汪德熙文集

SELECTED WORKS OF WANG DEXI

原子能出版社

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中国原子能科学研究院
核工业研究生部 编
中国核学会

EDITED BY
CHINA INSTITUTE OF ATOMIC ENERGY
GRADUATE SCHOOL OF NUCLEAR INDUSTRY
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内 容 简 介

本文集收集了我国著名高分子化学家、核化学化工专家、中国科学院学部委员汪德熙教授 1935 年至 1993 年公开或未公开发表的部分文章，重点涉及纤维素、有机电解还原、糠醛塑料、不饱和聚酯玻璃钢、核燃料循环、冠醚化学和高放废物最终处置等领域，反映了汪德熙教授半个多世纪以来的主要科研生涯和学术贡献。

本文集可供广大科技工作者和大专院校师生阅读。

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序　言

汪德熙教授是我国著名的高分子化学家，核化学化工专家，中国科学院学部委员，全国“五一”劳动奖章获得者。

汪德熙教授1913年生于北京的一个书香门第，原籍江苏灌云县。1935年毕业于清华大学化学系，接着在该校从师著名化工专家张大煜教授攻读研究生，进行电解还原法制备有机偶氮化合物和用农村纤维素原料制备人造丝浆料的研究。两年后“七七”芦沟桥事变爆发，清华大学南迁，他曾去八路军冀中军区从事炸药研制工作。1938年底应导师张教授之邀，赴昆明西南联大任助教，并继续进行纸浆的研究工作。通过反复试验，他将碱法蒸煮改用两步法，节省了耗碱量和漂白所需的氯量，所得纸浆的α，β，γ纤维素含量完全符合人造丝用浆的要求。1940年考取清华大学赴美公费留学，次年9月进入美国麻省理工学院化工系，以电解还原葡萄糖制备可代替甘油的辛六醇为题进行博士论文研究。由于研究对象当时被列为军控物资，因而他的研究成果未能发表，至今仍留在麻省理工学院的图书馆里。1946年5月获博士学位后，毅然回国。1947年1月任天津南开大学化工系教授。

1949年新中国诞生后，汪教授夜以继日地努力工作。他用国产邻苯三酚和糠醛制备塑料，取得了创造性的研究成果，这在国际上属首创。1952年高等学校院系调整，他转入天津大学化工系，任系主任，并讲授“化工原理”、“高分子化学”等多门课程。在担任行政领导和教学工作的同时，继续在高分子化学科研领域辛勤耕耘，将方向瞄准能代替钢铁的不饱和聚酯玻璃钢，成功地制成小汽车壳体。他通过选择引发剂、促进剂及控制它们在反应物中的浓度和聚合反应速度，使加工成的小汽车外壳，不仅强度达到要求，而且光亮美观。在这一领域，他和他指导的研究生及青年教师一起完成了多篇论文。

1956年，他被邀请参加全国十二年科学技术发展远景规划的制定工作，主持《稀有金属》、《钛冶金》这两个专题规划的编写，由于预见性强、水平高，受到有关方面的重视。

1960年，我国原子能事业处于加速发展时期。当时二机部通过中央有关部门从高等院校、研究院所以及化工、石油等部门选调了包括汪德熙教授在内的多位专家、学者来部，以加强对各项工作的领导。汪教授被任命担任原子能研究所副所长，主要负责核化学、化工与分析等方面的科研、生产的组织领导工作。他以高度负责的精神，坚持实事求是，倡导“三严”作风，从而保证了各项工作的进度和质量。

60年代初期，在完成核武器引爆装置点火中子源的研制任务中，作为分工负责的副所长，汪教授起了重要的领导和组织作用。当时按三种方案组织三个小组攻关，齐头并进。他对三个组的工作都很关心，深入实际，帮助解决困难，他还亲自到实验现场指导研制工作，给年轻的科技工作者留下了深刻的印象。经过论证，其中一种方案被正式采用，在我国首次核武器试验中

发挥了重要作用。另外两项也为后来核武器的研制及其它应用工作打下了基础。这三项科研成果均荣获1978年全国科学大会奖。汪教授还直接组织各方面力量，完成多次核试验爆炸当量的测定，并提出用几种方法进行核对，按时提供了测量数据，受到有关方面的肯定，该项成果也荣获全国科学大会奖及国家发明奖。在二氧化铀、四氟化铀、六氟化铀生产技术攻关过程中，汪德熙教授主要负责抓分析方面的工作。这些产品的分析，要求达到相当高的灵敏度和准确度。他亲自讲授分析化学中的误差理论及数据处理，以保证分析工作的质量。这些分析方法最后都通过验收，在实际生产中发挥了重要作用。在放射性三废处理方面，在汪教授的领导下，进行了水泥固化、沥青固化、玻璃固化的研究。他还积极促进我国与国际原子能机构成员国之间在这一领域的技术交流与合作，从1988～1992年，汪教授担任了国际放射性废物管理顾问委员会的委员。

汪德熙教授在原子能事业发展中最为突出的贡献是在核燃料后处理方面。他积极支持将原来根据前苏联资料设计的沉淀法工艺流程改为萃取法，并提出在萃取过程中溶剂辐射分解造成的乳化，可能是一个关键性技术问题。他向二机部领导建议进行试验。1964年初，二机部成立了由部内外有关专家组成的调研组，由汪德熙教授任组长，到国内多个科研单位和工厂考察萃取设备运行情况，调查乳化问题和溶剂质量。接着，汪教授又直接领导了模拟强辐射条件下的乳化实验和多次萃取循环热试验。他亲临现场指挥，帮助解决技术问题。热试验的结果充分显示了萃取工艺的优良性能，为二机部领导决策将沉淀法改为萃取法提供了重要依据。1968年1月，按萃取法流程设计的后处理中间工厂投产一次成功，及时为核武器提供了首批钚装料。萃取法的实现使大型后处理厂取得了良好的效益，缩小了厂房面积，减少了不锈钢用量和试剂消耗，节省了大量投资，而且建厂工期提前一年完成。在这一重大革新中，汪德熙教授起了重要的作用。

汪教授在承担繁重的领导工作的同时，经常深入图书馆调研文献，以敏锐的目光密切注视着科学技术发展的新动向，抓住前沿课题，组织力量开展研究工作。当他看到冠醚的独特性能有可能提高化学交换法分离同位素的分离系数时，他积极倡导成立了冠醚科研小组，通过一系列研究，取得了较好的结果，使锂-6，锂-7的单级分离系数达到1.036，铀同位素的分离系数达到1.0007～1.001。他积极支持液膜分离技术课题组的工作，这个小组开发了具有创造性的静电式准液膜分离技术，避免了常规液膜的某些缺点，已取得多项国家专利。

1980年，汪德熙教授被选为中国科学院学部委员。1983年，被任命担任中国原子能科学研究院第一任科技委主任，从建立组织、确立科技委工作秩序，到卓有成效地完成一系列重大科研项目的论证、长远规划的审议以及成果评价等工作，发挥了科技委在重大科学技术问题决策中的参谋作用。他还积极支持建立我院青年科学基金和举办一年一度的院“五四”青年学术报告会，有力地促进了青年科技人才的成长。同时他还兼任核工业部科技委常委。1990年底当选为中国核学会第三届理事长。他长期担任《核化学与放射化学》主编和《核科学与工程》常务副主编，为提高学报水平和反映核科学技术最新研究成果作出了重要贡献。

汪教授关心并促进我国核电的及早发展，曾多次在国家计委、国家科委和中国核学会组织的会议上作报告、提建议。例如他主张在我国建立经济、合理的核燃料循环体系，主张在我国建

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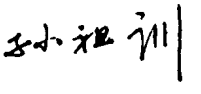
立动力堆后处理厂；在铀同位素分离方面，建议除搞离心法外，激光法、化学法亦应予以安排；他主张对放射性废物加以多层封闭，希望早日确定废物最终处置方案，建立国家废物库等。他的建议得到专家们的支持，并被有关领导部门采纳。

汪教授高瞻远瞩，重视人才的培养。在他的积极倡导和促进下，1985 年成立了核工业研究生部，他被任命为第一任研究生部主任。他呕心沥血，到处奔波，从报批到组建，从经费到设施，从课程设置到教师聘任，都亲自过问，一一落实。他自编“化工热力学”教材，以 70 多岁的高龄重登讲台，为研究生讲课。现在他任研究生部名誉主任，还为研究生部所办的“核电英语培训班”学员中的“尖子”学生开“小灶”，深受学生们的欢迎。研究生部能成为培养高层次专门人才的阵地，与汪教授的努力是分不开的。在他领导并担任教学工作的同时，继续抓住一些前沿性的课题指导硕士生、博士生进行研究，例如关于放射性核素在地质层和各类屏障材料中的吸附、滞留、扩散、迁移以及在地下水中的化学行为的研究。近年来他在“分离科学技术”“锕系元素化学”领域已培养出多名硕士生和博士生。他还曾亲自为中国原子能科学研究院的“英语班”讲课，培养了一批英语口语人才，有力地促进了院国际学术交流的广泛开展。

汪教授治学严谨，对工作要求严格，善于协调各方面的力量，共同做好工作。他关心国家大事，重视对青年的思想品德教育，言传身教，堪称楷模。他热情乐观，对生活充满信心。今天，虽已届杖朝之年，犹精神矍铄，活力充沛。他有一副歌唱家的好嗓子，在音乐方面的素养是早就为人们所称道的。在本文集的后面附有一篇他关于音乐的论述，可见他生活情趣的广泛。

总之，汪德熙教授是一位德高望重、卓有成就的科学家。这本文集不仅是他科研教学生涯的一个历史记录，而且将给我们，特别是中青年科学工作者以很大的教育与启迪。我们祝愿汪教授健康长寿，为我国的核科技事业作出新的贡献。



（中国原子能科学研究院院长）

1993 年 5 月

Preface

Professor Wang Dexi, formerly a polymer chemist, now a famous expert of nuclear chemistry and chemical engineering, member of Academia Sinica and the awardee of National "May 1st" Labor Medal, was born in a scholarly family in Beijing in 1913. His ancestors came from Guanyun County of Lianyun Gang City in Jiangsu Province.

After graduating from the Chemistry Department of Tsinghua University in 1935, he took two years' graduate course in the same university and , with Dr. Zhang Dayu, a celebrated professor of industrial chemistry as his advisor, he devoted himself to the studies on the preparations of organic azo compound by electrolytic reduction and of rayon pulp with farm cellulose byproducts as raw materials. Then the "July 7th" Lugouqiao Incident broke out and Tsinghua University had to be moved southward. He then once worked on the development of explosives for Jizhong (Central Hebei Province) Military Command of the Eighth Route Army.

At the end of 1938, at the invitation of Professor Zhang , he joined the Southwest Associated University, Kunming, as an assistant in the Department of Chemical Engineering, where he continued his studies on the pulp preparation. After repeated tests, he tried with "two-step" instead of "one-step" alkali digestion method to reduce the consumption of alkali and chlorine required for bleaching and succeeded to obtain a pulp, of which the contents of α, β and γ cellulose completely met the requirements of pulp for rayon fabrication.

In 1940, he was granted a scholarship for graduate study in the United States and entered the Department of Chemical Engineering of Massachusetts Institute of Technology (MIT) in September 1941. His doctoral dissertation was on the preparation of sorbitol, a possible substitute for glycerin, by electrolytic reduction of glucose. During those years, sorbitol was classified as a controlled material for military purpose. As a result, this piece of work was not published.

In May, 1946, he received his doctorate and came back from the U. S. without hesitation. In January, 1947, he joined the Department of Chemical Engineering of Nankai University, Tianjin, as a professor.

After the birth of New China in 1949, professor Wang worked hard day and night to synthesize plastics with home-made pyrogallol and furfural and obtained a thermosetting plastic, which was the first in the world at that time.

In 1952, following the reformation of high education system in China, he was transfered to Tianjin University as the Chairman of the Department of Chemical Engineering. He also taught several courses on "Principle of Chemical Engineering" and "Polymer Chemistry" in these universities. Besides administrative work and teaching, Professor Wang continued to plough in the field of polymer chemistry, aiming at the synthesis of the glass fiber reinforced plastic of unsaturated polyester, which could be a promising substitute for iron and steel. Af-

ter carefully screening the initiators and promoters, controlling their concentrations in the reactants to adjust the polymerization speed, he finally succeeded in making a car body which was both strong enough and beautiful. Together with his graduate students and young teachers, he wrote quite a few papers in this area.

In 1956, he was invited to join an experts team to draw up the "Twelve Years' Long-Range Plan for National Science and Technology Development". In this team, he was in charge of compiling recommendation reports on two special projects, "Rare Metals" and "Titanium Metallurgy", which were highly valued owing to their farsightedness and high academic level.

The year 1960 witnessed the period for quickening the pace of developing China's atomic energy. At that time, the central government authorized the Second Machinery Ministry (i. e. Nuclear Industry Ministry) to select a number of specialists and scholars from universities, research institutions and from chemical and petroleum industries to work under this ministry so as to strengthen the leadership of various departments of atomic energy researches. Professor Wang was among them and was appointed Deputy Director of Institute of Atomic Energy. He was mainly responsible for the organization of R and D work of nuclear chemistry and chemical engineering and analysis. With high conscientiousness, he sticked to the principle of seeking truth from facts and initiated a strict high quality working style. These were the guarantee for fulfilling various tasks on schedule with high quality.

Early in the 1960s, Professor Wang led and organized the development of the detonator of nuclear weapon——ignition neutron source. At first, three key-task teams were formed to work on three different schemes. He went into the midst of the young scientists to help them overcome difficulties. The young workers were deeply impressed by his working style. Later on, one of the schemes was adopted, which played an important role in China's nuclear weapons tests. The other two schemes also laid foundation for some other applications concerned with weapon development. All the above work was awarded the National Science Congress Prize in 1978.

Professor Wang also personally organized the scientific workers concerned to determine the TNT equivalent for several nuclear weapon tests. According to his suggestion, the measured data were checked with several methods before being sent out. This work was favorably appraised and also won the National Science Congress Prize and National Invention Award.

In tackling problems concerned with the production technologies of UO_2, UF_4 and UF_6, Professor Wang was in charge of the analyses of these products with reasonably high sensitivity and accuracy. He gave lectures on the error theory and data processing in analytical chemistry so as to ensure the high quality of the work. Finally, all the analytical methods were accepted and played an important role in quality control of these uranium compounds. In the field of radioactive waste treatment, work on cementization, bituminization and vitrification was carried out under the leadership of Professor Wang. He is also active in promoting

the technical exchange and cooperation between China and other member countries of IAEA in this area and had been invited as an advisor of the International Radioactive Waste Management Advisory Committee during 1988～1992.

Professor Wang's most outstanding contribution to the development of China's atomic energy is in the field of nuclear fuel reprocessing. He actively supported the proposal to change the precipitation process which was designed based on the former Soviet informations into solvent extraction process, and pointed out that the key problem would be the emulsification caused by radiolysis during the extraction process. He submitted a proposal to the ministry leaders, making suggestions to test and solve this problem. At the beginning of 1964, an investigation team including experts concerned from inside and outside the Second Machinery Ministry, headed by professor Wang, was formed to inspect the operation conditions of the solvent extraction setups in various research institutions and factories and investigated the emulsification problems and solvent quality. After that, Professor Wang led the emulsification experiments of the solvent extraction process with highly radioactive spent fuel dissolutions and several hot tests of the solvent extraction cycles. He directed on the spot to help the scientists there to solve the technical problem. The results of the hot tests fully demonstrated the excellent performance of solvent extraction process and provided important scientific basis for the decision-making of the ministry leaders to change the precipitation process into solvent extraction process. In January, 1968, a reprocessing pilot plant based on solvent extraction process was put into successful operation at one stroke. This plant timely provided the first batch of plutonium loading for China's nuclear weapon. The adoption of solvent extraction process to a large scale reprocessing plant resulted in the reduction of the plant's built-up area, lowering of the consumptions of stainless steel and the reagents, and the saving of enormous investment. This plant was built one year ahead of schedule and got very good beneficial results. Professor Wang played an important role in this major technical innovation.

One of Professor Wang's favorable practice is to go to the library to do literature survey. He is keen at grasping the frontiers of scientific problems and supporting researches in these areas. He is the first in our institute to notice the unique features of crown ethers which might increase the separation factor of isotope separation by chemial exchange method, and he actively initiated to establish a research group for crown ethers studies. Through a series of studies, fairly good results were obtained with single separation factor up to 1.036 for $^{6}Li/^{7}Li$ and 1.0007～1.001 for $^{235}U/^{238}U$. Professor Wang warmly supports the work of Liquid Membrane Group. This group has developed a new type liquid membrane called electrostatic pseudo liquid membrane. This technology avoids some drawbacks of the conventional liquid membranes, for which this group has taken out several Chinese patents.

In 1980, Professor Wang Dexi was elected to be the member of Academia Sinica. In 1983, he was appointed the first Chairman of Science & Technology Committee of China Institute of Atomic Energy. He built the functional structure and established working principles

of this committee. Under Professor Wang's leadership, this committee effectively audited a series of major research projects, examined the long-range plans and evaluated some major research results, thus giving full play to the role of advising on the decision making of the major scientific and technological problems. He also actively supported to establish the Youth Science Foundation of the institute and the "May 4th" Youth Academic Symposium which is held once a year. These have forcefully promoted the growth of the young scientists. He holds a concurrent post as the member of the Standing Committee of Science & Technology Committee of Nuclear Industry Ministry. In the end of 1990, he was elected to be the third president of the Chinese Nuclear Society. He has been serving as the Chief Editor of "Journal of Nuclear and Radiochemistry" and the Standing Deputy Chief Editor of "Nuclear Science and Engineering" for many years, making considerable contributions to raising the academic level and reflecting the most up-to-date developments in neclear science and technology.

Professor Wang showed great concern for China's nuclear power development and promoted its start. He gave lectures and put forward proposals at the meetings sponsored by National Planning Committee, National Science Committee and the Chinese Nuclear Society. For instance, he stands for the establishment of an optimized national nuclear fuel cycle system and the construction of fuel reprocessing plant for power reactors in China; for the uranium isotope separation, he suggests that chemical method should also be looked into besides centrifugal and laser methods; he advocates on the multi-barrier isolation method for the disposal of highly radioactive wastes and proposed an early start of the ultimate disposal projects for nuclear wastes and building of National Waste Repositories. His proposals have been supported by experts and adopted by the leading authorities concerned.

Showing great foresight, Professor Wang pays great attention to personnel training. As initiated and promoted by him, the Graduate School of Nuclear Industry was founded in 1985 and he was appointed to be the first director of the school. Taking infinite pains, he rushed about from place to place for running the school. He concerned himself with setting up the various departments of the school, the raising of funds, the collecting of facilities, the offering of courses and the appointment of teachers, etc. In his advanced age of 70s, he returned to the platform to give lectures to the graduate students on "Chemical Engineering Thermodynamics", wrote outlines and designed problems for the course. He is now the honorary director of the Graduate School. He renders special trainings to the top students from the "Nuclear Power English Training Course" run by the graduate school, for which he is warmly received by the students. It is with Professor Wang's efforts that the graduate school may become the base for training the qualified scientists. Besides the administrative and teaching activities, Professor Wang continues to direct his master and doctorate students to study in some frontiers of science and technology, such as the sorption, retention, diffusion and migration of the radioactive species in the geological formations and various barrier materials and their chemical behaviors in the underground water. In recent years, he has trained quite a few master and doctorate students in the fields of separation science and technology and actinides chemistry.

He also lectured in the "English Training Course" of our institute to improve the spoken English of our scientists.

Professor Wang possesses rigorous scholarship and is strict with his work. He is skillful in coordinating people from various departments to work well jointly. He concerns himself with state affairs, and pays attention to the ideological and moral education for the young generation. He teaches by personal example as well as by verbal instructions. He is enthusiastic, optimistic and full of confidence to life. He is now entering into his advanced age of 80, but still healthy and hearty in spirit and brimming with vigor. He has a beautiful singer's voice and his music accomplishment has long been known. An article of his exposition about music is attached in the end of this selected works, as an example to show some of his delights of life.

To sum up, Professor Wang Dexi is a fruitful scientist of noble character and high prestige. This selected works not only acts as a historic record of his career of scientific researches and teachings, but also serves as an enlightenment to us, especially to the young and middle-age scientists. We wish Professor Wang good health and a long life, making yet new contributions to the cause of China's nuclear science and technology.

Sun Zuxun
President, CIAE
May, 1993

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目　录

Electrolytic Reduction of Meta-Halogen-Nitrobenzenes to the Azo-Compounds

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The course of the electrolytic reduction of aromatic mononitro-compounds has been thoroughly studied by Haber[4] and it has been found that azoxy-, azo-, and hydrazo-compounds were the normal products of the reduction. Many methods for carrying out the electrolytic reduction were found in literature, but the best procedure for alkaline medium was described by Elbs[1] and Müller[5]. Following Müller's method, however, it was impossible to obtain the azocompounds of the mono-halogen derivatives of nitrobenzene by electrolytic reduction, since the corresponding azoxy-compounds were sparingly soluble in the medium (75% alcohol saturated with sodium acetate) and could not be further reduced. This was the property utilized by Elbs and Kremann[2] to prepare *m* -dichloro-azoxy-benzene. By modifying the apparatus described by Müller, using a rotatory cathode instead of a stationary one, and using an alcohol solution without sodium-acetate, the present authors have found it possible to reduce meta-chloro-, meta-bromo-, and meta-iodo-nitro-benzene with fairly high yields.

EXPERIMENTAL

The electrolytic cell consisted of a 400 cc. beaker in which stood a porous pot, 10cm. high and 5 cm. in diameter. The anode consisted of a rectangular strip of lead sheet bent into the form of a cylinder. The rotatory cathode consisted of a 100-mesh nickel wire-gauze cylinder. A long stout copper wire was threaded through the meshes of one end of the gauze-cylinder and welded. The remaining part of the copper-wire was then bent to such a position that the cylinder would rotate around it as axis, and, after passing through a mercury seal, the other end was sealed onto a glass rod fitted to a motor. The connection between mercury and the copper axis was made by welding a short copper-wire which was bent in such a way that it would rotate freely in the mercury seal around the axis. Another copper wire dipped into the latter and served to connect with the outside circuit.

Anolyte : Saturated solution of sodium carbonate.

Catholyte : 1/20 mole of the meta-halogen nitrobenzene in 60 cc. of 75% alcohol. (The *m* -chloro-nitrobenzene used was prepared from *m* -nitroaniline through Sandmeyer-Gatterman reaction, the *m* -bromo-nitrobenzene from nitrobenzene by direct bromination with iron powder as catalyst, and the *m* -iodo-nitrobenzene also from *m* -nitroaniline through Sandmeyer-Gattermann reaction.)

The anolyte and catholyte were heated to 70 C. and poured into the cell and pot respectively. The rotatory cathode was set in motion and the electrolyzing current adjusted to 5～6 amp. Fresh, cold 95% alcohol was added from time to time into the pot to compensate the loss by evaporation. After the theoretical amount of electricity (5. 35 amp. hrs.) had been passed through, the catholyte was poured out into a beaker, and the pot and the cathode washed clean into the latter with a mixture of alcohol and acetic acid. After allowing to cool to room temperature, the mixture was filtered and the precipitate washed with alcohol and then with water. The crude products were in all cases orange-yellow in color, and did not give definite melting points, because they were contaminated with some azoxy- and possibly a little hydrazo-compound as impurities.

Method of Purification: Since the azo-, azoxy-, and hydrazo- compounds exhibited nearly the same solubility behavior in ordinary solvents, it was quite difficult to separate them by recrystallization. For the bromo-cmpound, it was found that pure 3, 3′-dibromo-azobenzene might be obtained by repeated recrystallization from a mixture of alcohol and acetic acid, but the yield was low and the process laborious. For the other two compounds the pure azo-compounds could not be obtained even by this method. Basing upon the fact that the azoxy-compound would undergo a rearrangement into an alkali soluble compound[7] and the oxyazo-benzene and hydrazo-compounds a rearrangement into an acid soluble product —— benzidine[3,5], on treatment with concentrated sulfuric acid, while azo-compounds are not affected by this treatment, the present authors worked out a very satisfactory method for this purification.

The dry crude product was dissolved in the least amount of hot concentrated sulfuric acid. The solution was stirred and kept at 250 C. for a few minutes. It was then cooled, poured into a sufficient amount of crushed ice with vigorous stirring, filtered and washed with water. The precipitate was transferred into cold dilute sodium hydroxide solution and stirred. The mixture was filtered again and washed first with dilute alkali and then thoroughly with water. It was then dried. It might be further recrystallized from a mixturc of alcohol and acetic acid, whereby fine crystals with sharp m. p. were obtained. The final results obtained are shown below:

RESULTS

Average Yield of Products

Products	3-3′-dichloro-,	3-3′-dibromo-,	3-3′diiodo-azobenzene
Quantity of elect. used	5. 6 amp. hrs.	5. 44	5. 45
Current eff. for crude products	5. 8g, 89%.	6. 9g, 80. 3%	8. 9g, 78%
Current eff. for purified products	4. 8g, 74%.	5. 9g, 70%.	7. 2g, 65%

Porperties of the Pure Products

(1) 3-3′-*Dichloro-azobenzene*: Orange needles from a mixture of alcohol and acetic acid,

m. p. 100～101 C. It was found to be identical with that of Laubenheimer[5] and was insoluble in cold alcohol, cold acetic acid, and water; quite soluble in hot alcohol and acetic acid, ether and benzene. This compound had already been prepared electrolytically by Wülfigg[8], but in presence of sodium acetate and with lower yield; no exact procedure was given.

(2) 3-3′-*Dibromo-azobenzene*: Orange-red needles from a mixture of alcohol and acetic acid; m. p. 124～125 C; insoluble in warm alcohol or cold acetic acid; quite soluble in boiling alcohol; very soluble in hot acetic acid, ether and benzene. It was identical with the compound described by Gabriel[3].

(3) 3-3′-*Diiodo-azabenzene*: Long dark red needles from acetic acid or a mixture of acetic and alcohol; m. p. 150 C. It was identical with the compound described by of Gabriel[3]. It was found to be hardly solube in hot alcohol or cold acetic acid, but easily soluble in boiling acetic acid, cold benzene and ether.

All these products were found to be soluble in concentrated sulfuric acid, forming red solutions which darkened on heating. A drop of such a solution on a porcelain spot plate appeared yellow in color. This behavior might serve as a simple test to differentiate them from the azoxy-compounds whose solutions in concentrated sulfuric acid were also red, but a drop on spot plate appeared still red.

SUMMARY

(1) The meta-halogen-nitrobenzenes were electrolytically reduced to the corresponding 3-3′-dihalogen-azobenzenes with fairly high yields by using a rotatory nickel gauze cathode and a catholyte of 75% alcohol without sodium acetate.

(2) A new procedure was worked out to purify the reduction products by utilizing the different behavior of azoxy-, azo-, and hydrazo-compounds against concentrated sulfuric acid.

(3) The purified products were found identical with the known ones, and their physical properties and solubility behavior are described.

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