and I think to this expert will have a clear idea of ~~what~~ I am talking about.

2. ~~About identify the Geneva and~~ the nature of gases evolved ~~from~~ the above papers will provide ~~with~~ necessary information. I am herewith sending the photocopy of a few Cables exchanged by me collaborator with ~~NASA~~ Dr. A Smith of NASA, Ames Research Center, Moffett Field, Calif. Cables which will answer the question. ~~The photocopy of this paper~~ "The paper with Smith & Nelson reprint also ~~was written~~ has the details of this collaboration. " ~~in experiments~~ . . . . . with other ~~the evidence~~ is the answer was written after the ~~Collaboration~~ and the work with D_2O and $NaH^{14}CO_3$ indicating water splitting, fixation of nitrogen and ~~Carbon~~ inorganic carbon by these particles. This paper is in my file with you. Please send a photocopy of the paper which is in my file with you to the Expert.

A. I have written my view.

B. no comment.

C) 1— ~~XX~~ I explained to you about the ~~expert~~ working cost of the Gas chromatograph.

2— total is only Rs 1,80,000 per year. as suggested by the ~~ex~~ expert,

D— ~~XX~~ He has suggested the same fees as I have per year

I am sure the Expert will ~~do~~ revise his opinion after you send ~~him~~ the literature which I have suggested. Some of these are in my file

and am I am sending herewith.

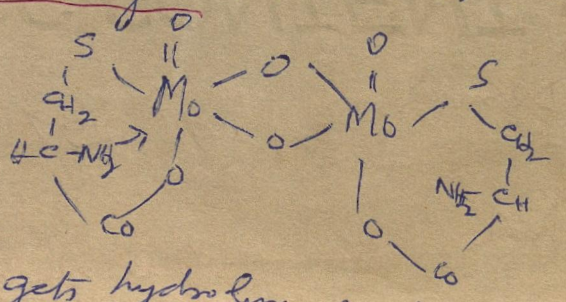
Expert No 3.

~~[illegible]~~ I suggested that the expert be sent the photocopy of the following ~~[illegible]~~ papers:

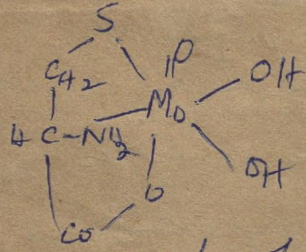
1. ~~[illegible]~~ Madurai — with you
2. Folsom — with you
3. Bombay. — I am sending him with
4. Delhi Dr. — I am sending him with
5. Delhi — I am sending here
6.

This will give him all the information he needs ~~about the~~ ~~the~~ About the role of molybdenum ~~[illegible]~~ [in fixation of nitrogen mainly ~~of~~ photochemical splitting of water] Schrauzer & ~~[illegible]~~ and coworkers are doing some good work. A summary of this has been dealt in [with this line] my paper in Bombay [Group discussion] ~~Symposium~~ I am sending. This paper contains all ~~the expert wants and also what the search~~ has upto date review of the work on ~~[illegible]~~ photochemical splitting of water ~~[illegible]~~ excluding Electro photochemical one in which we are not interested. Mo being a part in nitrogenase in catalysis is good to believe that it will help in ~~to~~ photochemical splitting of water. ~~Hence after the detection~~ of ferredoxin-like material ~~in these [illegible] microbes the [illegible]~~ were detected in the particles. [The particles were then ...] Nitrogenase-like activity [also] ~~was [illegible] in these particles~~ because it is Mo-Fe-protein. In nitrogen fixers the hydrogen needed for the fixation of nitrogen by nitrogenase is obtained from organic sources ~~[illegible]~~ [by the help of] ATP ~~[illegible]~~.

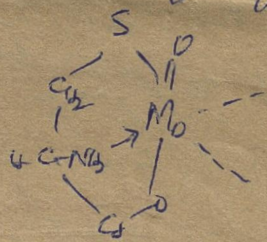
~~Here~~ The nitrogenase activity is tested by the ability of the nitrogenase-enzyme system to reduce $CH \equiv CH$ to $CH = CH$ and in typical nitrogenase activity organic material is used a electron donor ~~as in photosystem I~~. Here with these particles ~~the [illegible] only~~ are able ~~to do~~ show nitrogenase-like activity that ~~convert~~ conversion $CH \equiv CH$ to $CH_2 = CH_2$ in the over head space of mixture of organic molybdenum & microelements and water only on exposure to light. Thus this nitrogenase-like activity is like that of



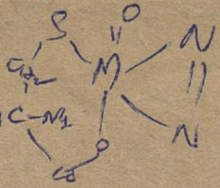
complex of Schrauzer ( ). ~~These~~ Which gets hydrolysed of Mo_{VI}



which on reduction forms Mo_{IV}



which combines with mol. N_2 to form



Our particles are able to utilise water as electron donor on exposure to light for ~~this~~ the conversion of Mo_{VI} to Mo_{IV}.

I resent the use of the term "Cook book approach" by the ~~auth~~ expert. Please send the literature I have ~~[illegible]~~ referred also to him. If even then he holds his ~~old~~ ~~[illegible]~~ earlier view it is upto to you to decide.

With regards

Yours

एक $(CH_3)_2C(OH)CH_2-COOC_2H_5$ हाइड्राक्सी एस्टर बनाने के लिये मूल से इसका संश्लेषण एसिटो एसिटिक एस्टर और मैग्नीशियम आयोडाइड उपयोग करते हुये प्रारम्भ किया गया। अभिक्रिया बिना ऊष्मा लगाये हुई और मिश्रण खूब बुलबुले उठते रहे। परन्तु जल उपघटन के उपरान्त केवल एसिटो एसिटिक एस्टर प्राप्त हुआ। क्या अभिक्रिया हुई? बुलबुलाहट किस कारण हो रही थी?

गलती से
$C_6H_5-CH=CH\,C(OH)CH_3$ बनाने के लिये ~~स्थित~~ स्थित मैग्नीशियम ब्रोमाइड के विलयन में उपाधिक्य मात्रा में $C_6H_5CH=CH\,CO\,CH_3$ डाला गया और अभिक्रिया तब चलाई गई जब तक चूरा स्थित मैग्नीशियम ब्रोमाइड समाप्त न हो गया। मिश्रण को तनु सल्फ्यूरिक अम्ल से अभिक्रिया कराने पर एक पदार्थ प्राप्त ~~हुआ~~ हुआ जो आयोडीन और सोडियम हाइड्राक्साइड से अभिक्रिया करने पर ~~आयोडोफार्म~~ आयोडोफार्म की खूब गंध देता था। क्या बन गया? यह किस प्रकार बना?

(1B) (1) ~~How will you~~ establish the structure of molecule of
α terpineol
α– टर्पिनाल की संरचना स्थापित कीजिये।

(2B) (2) ~~Write short notes on~~ Discuss any one of the following
निम्न में किसी एक की विवेचना कीजिये
(a) Structure of protein प्रोटीन की संरचना
Discuss the (b) ~~amino acid sequence~~ of
(IB) Structure of oxytocin
आक्सीटोसिन की संरचना का विवेचन कीजिये

(3B) (3) Give one method of synthesis of ~~any two~~ of the following.
निम्न की संश्लेषण की एक विधि लिखिये
(a) adenine एडिनिन
(b) ~~Guanine~~ Guanine.
ग्वानीन

(IIB) (4) How do you determine the sequence of amino acids in protein molecule.
प्रोटीन में अमीनो अम्ल की श्रृंखला क्रम आप किस प्रकार ज्ञात कीजियेगा।

(IA) 1. Account for the different bond lengths of C–H bonds in acetylene, ethylene and ethane.
एसिटिलीन, एथाइलीन और इथेन के C–H बंध की
2. बंध लम्बाई विभिन्न होने का कारण बतलाइये

(2A) 3. Discuss the isomerism of diphenyl. Under what circumstances the ortho substituted of diphenyl show optical isomerism.
डाइफ़ेनिल के समावयवता का वर्णन करो।
4. किन परिस्थितियों में डाइफ़ेनिल के ऑर्थो प्रतिस्थापी प्रकाशिक समावयवता दिखाते हैं।

IIA
3A
IA
IIIA
IIB
IC
2C

~~I A~~ Write ~~short~~ notes on any ~~two~~ of the following
(a) Beckmann's transformation — निम्न पर ~~लघु~~ टिप्पणी
(b) Walden inversion. बेकमैन रूपांतरण कीजिये :
~~(c) Asymmetric synthesis~~ वाल्डन प्रतिलोमन।

3A What are free radicals? Discuss the condition which favour the stability of ~~carbon~~ free radicals.
मुक्त मूलक क्या है? उन स्थितियों का वर्णन करो जो मुक्त मूलक को स्थायित्व प्रदान करती है।

~~Why.~~

I A 1. Discuss ring-chain tautomerism ~~giving~~
~~acid on ozonation and subsequent~~
~~Do~~ taking suitable examples. उचित उदाहरण देते हुये
~~hydrolysis~~ gives वलय - श्रृंखला चलावयवता की विवेचना कीजिये।

III A ~~Write short notes on~~
~~(a) Beckmann's transformation~~ ~~Account for~~
their formation.

What is asymmetric synthesis? Discuss
a asymmetric synthesis taking a good example.
असममित संश्लेषण क्या है? एक अच्छा उदाहरण लेते हुये असममित संश्लेषण की विवेचना कीजिये।

III B Give critical account of any of the following
~~structure~~
निम्न का आलोचनात्मक मूल्यांकन कीजिये :
(a) Molecular Structure of lactose (क) लैक्टोस की आणविक रचना।
(b) Molecular Structure of Sucrose. (ख) सुक्रोज की आणविक रचना।

C

ऐरोमैटिसिटी क्या है? छः, पांच या सात कार्बन परमाणु वाले ऐरोमैटिक ~~यौगिक~~ ~~प्रकृति~~ के यौगिक के विशेष निर्देश देते हुये ऐरोमैटिसिटी की आधुनिक कल्पना की विवेचना कीजिये

I C 1. What is aromaticity? Discuss the modern concept of aromaticity with special reference to aromatic nature of rings with 5, 6 and 7 carbon atom rings.

2C 2. Discuss the reaction mechanism of the following
(a) Diels-Alder ~~reaction~~ addition
(b) Benzil - benzilic acid ~~rearrangement~~ transformation
निम्न की ~~क्रियाविधि~~ अभिक्रिया ~~विधि~~ की विवेचना कीजिये
डायल - एल्डर योग
बेंजिल - बेंजिलिक अम्ल रूपांतरण।

निम्न के ~~यांत्रिकी~~ की विवेचना कीजिये:

(a) क्रियाविधि

2. Discuss the mechanism of the following

(a) Friedel-Crafts condensation फ्रिडिल-क्रैफ्ट संघनन

(b) Claisen Condensation क्लाइजन संघनन

3. ~~Discuss~~ Describe the synthesis of the following — निम्न के संश्लेषण का वर्णन कीजिये।

(a) Acridine. (a) एक्रीडीन

(b) indole. (b) इंडोल

4. ~~Discuss~~ the synthesis of :

(a) Carbazole,

(b) isoquinoline.

5. How is piperine ~~isolated~~ obtained from the plants? Discuss its molecular structure.

पाइपेरीन किस प्रकार पौधे से किस प्रकार प्राप्त की जाती है इसके धातु रचना की विवेचना कीजिये

6. Describe the procedure of extraction ~~coniine~~ nicotine from its source? Discuss its structure.

निकोटीन अपने स्रोत से किस प्रकार निष्कर्षित की जाती? इसके धातु रचना की विवेचना कीजिये।

(3C B) ~~One~~ To prepare a hydroxy ester, $(CH_3)_2C(OH)\cdot CH_2\cdot COOC_2H_5$ by mistake the synthesis was started using acetoacetic ester and methyl magnesium iodide. The reaction took place without application of heat and the mixture bubbled merrily. How on hydrolysis only acetoacetic ester was obtained. What reaction has taken place? What was bubbling due to?

$CH_3CO\cdot CH_2COOC_2H_5 + CH_3MgI \rightarrow CH_4 + (CH_3\text{-}COCH\cdot COOC_2H_5)_2Mg$

$\downarrow$

$CH_3CO\cdot CH_2COOC_2H_5 + CH_3OMgI$

(III C B) To prepare $C_6H_5CH=CHC(OH)CH_3C_2H_5$ ~~slight excess of~~ $C_6H_5CH=CHCOCH_3$ was added to a solution of ethyl magnesium ~~iodide~~ bromide and reaction continued till all ~~the reaction~~ the ethyl magnesium iodide was consumed. On treating the mixture with dilute sulphuric acid ~~I got~~ a product which gave a copious precipitate of iodoform when treated with iodine and sodium hydroxide. ~~It was mistook for~~ What is formed? How has it formed?

$C_6H_5\text{-}CH(C_2H_5)CH_2\text{-}CO\text{-}CH_3$: 4 Phenyl - 2-hexanone.