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ACHARYA PRAFULLA CHANDRA RAY: SOME IMPORTANT CONTRIBUTIONS IN CHEMICAL RESEARCH

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Acharya Prafulla Chandra Ray, noble son of our country was the pathfinder and originator of chemical research in modern India. He was a life long campaigner of promoting teaching and research in chemical sciences and developing chemical industries in our country. He was not only a devoted scientist, he was also a great philanthropist and a staunch nationalist. He lived a saint like simple life strongly adhering to the practice of plain living and high thinking. Swadeshi was his motto. Establishment of "Bengal Chemical and Pharmaceutical Works" is his efforts in this direction. Thus he paved the way for the then British ruled India becoming self reliant in the manufacture of drugs and food chemicals. So he was a pioneer of chemical industry in India. As a social worker and social reformer he rendered paramount services to his motherland. His love for knowledge of literature and history was remarkable. The History of Hindu Chemistry composed by him was the result of long and painstaking research extending over a period of 15 years and gives us the achievements of the ancient Indians in the domain of science. Above all he was really a true Acharya, whose life and teaching radiated the great inspiration to all. For his versatility he became a legend in his life time. In recent years when there is a trend in the erosion of values almost in every sphere of our life, it is hightime to make a sincere retrospection of Acharya Ray.

In this article some of these outstanding research areas will be highlighted with a short biographical sketch.

In an age of intellectual awakening on August 2, 1861, Prafulla Chandra Ray was born in a wealthy and cultured family, in the then undivided Bengal. After his early education in rural background and subsequent schooling and college education in Calcutta, he went to Edinburgh University with Gilchrist Scholarship for higher studies and research. Prafulla Chandra Ray had his grooming as a chemist initially from Alexander Peddler at Presidency College, Calcutta and subsequently during his graduate studies at Edinburgh University (1885-1888) from Prof. A. Crum. Brown. a notable chemist and teacher of that University. Prafulla Chandra was introduced to research by Prof. Brown. His doctoral work was on the chemistry of double sulphates. Mendeleeff's periodic law (1869) and periodic classification of elements on the basis of atomic weights was the hottest research topic on those days. Naturally young Prafulla Chandra

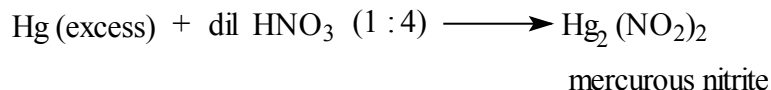
took up for his doctoral research, chemical investigation on the double sulphates of Copper Magnesium group metals with a view to find any chemical relationship, like isomorphism, existing among them. In 1887, he was awarded the D. Sc. Degree of the University of Edinburgh on the basis of the thesis "Conjugated Sulphates of Copper Magnesium group : A Study of Isomorphous Mixtures and Molecular Compositions." Later he published the paper on this work, in 1891 while working at Presidency College. This research theme however continued to reverberate in his thought during his later works (1927-1930), wherein he established the chemical homology existing among tetraalkyl ammonium, tetraalkyl phosphonium and tetraalkyl sulphonium cations with the alkali cations and isomorphism of sulphates, tetrafluoroberyllates and monofluorophosphates. He was elected Vice-President of the University of Edinburgh Chemical Society and was awarded Hope Prize Scholarship which enabled him to continue his work in that University for another year. In 1888 he returned to India. Though he had a Doctorate in Science, it became difficult to receive recognition in his own country. For about a year he spent his time working with his famous friend Acharya Jagadish Ch. Bose, in his laboratory. In June 1889, he joined Presidency College as an Assistant Professor. In 1890 he rented a small house at 91, Upper Circular Road, where he stayed for 27 years. He had a small laboratory in his house. It was here that the "Bengal Chemical & Pharmaceutical Works" was started before the publication of his first research paper in India.

When Ray joined, Presidency College did not have any good chemical laboratory. In 1894 a new chemical laboratory equipped with imported instruments was commissioned as a result of efforts of Ray, Prof. Peddler and Principal Tawney. Here in this laboratory we saw the dawn of pure chemical research.

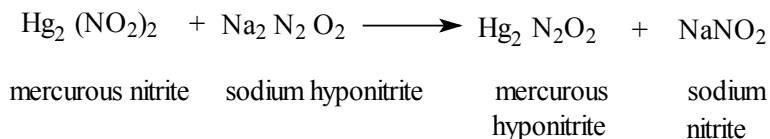
The adulterated food stuffs (oils, ghee, milk etc.) available in the market led Prafulla Chandra to determine the extent of adulteration by chemical analysis and publish the results in the form of paper entitled "Chemical Examination of Certain Indian Foodstuffs, Part I, Oils and Fats" in 1894 in the Journal of Asiatic Society (Bengal).

The first notable work of Sir P. C. Ray which brought him international recognition was the isolation and characterisation of mercurous nitrite in 1895. Ray conducted systematic chemical analysis of a number of rare Indian minerals with the object of discovering in them some of the missing elements in Mendeleeff's periodic table. In this process he isolated mercurous nitrite, which was not known then. Describing this event Ray wrote in his autobiography "the discovery of mercurous nitrite opened a new chapter in my life." The discovery of mercurous nitrite was an accidental one. He wanted to prepare water

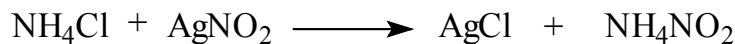
soluble mercurous nitrate, an intermediate for the synthesis of calomel, Hg_2Cl_2 by the action of cold and dilute nitric acid (1: 4) on mercury. He suddenly discovered the formation of bright yellow crystals of mercurous nitrite.



The discovery of mercurous nitrite and other metal nitrites found a significant importance in the field of chemistry, because mercurous compounds are highly unstable. In aqueous solution, mercurous nitrite is converted to mercuric nitrite with the formation of some amount of mercury. Such type of reaction is called disproportionation reaction.



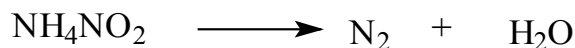
In 1896, Ray first published his findings in the Journal of Asiatic Society of Bengal which was immediately noticed by Nature, the famous international science journal. The discovery of mercurous nitrite prompted Ray to synthesize the nitrites of alkali and alkaline earth metals and of copper, silver, gold and also to study the thermal decomposition and physico chemical change of those nitrites. Such chemical studies led him to the conclusion that the compounds of nitrites have got certain degree of stability. Prafulla Chandra now prepared mercurous hyponitrite by treating mercurous nitrite with aqueous solution of sodium hyponitrite. Similarly was prepared mercuric hyponitrite from mercuric nitrite.



Synthesis of large number of hyponitrites of various metals and their chemical studies became a very fascinating task to him.

Another notable contribution made by P. C. Ray was the synthesis of ammonium nitrite (NH_4NO_2) in pure form. Before Ray's synthesis it was used to be believed that ammonium nitrite undergoes fast thermal decomposition (at $32/33^\circ\text{C}$) yielding nitrogen and water, as shown in the given reaction.

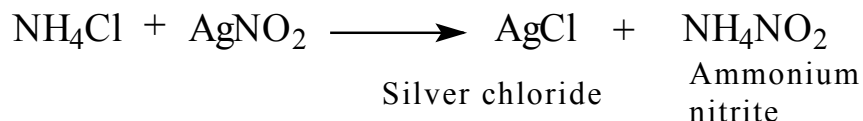
Mausumi Roychowdhury



(amm. nitrite) (nitrogen) Water

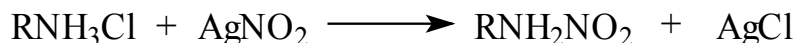
But Prafulla Chandra synthesized pure ammonium nitrite from the reaction between ammonium chloride (NH_4Cl) and silver nitrite

(AgNO_2) in double decomposition reaction and found that it is stable even at 60°C .

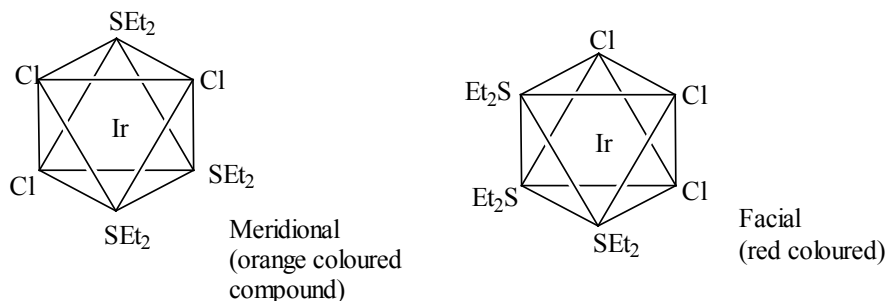


He heated ammonium nitrite to vaporise and measured its vapor density. He observed that NH_4NO_2 retains its identity even in vapor state. Ray along with his coworkers, Nilratan Dhar, Tinkori De published the paper "Vapour density of ammonium nitrite" comprising the results of above research works in the Journal of Chemical Society (London). For his enormous contribution towards chemistry of nitrites, P. C. Ray was designated by Prof. Armstrong as the "Master of nitrites".

Ray was also interested in the synthesis of simple alkyl and aryl ammonium nitrites. They were synthesised by the action of silver nitrite (AgNO_2) on alkyl or aryl ammonium nitrite (RNH_3Cl where R = alkyl or aryl gr) as shown by the following equation



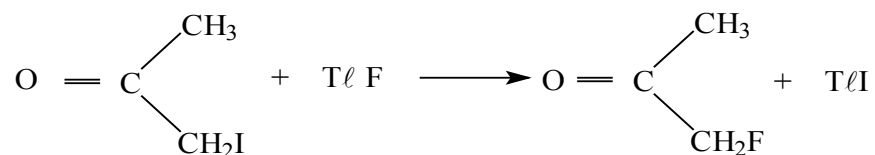
P. C. Ray found great interest in chemistry of complex salts. He prepared many complex salts of Iridium, platinum, palladium, gold etc and studied their chemical properties. In this endeavour to prepare these compounds he selected many types of sulphides and disulphides e.g. methyl or ethyl sulphides or diethyl sulphide etc, as ligands for co ordinating with metal. But the reaction between iridium tetrachloride and diethyl sulphide Ray synthesised trichlorotris diethyl sulphide Ir(III). $[\text{IrCl}_3 \cdot 3\text{Et}_2\text{S}]$ which exists in two isomeric forms, one facial and another meridional.



With the idea of capability of forming bonds of organic thio compounds with metals Ray synthesised a large number of compounds of platinum (Pt) of various valencies. For this purpose reactions were carried out by subjecting the thio compounds to the treatment with chloroplatinic acid. Khitish Ch. Basu, Bires Ch. Guha, Dinesh Ch. Sen, Sailesh Ch. Sengupta, Nripendranath Ghosh were involved in the above research work. Ray published the papers comprising the results of above investigation in 1923-24.

Thus, chemistry of metals and their compounds had always been the pivotal theme of his research work. Although he was greatly influenced by Alfred Warner's epoch making theory (1893) of coordination compounds, he did not hesitate in pointing out certain of his inadequacies in respect of variable valency of platinum group metals and it was possibly he, who for the first time (1926) proposed metal-metal bonding in complexes, a common feature in platinum metal chemistry, not pronounced in Warner's postulates. In addition to these, during the course of his long continued research life he extensively studied the chemistry of organic sulphur compounds and fluorination of organic compounds. Some of his works in this area are briefly narrated below.

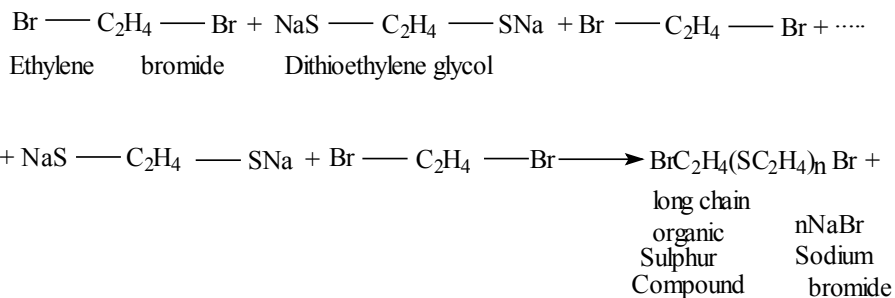
Ray prepared monofluoroacetone in high yields by the reaction of thallos fluoride with monoiodo acetone.



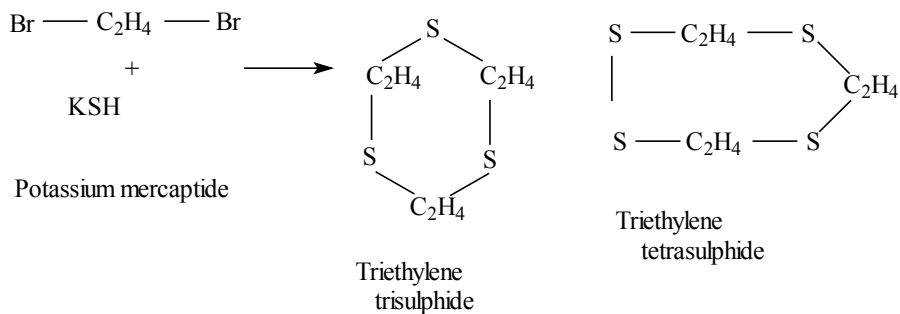
Applying this methodology Ray could synthesise methyl fluoroformate and fluoroacetal. Pulin Bihair Sarkar, Anil Chandra Ray were involved in this research work.

Mausumi Roychowdhury

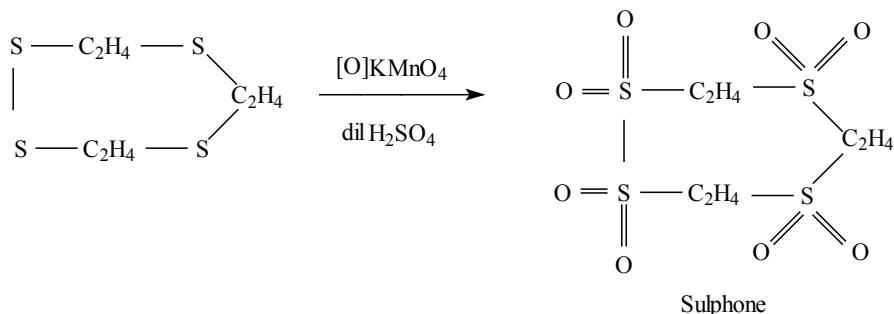
He had also a remarkable contribution in the synthesis of long chain organic sulphur compounds, which constituted an important part of his huge creative research work. The crystal of such organic thio compound of molecular weight 3064 was first prepared by him by the reaction of dithioethylene glycol and ethylene bromide, represented by the following equation.



His research on this area was not only confined in open chain compounds but was extended in cyclic systems also. He used potassium mercaptide and ethylene dibromide as starting materials for the synthesis of cyclic sulphides which on oxidation with potassium permanganate produced sulphones.



Mausumi Roychowdhury



His last research paper "Synthesis of Bis thiocamphors" was published in Nature, 1936, 138, 548. On passing hydrogen sulphide and dry hydrogen chloride gas over alcoholic solution of camphor, the compound bis thiocamphor was synthesised. This method finds wide application in the synthesis of thioketones. P. C. Ray pioneered this type of research works in 1934.

Prafulla Chandra joined the chemistry department of the University College of Science as Palit Prof. of chemistry on Nov. 1, 1916. In 1936 at the age of 75 he retired from active service and became Professor Emeritus. Long before that, on the completion of his 60th year in 1921, he made a free gift of his entire salary to the Calcutta University from that date onward, to be spent for the furtherance of chemical research and the development of Department of Chemistry in the University College of Science. He had published about 120 research papers mostly in research journals of international repute. A glance over his research papers would take one from the pre electron era of isomorphism, chemical homology and isomerism, through the days of electrochemistry and electronic concepts of chemical bonding to the days of spectroscopy, structure, stability and reactivity. Apart from his own research works, his greatest contribution to chemistry of course, had been the foundation, of the Indian Chemical Society (1924), a forum for publication of research findings of the chemists in India which was then under British rule and the creation of a talented school of chemistry in the University College of Science, which was later spread out all over the country by his many illustrious disciples like R. L. Dutta, H. K. Sen, B. B. Dey, J. N. Rakshit, N. R. Dhar, J. C. Ghosh, J. N. Mukherjee, P. Ray and others. They in turn later gradually set up many such flourishing schools of chemistry in different parts of the world. Thus was established the solid foundation of chemical research in India. This is why Acharya Ray is aptly called the doyen of chemical sciences in India. His life and work will serve as a light and inspiration to the present and future generation.

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