KRISHNA KAMINI ROHATGI-MUKHERJEE

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KKRohatgi Mukherjee

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(1924-2009)

Elected Fellow 1984

FAMILY BACKGROUND

KRISHNA KAMINI ROHATGI was born in a joint family on 2nd August, 1924 in Patna, Bihar. She was the second child of late Binay Krishna and Shakuntala Rohatgi. Her family migrated to Kolkata from Patna more than two hundred years ago. Her father was a student of chemistry who unfortunately could not complete MSc course in Calcutta University and later on became a businessman by profession. Her mother Shakuntala Devi always inspired her children for modern education. Her parents maintained strict disciplines and taught high moral values to their children. They were believer of modern education, particularly science education. Her father established a family library and chemistry laboratory in the house for science education to his children. As a part of the proper education her parents arranged for training of music and painting of their children. It is no wonder afterwards their daughter Krishna Kamini became an expert sitar player and good painter too. She was involved in the nationalist movement of India following her father who was a strong nationalist and involved in Swadeshi Movements (even during the turbulent days of the 1942 Quit-India Movement).

She grew up with her six brothers and five sisters. Being second child of her parents she had the responsibility to guide younger brothers and sisters to their studies and as a loving and affectionate elder sister and often she had to oblige most of their childish demands. The affection and mutual respect between all brothers and sisters grew with time. All the time she was highly respected by her brothers and sisters as the guiding spirit to their family for all moral values.

EDUCATION

Her school education started in Gokhale Memorial Girls' school, Calcutta. From her childhood she was exposed to three languages Hindi, English, Bengali and in her school days she learned and loved Sanskrit. She passed Matriculation in the year 1939 and obtained first class with distinction in vernacular. After Matriculation she was admitted in Ashutosh College, Calcutta and passed Intermediate of Science (ISc) examination in 1941 with distinction (Star) in Chemistry. For her brilliant results she received (i) Free Studentship, (ii) State Government Scholarship, (iii) Nawab Abdul Latif and Father Lafont Science Scholarship. In the year 1943, she passed BSc

Examination with honours in Chemistry from Scottish Church College under Calcutta University. She stood first among all women candidates in science and received (i) Basanti Debi Medal (Calcutta University) and (ii) Kunj Behari Basak Medal (Scottish Church College). In the year 1945, she passed MSc in Pure Chemistry with specialization in Physical Chemistry from Calcutta University and stood first class second in order of merit. She received (i) the University Silver Medal and (ii) Jogmaya Debi Gold Medal for standing first amongst all women candidates in science subjects. She published two papers based on her MSc thesis.

RESEARCH CAREER

She started her research career at the Department of Chemistry at College of Engineering and Technology, Jadavpur, Calcutta (at present Jadavpur University) in 1948 under Professor Sachindra Nath Mukherjee, DSc. Professor SN Mukherjee introduced her to the subject on fluorescence of anthracene in solution and its quenching by chlorinated hydrocarbons and this topic drew her interest throughout her entire research career. She joined with Professor EJ Bowen, FRS at Oxford in 1950 and continued the work on fluorescence studies of anthracene to get DPhil (Oxon) in 1952 on the thesis entitled "*Photochemistry of Anthracene Derivatives*". From then onwards she remained the Senior Member of the St. Annes' College, Oxford University.

In the year 1954, she was awarded Sir PC Roy Research Fellowship for two years in Department of Chemistry, University College of Science, Calcutta University. During this period she used to deliver special lectures in Photochemistry in M Sc classes and she continued to lecture on the subject till 1970. In the year 1956 as Fulbright/Smith Mundt Grantee, she went the University of California, Berkeley, USA and engaged in research on determination of life times of excited molecules by using phase shifting technique.

She joined Jadavpur University in 1958 as Reader in Physical Chemistry. For her initial research work, her father had given a gift of an instrument, Lumetron, which is still there in the Department. With years passing by, she fluorished in her research in the fields of Photo physics and Photochemistry. She became Professor of Chemistry in 1974. In between, she spent one year (1963-64) as Assistant Professor of Chemistry at IIT, Kanpur and one year (1973-74) as Visiting Scientist at the School of Life Sciences, Jawaharlal Nehru University (JNU), New Delhi. She acted as Head of the Department of Chemistry, Jadavpur University for three years (1979-1982). She retired as Professor of Chemistry on 1989 and then continued her teaching and research in the Department as the INSA Senior Scientist from 1990 to 1993. She was awarded CV Raman Gold Medal by Indian Science Congress Association in 1990.

RESEARCH HIGHLIGHTS

Research in Photochemistry and Photophysics

- Even in early fifties, modern approach to systematic study of photo physics and photochemistry was hardly introduced in India. Professor Rohatgi-Mukherjee initiated such studies with available instruments and light sources after returning from Oxford.

(a) Photochemistry of Anthracene with Chlorinated Hydrocarbons

The research problem taken up in Oxford under the supervision of E J Bowen was actually initiated in India but was carried out more systematically and quantitatively as a doctoral project. The reaction between anthracene and chlorinated hydrocarbons in deoxygenated solutions has led to the concept of excited state electron transfer reactions. Although the initial idea was incorporated in the thesis, it is later firmly established by Naqvi, Ware, Carrol, Whitten and others. In the presence of oxygen, photoperoxidation of anthracenes occurs in halocarbon solvents. It was established that intermediate formation of singlet oxygen O_2 ($^1\Delta_g$), generated by interaction of ground state oxygen $^3O_2$ with triplet photosensitizer which plays the major role in photooxygenation reactions.

(b) Photophysics of Laser Dyes: Hypochromism and Exciton Interactions in Self-aggregation Phenomenon

A systematic study of photo physics of dyes and aggregation phenomenon has a great relevance in the development of dye-lasers. An understanding of the nature of bonding in dye aggregates through its thermodynamics, is important for a number of problems such as, stacking interactions in bimolecules, hypochromism and conformation in polypeptides, energy and electron transfer in physicochemical and biological system, such as photosynthetic reaction centres, metachromasia and staining properties of dyes for biological specimens, tuning of dye laser, etc. With these objectives in view, detailed studies of the absorption and emission characteristics of a series of halofluoresceins (anionic) and rhodamine (cationic) dyes were taken up as a function of concentration. The observation of concentration quenching of fluorescence revealed the importance of dye dimers as energy traps. From spectroscopic studies, dimerisation constants and the thermodynamic parameters ΔG, ΔH and ΔS were evaluated after separation of the dimer spectra. It was established that aggregation at p_H 12 for fluorescein is an enthalpy directed phenomenon, in which water molecules participate in dimer formation, but in rhodamines and halofluoresceins it is entropy directed hydrophobic interactions.

From a detailed study of photophysics of halofluoresceins (from fluorescein to rose Bengal) it was established that increased oscillator strength (f) in absorption was responsible for increase in aggregation tendency along the series. Aggregation also caused splitting of absorption band due to exciton interaction. The ratios of transition moments integrals of split bands were found to be a function of the angle θ between the main oscillators of the two molecules. The angle of twist θ, the geometry of the dimers and the extent of the split ΔE due to exciton interaction were calculated to establish the stacking pattern. Iterative methods were developed to separate dimer spectra from the total absorption spectra to give correct value of the angle of twist and dimer geometry. Hypochromism due to aggregation was observed for more aggregation of dyes. This work was highly appreciated and extensively quoted. In later works energy levels of aggregates were calculated from quantum mechanical considerations of in phase and out of phase interaction between transition moments.

The energy transfer phenomenon between dyes of similar or closely related spectral characteristics which simulate energy transfer in antenna chlorophyll of photosynthetic reaction centre and in many biopolymers, was studied. Energy transfer occurs by Försters mechanism. Methods were developed to obtain true quantum efficiency of such coupled systems with overlapping absorption and emission bands of energy donors and acceptors.

Solvent effects on the photo physics of rhodamine dyes were studied in water ethanol mixed solvents. The three forms, the acid, basic and ester, of the dye are found to be sensitive probes of solvent structure.

With a view to develop laser materials, some mixed chelates of rare earths were synthesised. Spectral studies on these compounds suggested that the emission characteristics of these chelates can be improved by the distortion of micro symmetry around the metal ion. The effect depends on the enhancement of the symmetry forbidden electric dipole transition.

(c) PhotoPhysics and Photochemistry of Anthracene Sulphonates

Anthracene molecules can be made water soluble by inserting substituents like -SO_3H in various positions. Because of their convenient absorption spectra and useful fluorescence characteristics, the water soluble anthracene sulphonates are used as substrates, sensitizers and probes in photo physical and photochemical studies in aqueous environments and have been widely used in biological systems. Subtle changes occur in the physico-chemical properties on excitation. The substitutional positions and the number of substituent incorporated, have been observed to influence the photo physics and photochemistry of these sulphonates, changing their fluorescence quantum yields Φ_f, dipole moments and even leading to exciplex formation in aqueous solutions with H_2O molecules and formation of hydrated electrons. Photo peroxidation, concentration depolarization, energy transfer and kinetics of concentration quenching of fluorescence of variously substituted anthracene sulphonates have been studied. They all demonstrated variation reactivity for substitutionally different molecules.

The phenomenon of fluorescence quenching and triplet state quenching helps to assess the interaction in the excited states. The quenching of these energy states by small inorganic anions like halides and azides occurs by electron transfer mechanism. Quenching studies on variously substituted anthracene sulphonates have established the importance of hydrophobic hydration in the excited state interaction, which has important bearing on the study of biological molecules such as proteins and nucleic acids and their complexes.

The electronically excited anthracene sulphonates are efficient generators of singlet oxygen $O_2(^1\Delta_g)$, which occurs by energy transfer from the triplet state of the photo sensitizer. The singlet oxygens thus generated cause photosensitized reactions and photoperoxidation of anthracene sulphonates and other compounds, either by energy transfer or by electron transfer mechanism. The photooxidation of I^- occurs by charge transfer interaction, since the reaction is solvent polarity and protonicity dependent. Systematic studies on variously substituted anthracene sulphonates have been used to establish mechanistic details of formation of singlet oxygen as intermediates in photooxigenation reactions.

(d) Photo Electrochemical Conversion of Light Energy to Electrical Energy

Electron transfer or charge transfer photochemistry on micelles, on electrode surfaces and in solutions have been actively investigated for their role in solar energy conversion and storage, using photosensitized redox reactions in suitable electrochemical devices. Production of hydrogen by photo splitting of water using diammonium tetrathiomolybdate as photo catalyst has achieved some success.

Photoinduced reactions involving porphyrins and metalloporphyrins have been studied in electrochemical cells for the conversion of light energy to electrical energy by suitable modification of electrode surfaces. The photoelectroactive materials can be deposited either by dip-dry method or by electro initiated polymerization on Pt or SnO_2 electrodes. The electro initiated polymerization on laboratory synthesized meso-tetrakis (p-vinyl-phenyl) porphyrin, on transparent SnO_2 electrode was initiated through the vinyl group by oxidative scanning using cyclic voltammetry. For zinc meso-tetrakis (p-vinyl-phenyl) porphyrin, the reaction is (p = porphyrin),

$pZn(II) \underset{+e}{\overset{-e}{\leftrightarrow}} p^{+}Zn(II) \rightarrow$ chain propagation through vinyl group, generating - C·H-C·H radical. Stable conducting adherent films were formed by stacking interaction between layers. The counter ions of the conducting electrolyte tetra butyl ammonium salts appear to play a dominant role in photocurrent generation in the order ClO_4^- > BF_4^- > Cl^-. The smaller size of Cl^- ion leads to ion pairing, obstructing electron flow and photocurrent generation.

. The glassy carbon electrode has been modified by covalent attachment of 5-amino-phenyl (10,15,20) tri phenyl porphyrin (NH_2P) by amide linkage after suitable preparation of carbon electrode. The immobilized NH_2P is electrochemically active and because of unidirectional linkage on carbon electrode, acts like a molecular wire. When studied by cyclic voltammetry, about 50mV to 100mV was obtained for ΔE of oxidative and reductive peaks. Although a comparatively good photocurrent was generated, the fill-factor was poor (ff = 0.32). No peak was observed when prepared by dip-dry method. Electrochemical behaviour was also observed when tetra phenyl porphyrin was immobilized on the surface of montmorillonite clay and films cast on SnO_2 or glassy carbon electrodes. Photovoltage of 300mV in open circuit was obtained but photocurrent was very poor.

(e) Photochemistry of Water Soluble Porphyrins in Organized Media

Absorption and fluorescence characteristics of laboratory synthesized free base H_2TTPX_4, where X = $-SO_3H$, -COOH and -OH and their metal analogues have been studied in aqueous solutions and in polyvinyl pyrrolidone (PVP) matrices from p_H range 2 to greater than 12 at high p_H the substituent groups are ionized and they bind to water soluble PVP. The macrocycles have different hydrophobicity parameters and different charge delocalization capacity. Their singlet and triplet state photo physics and quenching by electron acceptors like MV^{2+} and (1,5 anthraquinone disulphonate)$^{2-}$ have been studied in homogeneous aqueous solution and bound to PVP matrix. Their binding constants are small and similar showing that water soluble porphyrins are embedded in hydrophobic pockets in the polymer matrix and are partially available to outside quenchers. From flash photolysis studies, formation of long lived porphyrin radical cations and quencher anions were identified. The generation of long lived radical ion pairs in polymer matrix is a step towards photochemical and photo electrochemical conversion and storage of solar energy.

Some studies on molecular interactions in micells, liposomes for solar energy conversion had been initiated. Electron transfer from a donor in the inner pool to an acceptor in the outer pool, sensitized by liposome encapsulated photo sensitizers like chlorophyll complex and ZnTTP have been studied to simulate photo redox chemistry in bio systems and solar energy conversion. Production of hydrogen by photo splitting of water using diammonium tetrathiomolybdateas photo catalyst has achieved very good success.

ACQUAINTANCE WITH SCIENTIFIC COMMUNITY

One of her unique character was to keep contact with scientific personalities [illegible] of her own research field but all other allied research fields. She attended as many conferences as she could, of course taking full care teaching load. She participated in:

- IV International Photobiology Congress, Oxford (1964)
- International Conference on Molecular Luminescence, Budapest (1966)
- V International Photobiology Congress, Hanover, USA (1968)
- International Conference on Molecular Luminescence, Chicago (1968)
- International Conference on Photochemical Conversion & Storage of Solar Energy, Canada (1976)
- IUPAC Symposium on Photochemistry, France (1976)
- VI International Photobiology Congress, Rome (1976)
- International Conference on Photochemical Conversion & Storage of Solar Energy, Cambridge (1978)
- International Photochemistry Conference, Cambridge (1978)
- 10th International Symposium on Photochemistry, Interlaken, Switzerland (1984)
- IX International Congress on Photobiology, Philadelphia, USA (1984)
- First European Congress of Photobiology, Grenoble, France (1986)
- International Conference on Molecular Luminescence and Photophysics, Torun, Poland (1986)
- She attended Tenth International Photobiology Congress as President of the Congress at Jerusalem, Israel (1988).

She travelled abroad quite frequently. She went to UK to work on flash photolysis technique with Sir George Porter, FRS, NL at Royal Institution of Great Britain sponsored by British Council (1978). She visited USA as Visiting Scientist at Radiation Laboratory, University of Notre Dame, Indiana (1984) and visited Poland under Inter Academy Exchange Programme (1986).

OTHER ACADEMIC INVOLVEMENTS

In spite of the heavy burden of research work, she took the initiative of approaching national funding agencies for development of infrastructure of teaching and research in the department. The culture of research work in a group in the department was first conceived by her. In and around 1980, under her leadership, a departmental project on conversion and storage of chemical energy was sponsored by University Grants Commission and was successfully implemented with the help of many departmental colleagues. The successful completion of the project led the way to bigger projects being carried out in the department currently.

She could look forward ahead of others. At present, training of college teachers in the form of Orientation course and Refreshers course etc. is compulsory. But back in 1966-68, she felt the necessity of such training and organized three consecutive summer institutes for college teachers, collecting funds from University Grants Commission, India and National Science Foundation, NSF/USAID USA. As the Director, she brought eminent teachers and scientists from USA to participate in the summer institute. Following this she was invited to the Indo-US bi-national conference on Chemical Education. She visited a large number of Universities in USA under College Science Improvement programme.

She was also very much concerned about the curriculum followed in the undergraduate and post graduate classes. She was a Member of the Syllabus Committee set up by the University Grants Commission. While attending the meeting, she always took note of experiences of her colleagues to frame the curriculum.

The reflection of her broader scientific outlook on interdisciplinary research is brought out in the role she played to establish the scientific forum known as the Indian Photobiology Group (later renamed as the Indian Photobiology Society) in 1964. The Society is now one of the best forums for exchanging ideas of Physicists, Chemists, Biologists, Medical Experts etc. She initiated the society, nurtured it and maintained its objectives as a true guardian of the Indian Photobiology Society. The Society is now recognized worldwide and became affiliated to the Association International de Photobiologie (AIP) in 1964.

HONOURS AND DISTINCTION

She participated the Bi-national Conference on Chemical Education at Srinagar & Bangalore (1969) organized by UGC & NSF/USAID. She became the Director of All India Institute for Test Construction & Evaluation Methods in Chemistry sponsored by UGC (1970). She served on a number of committees set up by the Government of India such as National Committee on Environmental Planning and Co-ordination (1977-78). In 1978, she became the Member of the Editorial Board of the *Journal of Indian Chemical Society*. She became the UGC National Lecturer in 1980 and Vice President of Indian Chemical Society. She served as Member of Editorial Board of *Indian Journal of Chemical Education, Indian Journal of Chemistry*, Section A (1980-82). She served as the national representative to the committee of International Union of Pure and Applied Chemistry (1982-83). She was the Member of the Committee of Non-Conventional Sources of Energy (Government of India), Conversion on Chemical routes (1982) and Chemical Research Committee on Physical Chemistry, CSIR (1982-86).

She became the President of Chemistry Section of Indian Science Congress Association in 1985. She was the first from Asia to act as the President of the

International Congress of Photobiology (1988) and elected as Honorary M... the Association Internationalé de Photobiologie in the same year.

She was Member of Asiatic Society, American Photobiology Society, European Photochemistry Association, Indian Biophysical Society, Indian Science Congress Association, Indian Association for the Cultivation of Science, Solar Energy Society of India, First lady Committee Member of Indian Society of Lighting Engineers (ISLE).

SOCIAL AND CULTURAL ACTIVITIES

She associated herself in different social and cultural activities. She was President of Anamica a cultural organization in Calcutta (1959) and a Founder Member of the Organization (1956). She was President of University Women Association of Calcutta (1968) and served as a Member since 1960.

In her personal life, she was the wife of Professor Sushil Kumar Mukherjee, DSc, FNA, former Vice-Chancellor of Calcutta University and Kalyani University. Professor Sushil Kumar Mukherjee was a renowned scientist in the field of Chemistry, Agriculture and Soil Chemistry. Professor Sushil Kumar Mukherjee and she were associated with numerous organizations serving the society and humanity.

A RARE AND UNIQUE PERSONALITY

Each and everyone in the Jadavpur University campus knew her as the symbol of true academic personality. Prof. Rohatgi-Mukherjee used to come to the University driving her own car, by 10 O'clock. While getting down of her car, she used to pull a lady's bag full of books and papers with one hand, with a few more books and journals almost slipping out of her other hand. It was the same picture when she was leaving the campus. This one picture tells about her complete absorption in her work. She used to visit the library of the Indian Association for the Cultivation of Science, which is situated across the road, on a regular basis. It seems she used to relax not on a cup of tea, but by going through the different articles in some journal or other. Sometimes it happened that she was not satisfied herself by reading an article. She made a copy of it and distributed it to us for our information. This is an example of her greatness. She wanted to improve the information level of her associates and colleagues to keep them up to date.

Another important feature of her character which distinguishes her from the rest is that she never criticized any person even if the person criticized her on the wrong ground, due to jealousy or biasness. And, even more surprising, she helped those critics whenever they needed her helps irrespective of whether it was asked for or not. She used to help her students academically, and if needed, financially whenever possible. She never hesitated to help a student, sacrificing her own interest.

Personally, she was very sensitive to old values of the society. Sometimes we did not agree relating to seniority of age on some social systems or values, teacher-student relation as master-disciple relation, or the limits of duty and responsibility etc. Even if we did not agree, her concern and deep feeling of the effects of social changes made us think over changes and their consequences.

FUNDAMENTALS OF PHOTOCHEMISTRY

In spite of her numerous academic and social occupations, she always felt the need of a good text book on applied photo sciences particularly on photochemistry. She collected the modern and up to date information on the subject and wrote the book *Fundamentals of Photochemistry* which was first published in 1978. Some reviews and comments can be cited to find the quality of the book.

On 15th February, 1979; *NEW SCIENTIST* wrote

"--- represents a useful attempt to collect the information required for an understanding of the concepts underlying photochemistry and photobiology together into one relatively small volume. The choice of material is good and text well organized".

In November, 1979; *CHOICE* wrote

"A detailed closely packed discussion of photochemistry, including the fundamental quantum mechanical basis of photochemical processes and extending to applications such as photosynthesis and solar energy storage".

In *Photochemistry and Photobiology,* Vol. 29, p.1055

"The book in review does present some unique features. The emphasis of this book is slated towards the aspects of spectroscopy and photo physics, occupying roughly two thirds of the text". This reviewer recommends this book as an excellent introduction to spectroscopy and photo physics as applied to photochemistry of organic, inorganic and biological systems.

American Scientist in its Volume 68, 1980 wrote

"There is a need for an uptodate book for students that deals with basic photophysics and photochemistry essential for understanding such molecular photochemistry. This relatively slim volume goes a long way toward satisfying that need".

After several decades of the publication of the book, the same comment is applicable even today. Not only the book but many her academic achievements would go definitely a long way. One of such is the establishment of *Indian Photobiology Society* which would definitely go a long way. The other adjective used by the reviewer is the word slim meaning slender in some cases and in some occasion it means artful. Persons who were acquainted with her person knew even at her old age she was slim and graceful.

LAST DAYS

This great scientist and graceful academic personality passed away on 31st December, 2009 in her sister's place at Nagpur. For the last ten years she was suffering from the memory loss problem and ill health. In her personal life she did not have any offspring but on her passing away her students lost their affectionate mother and mentor, while her family members lost their idol of moral values.

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