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REVISION BIBLIOGRAFICA

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ABSTRACT

Ernest Baudrimont (1821-1885) was a French chemist that carried a detailed study of the derivatives of sulfur and phosphorus, the treatment of cholera and diabetes, the origin of mineral waters, and certain organic chemistry reactions. He demonstrated that soft sulfur was different from ordinary sulfur, he synthesized what he believed was carbon monosulfide, CS; he achieved the synthesis of many dialkyl sulfides starting from ethyl iodide instead of ethyl chloride and found that sulfur chloride reacted only and easily with metals forming volatile chlorides. He also demonstrated that succinite (pale amber) contained sulfur. He studied the reaction of phosphorus pentachloride with 25 elements, characterized the products and their properties, prepared phosphorus chloro and bromosulfides, as well as white phosphorus. He developed various potions for the prevention and treatment of cholera and studied the possibility of using yeast for the treatment of the effects of diabetes.

Keywords: amber, diabetes, cholera, mineral waters, phosphorus derivatives, sulfur derivatives.

RESUMEN

Ernesto Baudrimont (1821-1885) fue un químico francés que realizó un estudio detallado de los derivados del azufre y del fósforo, el tratamiento de la cólera y la diabetes, el origen de las aguas minerales, y ciertas reacciones químicas. Demostró que el azufre blando era diferente del azufre corriente, sintetizó lo que él creía que era el monosulfuro de carbono, CS, realizó la síntesis de muchos sulfuros de dialquil usando ioduro de etilo en vez de cloruro de etilo, y encontró que el cloruro de azufre reaccionaba solo y fácilmente con los metales que formaban cloruros volátiles. Demostró que la succinita (ámbar pálido) contenía azufre. Estudió la reacción del pentasulfuro de fósforo con 25 elementos, caracterizó los productos y sus propiedades, preparó el clorosulfuro y bromosulfuro de fósforo, así como el azufre blanco. Desarrolló varios brebajes para la prevención y tratamiento del cólera y estudió la posibilidad de usar la levadura para el tratamiento de los efectos de la diabetes.

Palabras claves: aguas minerales, ámbar, cólera, derivados del azufre, derivados del fósforo, diabetes.

INTRODUCTION

Life and career (Baudrimont, 1878; Joulie, 1885; Méhu, 1885, Wagner, 1886, Bonté, 2004)

Ernest Baudrimont was born in Compiègne (Oise) on September 2, 1821, the son of Marie Joseph Victor Baudrimont and Marie Angélique Virginie Coquin, and nephew of the famous pharmacist chemist Alexandre Baudrimont (1806-1880). At the age of 15, after finishing his elemental education, he moved to Paris and worked as assistant *préparateur* at the chemical laboratory of Jean Baptiste Dumas (1800-1884) in the Collège de France and afterwards, as préparateur of the chemistry course given by his uncle Alexander. In 1842 he entered by competition the Paris hospitals as pharmacy intern; his successful studies earned him the 1843 and 1845 Internat medals. In 1845 he received his diploma of bachelor ès-letters and in 1846 he earned his third and fourth medal, this time from the École de Pharmacie, and was also awarded his diploma of Bachelor of Sciences. In 1849 the Ministry of Agriculture and Commerce sent him as a pharmacist to different places in France to assist in the treatment of persons affected by the cholera plague. His successful performance earned him a silver medal from the Ministry and a gold one from the École de Pharmacie. In 1850 he was appointed préparateur at the École de Pharmacie de Paris and in 1852 he earned his degree of pharmacien de 1ère classe, after defending a dissertation on the formation and composition of mineral waters (Baudrimont, 1852). This work earned him the 1853 Capuron Prize of the Académie Nationale de Médicine de Paris. In 1854 he earned by competition the position of chief pharmacist in the civil hospitals of Paris. His first post was at the Sainte Eugénie Children's Hospital (today Trousseau hospital in Paris), a position he held until 1877 when he was appointed Director of the Paris Central Pharmacy of the Civilian Hospitals (after the retirement of Jean Antoine Regnault), a position he kept until his death. In 1864 the Faculty of Sciences of Pairs awarded him his degree of docteur ès-sciences physiques after successfully defending a thesis on the chlorides and bromides of phosphorus (Baudrimont, 1864). In 1865 he was appointed by competition, adjunct professor of chemistry by the École de Pharmacie de Paris, then, director of practical works (1866-1868) and adjunct professor of practical pharmacy (1872), a position he kept until 1874 when he was promoted to full professor. During this period, he also occupied several additional academic positions, for example, professor of chemistry and botany at the Association Philotechnique and professor of raw materials, at the École de Commerce,

Baudrimont died in Paris on September 14, 1885, after a long illness.

Baudrimont was fully recognized for his research, professional, and public activities. He was elected member of the Société de Pharmacie de Paris (1855), serving as its secretary, (1858), archivist (1866), and vice-president (1876); member of the Société d'Hydrologie Médicale (1855), the Société Botanique de France (1855); the Société Chimique de France (1859); Société de Médicine Publique et d'Hygiène Professionnelle (1877), and Académie de Médicine de France (pharmacy section) (1881), replacing Jacques Personne (1816-1880). He was corresponding member of Colegio de Farmacéuticos de Barcelona (1858), the Cercle Pharmaceutique de la Marne (1862), the Société d'Agriculture de Nancy (1869); the Société de Pharmacie de Bruxelles (1872), the Centro Farmacêutico Portugal da Porto (1874); and of the Société de Pharmacie de Meurthe-et-Moselle. He was also honorary member of the Sociedade Farmacêutica Lusitana (1876). Baudrimont received several important awards for his scientific achievements, among them, Officier d'Académie (1864) and Officier de l'Instruction Publique (1870) (two appointments awarded to distinguished academics), and awards from the French Minister of Agriculture and Commerce and from the École de Pharmacie (1850, 1854) for his contribution to the effort to control the cholera plagues of 1849 and 1854. He was a founder member of the Société des Pharmaciens and Chef des Hôpitaux Civils de Paris (1870) and in 1878 he was nominated Chevalier de la Légion d'Honneur.

Scientific contribution

Baudrimont wrote more than 80 papers and books (e.g., Baudrimont, 1852, 1864b, 1864c; 1865c; Chevallier & Baudrimont, 1895) on the subjects of inorganic, organic, and agricultural chemistry, vegetable principles, physiology, toxicology, etc. He also prepared a booklet describing his research activities and achievements (as usual for candidates to the French Academy of Medicine) (Baudrimont, 1878). He was a main collaborator of the dictionary of the alterations and falsifications of foodstuffs of Alphonse Chevallier (1828-1875) (Chevallier & Baudrimont, 1895). In addition to the subjects described below, he measured the relative amounts of gases flowing through an orifice of given diameter, for a given length of time (Baudrimont, 1856a); he analyzed fertilizers and artificial guanos, and established the criteria for appreciating their quality (Baudrimont, 1857ab); he studied the properties of iodine starch, cold or hot (Baudrimont, 1860b); analyzed the cinders of common eelgrass *Zostera marina* (Baudrimont, 1862a), examined the gas contained in the vesicles of the brown algae *Fucus vesiculosus* and *Fucus nodosus* (Baudrimont, 1865a); the fungus *Lycoperdon giganteum* (Baudrimont, 1867a); the action of chloroform on the liquor of Fromherz (Baudrimont, 1869); the falsification of cochineal (Baudrimont, 1870); the preparation, physical, chemical, and physiological properties of zinc phosphide (Baudrimont, 1879); etc.

Sulfur derivatives

Soft sulfur

Baudrimont observed that after leaving a mixture of fresh soft sulfur and turpentine in a closed glass tube for a few days, the fragments of sulfur became opaque and covered by a large number of small transparent and brilliant crystals, which also lined the sides of the tube (Baudrimont, 1856a). After several months, these crystals had achieved a noticeable size, which did not appear afterwards to increase. These were modifications of the symmetrical octahedron, which sulfur gave when it was crystallized at the ordinary temperature. The fact that this crystallization took place only at the surface of the sulfur and not in its mass indicated that it was not caused by the direct transformation of soft sulfur into octahedral sulfur. Baudrimont speculated that this phenomenon was caused by the greater solubility of the soft sulfur in the turpentine compared to that of ordinary sulfur, and to a return of the first sulfur to the latter state within the liquid itself, from where it was supposed to result the precipitation of a part of the body dissolved in the essence. He tested his hypothesis with the following simple experiment: A mixture of 5 g of ordinary sulfur in 50 g of turpentine was left alone at 15 °C for 24 hours. He found that 0.315 g of sulfur had dissolved, compared with 0.513 g of soft sulfur under the same conditions, representing, for 100 parts of turpentine, 0.630 g of ordinary sulfur and 1.016 g of soft sulfur. These results confirmed the assumption that soft sulfur was substantially more soluble in turpentine than ordinary sulfur. He also found that no crystallization took place with sulfur flowers, sulfur deposited from hyposulfites and polysulfides, as well as from aged soft sulfur (which had become hard). All these results indicated clearly that both sulfurs (ordinary and soft) were chemically different, as proved by their different solubility in the same solvent (Baudrimont, 1856b).

Sulfides

In 1796 Wilhelm Augustus Lampadius (1772-1842) accidentally discovered carbon disulfide when trying to determine how much sulfur the mineral pyrite (FeS_2) would furnish when heated with charcoal. He obtained a very sulfurous liquid that he suspected was a compound of hydrogen and sulfur and which he named *alcohol sulfur*. He was unable to determine its composition; he only reported that it was very volatile and seemed to be an alcohol containing sulfur (Lampadius, 1803). In 1802 Nicolas Clément (1779-1842) and Charles-Bernard Desormes (1777-1862) rediscovered this compound during their experiments on the nature of carbon that tried to demonstrate that it did not contain hydrogen (Clément and Desormes, 1802). They found that sulfur and carbon combined at high temperature and probably in different proportions. The most interesting product was one that was liquid at room temperature and pressure, which they prepared by passing vaporized sulfur through an ignited porcelain tube containing carbon in fragments and powder (it could also be prepared by heating antimony sulfide with carbon). The pure compound was transparent and colorless, had a disagreeable and pungent smell and was heavier than water. Submission of the compound to a series of different experiments showed that it was a combination of sulfur and carbon, with no traces of hydrogen; hence it should properly be called *carbureted sulfur*. Claude Louis Berthollet (1748-1822) repeated the experiments of Clément and Desormes and concluded that carbureted sulfur was actually a compound of sulfur and hydrogen and did not contain carbon (Berthollet, 1802). A few years later Louis Nicolas Vauquelin (1763-1829) replicated the experiments of Clément and Désormes, using a slightly modified apparatus that allowed distillation of the product of the reaction (Vauquelin, 1807). The resulting liquid (*liquid sulfur*) was slightly green due to the presence of sulfur; distillation yielded a perfectly translucent liquid, which caught fire promptly when coming close to an ignited body. He reported its reaction with sulfuric and nitric acids, KOH, ammonia, alcohol, etc. Passing its vapors over heated copper resulted in the formation of carbon and copper sulfide, indicating the presence of carbon and sulfur. In 1813 Jöns Jacob Berzelius (1779-1848) and Alexander Marcet (1777-1822) determined the correct formula of carbon disulfide as CS_2 and found that it reacted as an acid with alkalis to form thiocarbonates (Berzelius and Marcet, 1813). Berzelius and Marcet prepared the compound using the procedure of Clément and Désormes, by slowly volatilizing sulfur through red hot charcoal in a porcelain tube, condensing in water the oily liquid formed, and purifying it by distillation at a temperature not exceeding 100-110 ºC in a retort containing dry calcium chloride. Experiments with a Volta eudiometer proved that the compound did not contain hydrogen, and combustion experiments with pure oxygen and dissolution in baryta water showed that it contained carbon, and hence, that the compound was a true *carbon sulfuret* (carbon sulfide). Distilling the sulfide through ignited iron oxide and analyzing the resulting iron sulfide and gas mixture of SO_2 and CO_2 determined the proportion of carbon and sulfur. The results of these procedures indicated that the alcohol of sulfur contained, by weight, 84.83% sulfur and 15.17% carbon, that is, two atoms of sulfur to one of carbon (Berzelius and Marcet, 1823).

In a paper published in 1857 Baudrimont wrote that it was known that there existed a carbon sulfide CS_2 corresponding to the carbon dioxide CO_2, but it was not known if there was a carbon *sub-sulfide* corresponding carbon monoxide (Baudrimont, 1857b). He was now happy to announce to the Académie des Sciences that he had been able to synthesize this compound by several procedures, for example, by decomposing the vapors of carbon disulfide by means of platinum sponge or pumice stone heated red. In this reaction the disulfide separated into a large amount of sulfur and a gaseous product that could be shown to be the sub-sulfide. It was also obtained as a by-product during the standard production of carbon disulfide; by the decomposition of CS_2 vapors heated red, over carbon black, charcoal, and particularly, over fragments of bone char; by decomposing CS_2 vapors heated red with hydrogen; by calcining antimony sulfide with an excess of carbon; by reacting at red hot a mixture of carbon monoxide and hydrogen sulfide or of ethylene and sulfur chloride; and finally, as a byproduct of the hot decomposition of sulfocyanogen. The first method seemed to be the best; all the others yielded a mixture of hydrogen sulfide and carbon monoxide. The product could be purified by streaming it through solutions of lead acetate and of cuprous chloride followed by dissolution in HCl, drying, and collection under mercury. Carbon sub-sulfide was a colorless gas, smelling like ordinary carbon disulfide but not as disagreeable. Inhaled in large amounts it seemed to be anesthetic. It burned with a blue flame releasing CO_2, hydrogen sulfide, and a little sulfur. It was heavier than CO_2 and did not liquefy with a freezing mixture of ice and salt. It dissolved in water decomposing promptly into hydrogen sulfide and carbon monoxide. It was insoluble in alcohol and ether and was not absorbed by a solution of cuprous oxide. It was decomposed rapidly by aqueous solutions of NaOH or KOH. With limewater it yielded calcium sulfide and a volume of CO identical to that of the gas employed, and no calcium carbonate. A eudiometric analysis with oxygen produced an equal volume of CO_2 and SO_2, indicating that its formula was CS. This composition was also justified by the reaction with limewater (Baudrimont, 1857c).

Dialky sulfides

Baudrimont wrote that ethyl chloride was used to prepare a variety of alkyl sulfides. Reacting this chloride with an alcoholic solution of different salts yielded, by double decomposition, the corresponding thiol. Nevertheless, several motives (i.e., high volatility) made this chloride inefficient. For this reason, Baudrimont decided to study the possibility of replacing it with ethyl iodide, easier to obtain and manage (Baudrimont. 1862d). Thus, to prepare diethyl sulfide he dissolved 100 g of KOH in five times its weight of alcohol 88°; divided the solution in two equal portions, saturated one of them with hydrogen sulfide and then mixed it with the other portion in order to have the equivalent of potassium monosulfide, KS. This mixture was put in a retort provided with a distillation neck and water cooling. He now added 50 g of ethyl bromide and when the reaction subsided, he added another portion of 50 g of ethyl bromide. This operation was repeated two more times. The final liquid was mixed with 5 to 6 times its volume in water and left to rest. The mixture separated into two liquid phases, the upper one containing the diethyl sulfide, and the lower one, the aqueous alcohol. The ethereal layer was separated, distilled, and collected over calcium chloride. The same procedure was used to prepare ethyl mercaptan from ethyl bromide and potassium hydrosulfide, and other mercaptans (Baudrimont, 1862d).

Sulfur chloride

Baudrimont studied the action of sulfur chloride on various metals and their sulfides (antimony, arsenic, tin, aluminum, mercury, iron, zinc, magnesium, and sodium) (Baudrimont, 1867b). He found that the reaction in which metallic chloride was formed and sulfur precipitated, took place most readily with metals presenting volatile chlorides. Metals having non-volatile chlorides, such as sodium and magnesium, were practically not attacked by sulfur chloride. Thus, for example, the reaction of metallic antimony with sulfur chloride was spontaneous and highly energetic and yielded antimony trichloride and sulfur: $Sb + 3S_2Cl = SbCl_3 + 6S$. The action of sulfur chloride was so energetic that it also acted upon the resulting antimony sulfide causing its distillation and leaving a residue of sulfur alone: $SbS_3 + 3S_2Cl = SbCl_3 + 9S$. The reaction over yellow arsenic sulfide was even more intense, yielding liquefied products: $AsS_3 + 3S_2Cl = = AsCl_3 + 9S$. In opposition to these reactions, no action occurred when sulfur chloride was boiled with magnesium or sodium, even after 24 hours (Baudrimont, 1867b).

Sodium sulfide

According to Baudrimont, sodium sulfide, $Na_2S,9H_2O$, could be prepared by passing a stream of hydrogen sulfide through a concentrated solution of NaOH. The 1866 French Codex recommended a caustic solution of relative density 1.330 (30.20% NaOH) and that the gas be passed until it was absorbed no more. The resulting solution left alone and not in contact with air, deposited transparent and colorless crystals of sodium sulfide (Baudrimont, 1875). Many eminent chemists believed that this procedure actually produced a sodium hydrosulfide NaS,HS or NaHS, instead of the simple sulfide, and that it in order to obtain the true sulfide it was necessary to add an additional amount of NaOH, equal to the one employed in the first step. This criticism led Baudrimont to conduct a thorough examination of the Codex process and to conclude as follows (Baudrimont, 1875): (1) The Codex process yielded crystalline sodium sulfide; (2) the easy crystallization of the salt was due to is low solubility in NaOH, which was present in excess at the beginning of the process; (3) sodium hydrosulfide was much more soluble in the caustic solution than the sulfide, and was unable to precipitate at the beginning of the process; (4) addition of chloral hydrate to a solution of sodium sulfide resulted in the formation of a solution colored red intense. The presence of sodium hydrosulfide resulted in the deposit of a large amount of sulfur accompanied by a colorless liquid (Baudrimont, 1875). Baudrimont added that commercial caustic sodium always contained metal traces (iron, copper, silver), which were precipitated by hydrogen sulfide and redissolved by the excess of NaOH present. These impurities had to be eliminated previous to the crystallization process because they tinted brown the sodium sulfide crystals. For this purpose, it was enough to add a small first portion of hydrogen sulfide and leave the solution alone for 24 hours, followed by filtration and addition of the remaining amount of acid (Baudrimont, 1875).

Succinite (Baltic amber)

Succinite is a class of amber (fossilized tree resin) characterized by is high content of succinic acid. According to Baudrimont, many papers had been published regarding it properties. Although classified as a mineral, there was no doubt concerning its vegetable origin. Many theories had been proposed regarding its nature and source, but there was nothing certain about the plant that had given it place. The organized residues that sometimes it contained (flowers, insects, etc.), or its chemical composition, provided a clue to this question (Baudrimont, 1864a). Nicolas-Jean-Baptiste-Gaston Guibourt (1790–1867) suggested that its special resinous nature approximated that of analogous substances provided by certain *Hymanaea* or by *Pinus dammara* (Guibourt, 1839), but there were too many differences to accept this proposition. Also, there were too many varieties of succinite with different properties to assume they had a common origin. Whatever its composition, it seemed to contain the same immediate principles and a relatively constant composition. Baudrimont added that C. A. Recluz had shown that white and opaque amber contained more succinic acid than the perfectly transparent yellow sort (Recluz, 1839), and Auguste Drapiez (1778-1856) had analyzed it and found it to contain carbon, hydrogen, oxygen, and a small proportion of ashes consisting of lime, alumina, and silica (Drapiez, 1819). Baudrimont, however, thought that it contained another element not hitherto mentioned sulfur. He had found that heating a few fragments of succinite in a test tube up to the beginning of distillation resulted in the evolution of white fumes that turned black immediately a paper impregnated with acetate of lead, unmistakably denoting the presence of a sulfurized compound. All the samples of succinite he had examined showed this behavior. He determined the amount of sulfur present by oxidizing the sample with a mixture of KOH and potassium nitrate and converting it into barium sulfate. The results indicated that the amount of sulfur contained in yellow succinite was no more that about 0.50%. He could not determine in which form the sulfur was present in succinite. Was it contained in the essential oil, in the two soluble resins, or in the insoluble bitumen contained in the succinite? Anyhow, Baudrimont believed that it was combined with organic matter because distillation of the portion of yellow succinite soluble in ether yielded hydrogen sulfide. This finding suggested the possibility that succinite originated from vegetables that contained succinic acid and sulfurized principles, such as the *Cruciferae* (*Brassicaceae*), the *Alliaceae*, or the gum resins of the *Umbelliferae*. Baudrimont added that he had been unable to detect the presence of sulfur in substances analogous to succinite, such as copal and Dammar resins (Baudrimont, 1864a).

Phosphorus derivatives

Baudrimont did extensive research on the chemistry of phosphorus and its derivatives (Baudrimont, 1860a, 1861abc, 1862cd, 1864c, 1865b), and summarized most of it in his doctoral thesis (Baudrimont, 1864b). He mentioned that as a result he had investigated the action of phosphorus pentachloride on 25 elements (hydrogen, oxygen, sulfur, selenium, nitrogen, phosphorus, arsenic, antimony, chlorine, bromine, iodine, carbon, sodium, zinc, cadmium, aluminum, iron, tin, copper, lead, bismuth, mercury, silver, gold, and platinum). Some of his results were as follows:

Hydrogen

Streaming dry and pure hydrogen and phosphorus pentachloride into a glass tube heated red showed the formation of HCl, phosphorus trichloride that condensed on a refrigerated flask, and ordinary phosphorus. The high temperature slowly transformed the latter into red phosphorus. In addition, a gas was liberated that seemed to be a mixture of phosphine and the excess of hydrogen (Baudrimont, 1860a, 1864b). These results indicated that hydrogen acted simultaneously on the chlorine and the phosphorus of PCl_5.

Oxygen

The same process, conducted at the temperature dark red with dry and pure oxygen instead of hydrogen, showed the production of phosphorescence, the release of large amount of chlorine, and the formation of a residue of phosphorus pentachloride that slowly attacked the walls of the glass tube. In addition, inside a refrigerated flask, appeared a liquid, colored yellow by the chlorine, boiling at 110 ºC, condensing colorless, and being decomposed by water into HCl and phosphoric acid. This liquid was found to be phosphorus oxychloride, PCl_3O_2. According to Baudrimont, this reaction was the first example of the direct substitution of combined chlorine by oxygen (Baudrimont, 1860a, 1864b).

Sulfur

Heating a mixture of four equivalents of sulfur and of PCl_5 resulted in the immediate liquefaction of the mixture, yielding a yellow product that smelled like sulfur chloride (Baudrimont, 1864b). Upon heating, it started boiling at 100 ºC and the liquid fraction that passed between 125º and 150 ºC condensed into crystals very similar to those of PCl_5, but of a different nature. According to John Hall Gladstone (1827-1902) this fraction was a mixture of a liquid boiling at 118 ºC, having the possible formula $PCl_3,2S_2Cl$, and crystals of PCl_5S_4 (Gladstone, 1851). Charles Gerhardt (1816-1856) believed that the mixture of Gladstone was actually a mixture of sulfur chloride and phosphorus sulfochloride (Gerhardt, 1853-1856). According to Baudrimont, independently of the true answer, the reaction between sulfur and PCl_5 took place between 4 equivalents of the former and 1 of the latter: $4S + PCl_5 = PCl_5S_4$. His results indicated that an excess of sulfur did not change the result of the reaction (Baudrimont, 1864b).

Selenium

The reaction between four equivalents of selenium with one of PCl_5 was fast and complete (Baudrimont, 1864b). Distillation of the liquid product produced two unequal fractions; the first one was a colorless liquid boiling at 80 ºC that water decomposed into HCl and P_2O_3, and without traces of selenium. The second fraction was a red brown liquid, boiling above 100 ºC and composed of Se_2Cl. The actual reaction between selenium and PCl_5 could be represented as follows: $PCl_5 + 4Se = PCl_3 + 2Se_2Cl$. Baudrimont was unable to use the same reaction to produce $SeCl_2$. He also tried unsuccessfully to prepare phosphorus chloroselenide, PCl_3S_3, by the reaction of PCl_5 with antimony selenide, $SbSe^3$, phosphorus with $SeCl_2$, and PCl_5 with phosphorus pentasulfide, PSe_5. Anyhow, PCl_5 reacted energetically with warm $SbSe_3$ to yield PCl_3, $SbCl_2$, and Se_2Cl, which were difficult to separate one from the other (Baudrimont, 1864b).

Sodium

Pieces of sodium mixed with PCl_5 resulted in the metal being covered by a layer of sodium chloride, which stopped the complete action between the two substances. Addition of melted sodium to PCl_5 resulted in almost an explosion, accompanied by strong incandescence, forcing to add the sodium slowly and in very small portions. The resulting product was a mixture of sodium chloride and sodium phosphide. Addition of water produced phosphine, very flammable (Baudrimont, 1864b).

Platinum

Platinum sponge reacted readily with PCl_5, yielding PCl_3, $PtCl_2$, and a double chloride of platinum and PCl_5. The latter melted and sublimed when in the presence of an excess of PCl_5 (Baudrimont, 1864b).

Hydrogen sulfide

Georges Simon Sérullas (1774-1832) was the first to observe that hydrogen sulfide transformed PCl_3 into phosphorus sulfide, PS_3, and HCl. Baudrimont reported that the reaction occurred more rapidly and easily if hydrogen sulfide was bubbled through boiling PCl_3 (Sérullas, 1829; Baudrimont, 1864b).

Phosphorus chlorosulfide

Sérrullas was the first to prepare this compound by adding powdered phosphorus pentachloride to a flask full of dry hydrogen sulfide. In a short time. the contents turned into a colorless and transparent liquid, accompanied by HCl. Fractional distillation of the product yielded a liquid fraction, heavier than water, having a piquant aromatic odor, boiling at 125 °C, and containing by weight, 18.484% phosphorus, 18.914% chlorine, and 62.601% sulfur, corresponding to the formula PCl_2S_2 (Sérullas, 1829). According to Baudrimont, Sérrullas had not realized that the action of hydrogen sulfide could go to the complete sulfurization of phosphorus, if the vapors of hydrogen sulfide and PCl_5 were passed through a tube heated dark red: $PCl_5 + 5HS = PS_5 + 5HCl$. In 1846 August Cahours prepared it by reacting phosphorus pentachloride over organic substances, demonstrating a more general form for the production of PCl_2S_2 (Cahours, 1846). In 1855 Friedrich Wöhler (1800-1882) proved that this compound could also be prepared by reacting sulfur chloride with phosphorus, although he did not determine its formula (Wöhler, 1855).

Baudrimont wrote that during his work on the action of phosphorus pentachloride over a variety of substances he had observed the formation of Sérullas phosphorus chlorosulfide every time that the pentachloride came into contact with sulfur, free or as sulfide. Pursuing this observation, he was able to obtain the sulfochloride easily and in large amounts (Baudrimont, 1861a, 1864b). The reaction with antimony sulfide was fast and neat: $3PCl_5 + 2SbS_3 = 3PCl_3S_2 + 2SbCl_2$. The resulting liquid was distilled at a temperature between 125° and 135 °C. The passing chlorosulfide was always accompanied by a certain amount of antimony chloride, which could not be eliminated by repeated distillation. Baudrimont found that the impurity could be destroyed by treatment with a diluted solution of sodium sulfide, taking advantage of the fact that the chlorosulfide was destroyed very slowly by water, particularly cold water. Baudrimont wrote the phosphorus chlorosulfide was a very mobile liquid, boiling at 124.55 °C and having an irritating odor, which became aromatic when diluted. It fumed in contact with air and its vapors irritated the eyes strongly. It was slowly decomposed by HCl, hydrogen sulfide, and phosphoric acid, and was strongly attacked by nitric acid (Baudrimont, 1861a, 1864b).

Four short additional notes reported that phosphorus bromosulfide, $PBr_{,}2S_2$ could be prepared by a similar procedure (Baudrimont, 1861b, 1864b), the action of phosphorus pentachloride over various chemical elements (Baudrimont, 1861c, 1864b), metallic sulfides (Baudrimont, 1862b), and other chlorides. These papers also reported the physical and chemical properties of the different derivatives (Baudrimont, 1862c, 1864b). According to Baudrimont, phosphorus pentachloride reacted with oxygen producing phosphorus oxychloride ($POCl_3$). Sulfur and selenium did not react in the same manner, sulfur gave a combination between PCl_3 and S_2Cl; selenium yielded neatly phosphorus trichloride and Se_2Cl but did not produce phosphorus chloroselenide, PCl_3S_2. Iodine yielded ICl that combined with an excess of PCl_5 to form the compound PCl_5, ICl. The metals (e.g., aluminum, tin, bismuth, iron, and platinum) heated to 130° to 140 °C (the volatilization temperature of PCl_5) produced phosphorus trichloride and metallic chlorides, which then combined with the excess of PCl_5 to yield double chlorides. In all the above reactions, PCl_5 exerted an action equivalent to highly condensed chlorine (Baudrimont, 1861c). In the last paper, Baudrimont reported the synthesis of the double chlorides PCl_5, $SeCl_2$; PCl_5, ICl; PCl_5, Al_2Cl_3; PCl_5, Fe_2Cl_3, PCl_5,$2SnCl_2$; PCl_5,3HgCl; and PCl_5, $PtCl_2$ (Baudrimont, 1862c, 1864b).

Baudrimont reached the following general conclusions regarding the action of PCl_5 upon different compounds: (1) this compound was able to attack a large number of chemical elements, particularly the metals, chlorinating them and sometimes, yielding double chlorides: (2) it also attacked easily the sulfide, yielding PS_5 when the metallic sulfide was in excess, or a chlorosulfide, when the PCl_5 was in excess. Phosphorus trichloride yielded PS_3 when the metallic sulfur was in excess; (3) many metallic or semi-metal chlorides combined with PCl_5 to yield well-defined compounds; (4) most of these chlorides had a pernicious influence on the respiratory system and for this reason were difficult to purify properly. This danger led Baudrimont to cut short the extent of this research (Baudrimont, 1864b).

White phosphorus

Baudrimont wrote that when normal phosphorus (colorless and transparent) was stored under water without contact with a strong light, it became covered with a white and opaque crust of white phosphorus (Baudrimont, 1865b). Many conflicting opinions had been expressed about the nature of this substance. For example, Théophile-Jules Pelouze (1807-1867) believed it was a phosphorus hydrate (Pelouze, 1832) and Alphonse Dupasquier (1793-1848) attributed its formation to calcium salts originating from the water that covered the phosphorus (Dupasquier, 1844).

As a consequence, Baudrimont decided to carry on additional experiments to try to determine the nature of white phosphorus and a procedure for its manufacture (Baudrimont, 1865b). First, he found that white phosphorus was not a hydrate: a piece of white phosphorus, weighing 0.63 g was heated to fusion and found to lose only 0.03 g. Another fragment, completely opaque and weighing 2.72 g, was melted underwater and found to lose 0.01 g. These numbers were not in any atomic ratio. In a third experiment, be put a piece of phosphorus weighing 5.22 g under water for 5 months and found that its weight had decreased by 5 mg while becoming completely covered by a white opaque crust. If the crust was a hydrate, the weight of the sample should have increased and not decreased. Additional experiments proved that white phosphorus was not the result of phosphorus changing from an amorphous to a crystalline state. Phosphorus should not be compared with other vitrified amorphous bodies such as soft sulfur, vitreous arsenic, and barley sugar, because it could be crystallized by simple fusion, the same as common sulfur. A microscopic examination of white phosphorus showed no signs of crystallization; its surface was rugged and vermiculated, had irregular granulation, and did not present any sharp edge. A sample of phosphorus was melted under distilled and deaerated water and left to cool for 5 months in the absence of contact with air and in the presence of light. At the end of this period the phosphorus had not lost its transparency. More experiments showed that white phosphorus was not an allotropic state of normal phosphorus. Both states had the same properties: they were soft, released white fumes in contact with air, shined in the dark, had the same melting temperature, and were equally soluble in carbon disulfide (Baudrimont, 1865b).

Baudrimont believed that his results proved that the production of white phosphorus was not due to the action of water or to a slow crystallization; it only took place under the extended influence of aerated water. This assumption was confirmed by the following two additional experiments: (1) a piece of phosphorus kept in a limited mass of aerated water for a long time, became only slightly white. The same phosphorus, kept under water while constantly renewing the air, became slowly covered with a crust of opaque phosphorus; and (2) one piece of phosphorus was put in contact with a stream of ordinary water for six days; another piece was kept under still water for the same length of time and temperature. At the end of this time the first piece was substantially whiter than the second one. Baudrimont concluded that white phosphorus was simply ordinary phosphorus irregularly corroded on its surface, and degraded, so to speak, by the oxidizing action of the air dissolved in water. Diffuse light was found to accelerate this slow combustion (Baudrimont, 1865b).

Physiology

Cholera

Baudrimont wrote "that in the presence of the scourge, which has been raging on us for a long time, it is the duty of everyone to publish the information, which can be used to cure cholera and to ward off the attacks of this fatal epidemic" (Baudrimont, 1854). He added that in 1832 his uncle Alexandre-Édouard Baudrimont (1806-1880) had studied the secretions of people affected by cholera and other symptoms of the disease and developed a treatment that had proved to be very successful during the pandemic of 1849. This treatment was based on the use of alkaline salts, particularly, sodium bicarbonate in high dose. Independently of how long the patient had been sick, he was given a potion containing 10-12 g of sodium bicarbonate (or 5 to 8 g for a child), 30 to 40 g of standard syrup, and 100 to 120 g of cold water. This medicine never failed to stop the diarrhea almost immediately and completely but did not always stop other cholera-like effects as promptly; for these it was necessary to administer the same dose every 12 hours. Sometimes, despite this drug, vomiting persisted; a teaspoon of ether syrup given from time to time stopped it easily. Ammonia, breathed at intervals, dissipated headache and deafness as a whole. A remedy which was especially effective against the terrible pains which produced cramps, was the ammonia liniment massaged until rubefaction of the skin, in the calves, wrists, stomach, etc., preceded or followed by the application of energetic sinapisms. Baudrimont added that cholera patients had difficulty in eliminating urine; this effect should not be treated with diuretic herbal teas because they were almost always rejected by the stomach. Nitro enemas (5 to 6 g of potassium nitrate per enema) restored this secretion with ease. (Baudrimont, 1854).

During the 1849 plague Baudrimont added the following recommendations: (1) the effect of the potion mentioned above was improved significantly by addition of 8 to 17 drops of aqueous ammonia; (2) restoration of the different functions during convalescence was helped by drinking a mixture of 125 g of quinine wine, 30 g of syrup of orange peelings, and 2 to 4 g of canella tincture; (3) the bicarbonate potion should not only be used as a cure, but also as a preventive of cholera. This measure was supported by the fact that no cholera cases occurred in Vichy, where the population was used to drink the local mineral waters, known to contain sodium bicarbonate (Baudrimont, 1854).

Effect of yeast on a diabetic patient

Baudrimont wrote that during some experiments conducted on a diabetic person, it occurred to him to investigate the possibility of using yeast, not as a remedial treatment of the illness, but for converting into alcohol the glucose produced constantly by the body of the patient (Baudrimont, 1856c). The patient in question was a male boy, 11 years old, who was treated with an alkaline medicine, which did not result in a significant reduction of sugar in the urine (30 g glucose/liter). At a certain time, a physical indisposition of the patient led to a suspension of this treatment, which Baudrimont used to start the treatment with yeast. The first day the boy was given 0.20 g of yeast and this dose increased daily for 12 days until it reached 5 g per day. After the fifth day, the boy, who had a very tranquil personality, begun showing symptoms of drunkenness; he became sulky, noisy, nasty, thoughtless, and aggressive, even attacking one of his friends. Eventually, the intensity of these symptoms decreased, the thirst decreased to about one half, but his urine continued to be unchanged. Unfortunately, a serious physical indisposition forced a stop of the treatment. The boy died four days after a serous effusion on the brain. In spite of the scarce information collected, Baudrimont became convinced that yeast was able to transform into alcohol the sugar of diabetes. Nevertheless, he mentioned that the symptoms of drunkenness observed could have equally been a result of the brain illness (Baudrimont, 1856c).

Mineral waters

As mentioned above, Baudrimont obtained his diploma of pharmacien de 1er classe, after defending a thesis about the temperature and composition of thermal waters and the factors that modified these properties (Baudrimont, 1852). According to this publication, the temperature of a source of mineral water could be attributed to five different sources: (1) a central fire, (2) the heat of volcanoes, (3) electrical currents; very few scientists believed that the temperature of a mineral source was determined by the electrical currents generated by the contact of the different layers of the earth crust; (4) chemical reactions, and (5) particular combustions present in certain locations such as collieries. These temperatures could change by the presence of volcanoes, earthquakes, the location height, mixing with other sources, abundance of rains, melting of snow, overflow of rivers, etc. Some of the factors that determined the composition of the source were the composition of the terrains they went through, chemical reactions with the substances present in these terrains, the pressure, the temperature, etc. The same factors could also lead to a change in composition (slow or fast with time) (Baudrimont, 1852).

White spots in photographic proofs

Baudrimont wrote that the use of photography on paper presented, sometimes, the appearance of white spots on the proofs, which destroyed their value as works of art and rendered them unsuitable for sale (Baudrimont, 1872). The photographers claimed that they were due to the poor quality of the photographic paper, caused, particularly, by the calcium hypochlorite used in the bleaching of the paper. The manufacturers defended themselves stating that chemical analysis of the paper showed no presence of hypochlorite, a claim substantiated by the fact that not all the samples of papers obtained from the same batch, presented the defect. They accused the photographers of not washing the papers sufficiently, leaving upon them with a small amount of sodium hyposulfite, the developing reagent. Baudrimont was requested to carry adequate experiments to try to find the real cause of the problem.

The first thing he did was to perform a complete analysis of the papers and the glues used to manufacture the plates on which the images were adhered. These experiments provided no answer to the question but indicated that the defect occurred only on the surface of the image and never on the back of the paper. This result led him to study the altered proofs. For these purposes he artificially produced spots over an intact proof by means of calcium hypochlorite, sodium hyposulfite, and potassium cyanide. Once the papers were dry, he applied a solution of silver nitrate to the spots. This action showed that the white spots produced by the hypochlorite and cyanide remained totally unchanged, while those originated by the hyposulfite became promptly yellow and turned brown afterwards. He repeated this same test on proofs that had become altered spontaneously. Examination of the spots under a magnifying glass showed that they very rapidly developed a yellow tint, which then turned brown. These results proved clearly the argument of the paper manufacturers that the white spots were originated by the hyposulfite employed in fixing the positive image. If the wash following this step were carried in an incomplete manner, the photograph would eventually originate white spots (Baudrimont, 1872).

Action of chloroform on the Frommherz reagent

Baudrimont wrote that of the many papers describing the reaction of chloroform with a variety of reagents, only two spoke of the reaction with the Fromherz reagent (potassium cupro-tartrate) (Baudrimont, 1869). Charles Leconte studied the absence of sugar in the urine of women during lactation and mentioned that chloroform was one of the many substances that could reduce potassium cupro-tartrate (Leconte, 1857). In 1869 Eugene Maréchal stated that for a long time it had been believed that the urine of patients subjected to chloroform inhalations contained sugar. This belief was found to be wrong, the error originated from the reagent. These urines, treated with a few drops of Charles-Louis Barreswil's (1817-1870) reagent (cupric tartrate and alkaline potassium) and then heated, presented a very sensitive reduction due to the chloroform, very similar to that of glucose. Chloroform did not remain for a long time in the animal economy; it was soon found in the products of the eliminating organs and mainly in the urine (Maréchal, 1869).

Baudrimont wrote that it was known that chloroform was decomposed by KOH into a chloride and alkaline formiate. The formiate themselves were also known to reduce most metallic salts, particularly silver nitrate, mercuric chloride, and potassium permanganate. Hence, it was natural to assume that the decomposition of chloroform by KOH would go through the two reactions in series. This was easily confirmed by experience: heating a mixture of chloroform with a few drops of the Fromherz liquor resulted in turbidity, loss of the blue color of the reagent, and precipitation of the yellow hydrate of cuprous oxide, which turned red upon loss of its water. This extremely sensitive reaction did not take place with free formiates: no reaction took place when boiling the Fromherz liquor with a soluble formiate. These results meant that formiates acted on the potassium cupro tartrate only in their nascent state, that is, at the moment they were generated by the decomposition of chloroform by alkalis. These reactions could be represented by the following equation:

$$\mathbf{C_2HCl_3 + 5KO + 4CuO = 3KCl + 2Cu_2O + HO + 2(CO_2.KOwit)}$$

As seen above, all the carbon became potassium carbonate while the hydrogen became part of the water and the chlorine of potassium chloride. Baudrimont added that the reductive action of chloroform could also be expected to occur with all other similar bodies, such as chloral, trichloroacetic acid, and perchlorinated composite ethers. The same behavior should be expected from the corresponding brominated compounds. Thus, it was easy to show that bromoform reduced the Fromherz reagent, although less energetically (Baudrimont, 1869)

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