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REVIEW ARTICLE

WILLIAM ODLING: The composition of hippuric acid and water – Toxicology

WILLIAM ODLING: la composición de ácido hipúrico y agua – Toxicología

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ABSTRACT

William Odling(1829-1921) was a British physician and chemist who carried on important work about chemical nomenclature, classification of the elements, techniques for the toxicological analysis of arsenic, antimony and copper, analysis of river and cesspool waters, etc. Odling showed that the different opinions regarding the composition of hippuric acid were due to the use of different reagents to attack only one of the components of the acid and that the overall picture showed that hippuric acid had to be composed of benzoic acid and glycine. Odling studied in detail the use of the toxicological exams of Reinsch for detecting arsenic, antimony and copper, and of Marsh for arsenic, and determined the appropriate conditions for avoiding false results as well as increase the detection limits. Together with Dupré they showed that copper was naturally present in a large variety of organic matter (i.e. bread, flour, wheat, blood, flesh, human muscle, liver and kidney tissue, etc.). Together with Buckton they used alkyl derivatives of aluminum to prove that the correct formula of aluminum chloride was AlCl3 and not Al2Cl3. Odling used speculative arguments to show that the atomic mass of oxygen was 16 and that the molecular mass and formula of water were 18 and H2O, respectively.

Keywords: aluminum chloride; copper; hippuric acid; toxicology; molecular formula of water

RESUMEN

William Odling(1829-1921) fue un médico y químico inglés que realizó importantes trabajos sobre nomenclatura química, clasificación de los elementos, técnicas de análisis toxicológico del arsénico, antimonio y cobre, análisis de aguas de río y aguas servidas, etc. Odling demostró que las opiniones contradictorias respecto a la composición del ácido hipúrico se debían al uso de distintos reactivos para atacar solo uno de los componentes del ácido y que un estudio *global* demostraba que este ácido estaba compuesto de ácido benzoico y glicina. Odling estudió en detalle el uso de los procedimientos toxicológicos de Reinsch para detectar arsénico, antimonio y cobre, y de Marsh para el arsénico, y determinó las condiciones apropiadas para evitar resultados falsos, así como aumentar la sensibilidad de estos ensayos. Junto con Dupré demostraron la presencia natural del cobre en una gran variedad de materia orgánica (i.e. pan, harina, trigo, sangre, carne, músculo humano, tejidos del hígado y riñón, etc.). Junto con Buckton usaron derivados alquílicos del aluminio para demostrar que la fórmula del cloruro de aluminio era $AlCl_3$ y no Al_2Cl_3. Oldlin gusó argumentos especulativos para demostrar que la masa atómica del oxígeno era 16 y que la masa molecular y fórmula del agua eran 18 y H_2O, respectivamente.

Palabras clave: ácido hipúrico; cobre; cloruro de aluminio; fórmula del agua; toxicología

Life and career (Marsh, 1921, Webb, 1937, Fischer, 1996)

William Odling was born in Southward, London, on September 5, 1829, the only son of George Odling, a medical practitioner and surgeon of the police force. He received his elementary education at Stockwell Primary School and at Nesbit's Chemical Academy and Agricultural College. In 1845 he began his medical studies at Guy´s Hospital from where he received his M.D. degree in 1851. During his last year of studies he served as demonstrator at Guy´s and acquired additional chemical knowledge attending the lectures given by August Wilhelm Hofmann (1818-1892) at the Royal College of Chemistry, and also spending some months at the laboratory of Charles-Frédéric Gerhardt (1816-1856) in Paris. After graduation Odling continued teaching at Guy´s while serving as medical officer of health for the Lambeth district in central London (1856–1862). Between 1863 and 1868 he succeeded Edward Frankland (1825-1899) as Chemistry Lecturer at St. Bartholomew's Hospital Medical School, a position he abandoned in 1868 to become Fullerian Professor of Chemistry at the Royal Institution, replacing Michael Faraday's (1791-1867) who had died the year before. He kept this chair until 1873, when he began a private practice on water analysis. In 1872 he succeeded Benjamin Brodie (1783-1862) as Waynflete Professor of Chemistry at Oxford University, a chair he held until his retirement in 1912. In the same year he married Elizabeth Mary Smee; from whom he had three sons. In 1872 he left the Royal Institution to become a fellow of Worcester College, Oxford, where he stayed still his retirement in 1912. Afterwards, he remained active until his death on February 17, 1921.

Odling held many important scientific and public positions. He was one of the secretaries of the Karlsruhe international chemistry conference held in 1860 to try to reach an agreement on matters of chemical nomenclature, notation, and atomic weights; a member of the organization committee of the Institute of Chemistry, and its Vice President, and President (1883-188). In 1848 he was elected Fellow of the Chemical Society and served as one of the two secretaries (1856–1869), Vice-President (1869–1873), and President (1873-1875); He was also Censor (1878–1880 and 1882–1891), Vice-President (1878–1880 and 1888–1891), and President (1883–1888) of the Institute of Chemistry. In 1859 he became Fellow of the Royal Society of London as well as of the Royal College of Physicians, and in 1875 he was granted an honorary PhD by Leiden University, Holland. He was also member of a Royal Commission on Beer Materials.

Although he had the ability and training to do laboratory work, Odling preferred theoretical subjects. He worked and published extensively about chemical nomenclature, atomic masses, and the periodic classification of the elements (e.g. Laurent & Odling, 1855; Odling, 1855ab, 1857, 1859c, 1860, 1862, 1864abc). As a result of these, he proposed a methane type for carbon (Odling, 1855b; Oldling & Crookes, 1869) and developed some important concepts regarding the new concept of valence (Hodling, 1859a, 1860). Other research publications were related with tests for arsenic and antimony (Odling, 1855b, 1856b, 1859a), emanations from sewers and cesspools (Hodling, 1856a) tests of the water of the river Thames (Hodling, 1858), the atomic mass of oxygen and water (Odling, 1859b, 1863), the composition of hippuric acid (Hodling, 1865), the formula of aluminum chloride (Buckton & Hodling, 1865), on the revival of the phlogiston theory (Odling, 1872a), the structure of ozone (Odling, 1872b.), etc. etc.

Scientific contribution

wrote over 60 papers and books in the areas of toxicology, physiological chemistry, analytical chemistry, animal husbandry, etc. Many of his books were based on the lectures given in different institutions (Odling, 1858, 1859c, 1860, 1864c, 1866b, 1870b, 1883, 1916; Odling & Crookes, 1869). His work on chemical nomenclature and classification of the elements has been described in detail by his biographers (Marsh, 1921, Webb, 1937, Fischer, 1996) and will not be repeated here.

Hippuric acid

In a short note published in 1865 Odling offered an explanation why several researchers had reported widely different opinions regarding the composition of hippuric acid, an important physiologic compound (Odling, 1865). For example, Théophile-Jules Pelouze (1807-1867) and Hermann von Fehling (1812-1885) believed that hippuric acid was a compound of benzamide with some form of acetic or glycocholic acid (Pelouze, 1838; Fehling, 1838); for Adolph Strecker (1822-1871) and Nikolai Sokoloff it was a combination of benzoglycocholic acid with ammonia (Strecker & Sokoloff, 1851), and for Victor Dessaignes (1800-1885) a compound of benzoic acid and glycosine (Dessaignes, 1845). In this note Odling intended to show the origin of these discrepancies and how they could be reconciled.

It was well known those complex substances of vegetable or animal origin were the result of the combination of two or more simple molecules and that this combination was usually accompanied by the elimination of one or more molecules of water. The decomposition of such a complex molecule into its constituent parts was accompanied by the taking up of the same number of water molecules released during its formation. A very simple example was the formation and decomposition of an organic ester: formation of the ester was accompanied by the release of one molecule of water, its decomposition, by the taking up of one molecule of water. According to the published results, hippuric acid seemed to contain benzamide, or benzoglycocholic acid, or glycosine. Odlingbelieved that benzamide was a compound of benzoic acid and ammonia with elimination of water. Under appropriate conditions, the constituent reagents could be recovered by absorption of water. Benzoglycocholic acid was a compound of benzoic and glycocholic acids, formed by elimination of one molecule of water, and decomposed by addition of the same amount of water. Similarly, glycosine was a compound of glycocholic acid and ammonia formed by elimination of one molecule of water and decomposed by the addition of one molecules of water. Odling remarked that it was also possible that hippuric acid was formed by the combination of the three components benzoic acid, glycocholic acid, and ammonia, with elimination of two molecules of water.

These arguments could be used to explain the differences among the different views regarding the composition of hippuric acid. Since each researcher had attacked one or more of the components of the acid with a different reagent, it was expectable that different products would be formed. Oldlingmentioned that of the three possible components of hippuric, acid, glycocholic acid was the most easy to oxidize, thus treatment with lead dioxide destroyed the latter and left benzoic acid and ammonia combined in the form of benzamide. This result had led Fehling to assume that hippuric acid was a compound of glycocholic acid (or a similar acid) with benzamide. Since ammonia reacted with nitric acid to produce water and nitrogen, the reaction of hippuric acid with nitric acid destroyed its ammonia residue and left the remaining components as benzoglycocholic acid (Strecker's assumption). Similarly, boiling hippuric acid with acid or alkalis separated the benzoic acid and left the remaining compounds combined as glycosine (Dessaignes' model). In summary, Odling remarked that treating hippuric acid with different reagents left the ammonia and benzoic acid combined as benzamide, or the benzoic and glycolic acid united as benzoglycocholic acid, or the glycolic and ammonia residues as glycine (Odling, 1865).

Odling indicated that his arguments pointed to three possibilities: hippuric acid was the result of the combination of benzoic acid + (glycocholic acid + ammonia); or ammonia + (benzoic acid + glycocholic acid); or glycocholic acid + (benzoic acid + ammonia). He believed that the third possibility was the most plausible one (Odling, 1865).

Detection of arsenic, antimony, and copper

In 1841 Hugo Reinsch (1809-1884) described a procedure in which metallic arsenic was deposited on copper foil from diluted HCl solutions (Reinsch, 1841). This test took less time than that of James Marsh (1794-1846) (Marsh, 1836) because it was fast and worked on liquids containing organic matter. It could also be used to detect mercury and antimony, which also formed stains on copper foil; to distinguish these two elements from arsenic it was enough to heat the foil in a glass tube to volatilize the deposit, and also by the form of the deposit: mercury formed globules of the pure metal, arsenic crystals of the white oxide, and antimony an amorphous mass of its oxide, although the latter was also white but usually clearly different from that of arsenic. The main defect of the test laid in the fact that both HCI and copper could often contain arsenical impurities; this required carrying a blank test to determine the amount of the impurities.

In 1855 Odling wrote that the Reinsch's test had been widely adopted by British toxicologists because it was sensitive, practically free from failure, easy and rapid to apply, and did not require any special equipment (Odling, 1855c). According to Odling, a clear and positive indication of the presence of arsenic was for the grey metallic deposit upon the copper coil to yield a crystalline sublimate, which treated with nitric and hydrochloric acids and evaporated to dryness, left a residue giving a brick dust colored precipitate with silver nitrate. If the characteristics of the deposit were different, then it had to be subject to additional testing in order to determine the possible presence of antimony, bismuth, and sulfur. Oldling also addressed the question of the presence or absence of arsenic when the test did not yield the characteristic deposit (Odling, 1855c).

Although it was that known that down to an amount of 10.3 grain (1 grain = 0.0645 g) the Reinsch test would give, in succession, a deposit upon copper gauze, an obvious crystalline sublimate, and a brick dust colored precipitate of silver arsenate, Oldling showed that careful handling could actually lower the detectable amount to 0.2x10-3 grain (dissolved in a mixture of 10.65 cm^3 of water and 3.55 cm^3 of HCl of specific gravity 1.16). To do so it was recommended to use fine copper gauze for the precipitation of the arsenic, and conduct the sublimation in a hard glass tube, 5 cm long, 0.3 cm inch diameter, sealed at one end, and drawn out at the other end so as to form an almost capillary of about 2.5 cm long (the paper included a drawing of the sublimation apparatus). Proper performance of the test required using extremely pure HCl, free as much as possible of arsenic, nitric acid, and free chlorine. Odling found that the effect of dilution was not as great as was generally assumed; decisive results were obtained when the dilution amounted to 2,250,000 times the weight of arsenious acid (As2O3). Extended boiling with the acid seemed to compensate the increased dilution. One objection to Reinsch's test was that during the ebullition with HCl, arsenic was volatilized as trichloride; but Odling believed that this objection was of no practical consequences because the loss was inappreciably small, and might be provided against by using a small retort for the operation (Odling, 1855c).

It was generally believed that Reinsch's test was applicable only for the detection of arsenical compounds that are soluble in dilute HCl. In many cases of poisoning the decomposition of the organic matter led to a conversion of all the arsenic into its sesquisulfide (As2S3), which was usually considered to be insoluble in dilute HCl. In other words, the arsenic would not be extracted from the organic substance and tissues by boiling with dilute HCl. Repeated experimentation showed Odling that cooking of the tissue in diluted HCl, or even pure water, was enough for detecting the poison (Odling, 1855c).

In a following paper Odling discussed the merits of Reinsch's method for the detection of antimony, particularly in cases of poisoning (Odling, 1856b). The experimental procedure he followed was very similar to the one used with arsenic. A solution of one thousandth of a grain of anhydrous tartar emetic (a double salt of antimony and potassium, well known since the Middle Ages as a powerful emetic) in 100 grains of diluted HCl was contacted with a piece of clean copper foiling (exposing one cm^2 of surface) and boiled for about 5 minutes; a definite steel colored deposit was then seen to have formed. The coloring was not strong as with arsenic because tartar emetic contained 39% of the metal against 75.6 % in arsenic sesquioxide. Odling remarked that the amount of HCl employed should not be increased by more than 20 %, so as not to interfere with the sensibility of the test. Also, a dilution of 500,000 constituted the practical upper limit to the application of the test. Although the deposits obtained from arsenic and antimony were very similar, this was of no practical consequences owing to the ease with which the arsenical deposit was distinguished from that produced by arsenic (Odling, 1856b).

Odling suggested that to confirm the presence of antimony it was enough to submerge the coated copper in an aqueous solution of potassium permanganate (containing 0.152 g of the salt per 1000 g of water), and boil everything for one or two minutes. The permanganate decomposed and the antimony dissolved and could be precipitated by means of hydrogen sulfide from the solution acidulated with HCl (HHodling, 1856b).

Odling also examined the use of Reinsch's test for detecting bismuth, tin, silver, platinum, lead, cadmium, and zinc. The results indicated that the test could be used to detect down to one-thousandth of a grain of bismuth with a maximum dilution of 100,000. The results with tin were somewhat anomalous and not definite; the deposit with silver could be mistaken for that of antimony and the presence of nitric acid interfered with the brilliancy of the same. The deposit of platinum was initially shining but on exposure to air it resembled that of antimony, the one of lead was extremely light and did not exhibit a blue or violet color. The deposit of cadmium was more interesting because of its yellowish white color, and no deposit was formed with zinc (Odling, 1856b).

In an additional paper Odling reported that Marsh's test could be relied upon to detect small amounts of arsenic in the presence of organic matter, a problem that did not take place with Reinsch's test. In order to use Marsh's test in these situations Odling recommended boiling the specimen in concentrated HCl for about one hour and to filtrate the resulting liquid and evaporate it to dryness. This way the organic matter was completely destroyed and all the arsenic went into solution, without any perceptible loss (Odling, 1859).

The question if copper was or was not a normal constituent of organic structures had been discussed for many years. Some researchers believed that the presence of this element in animal or vegetable tissues or fluids was exceptional or abnormal, while others thought it was a natural constituent of living organisms, In 1858 Odling and Auguste Dupré (1835-1907) published a paper reporting that they have found that copper was present in a large variety of organic matter, such as bread, flour, wheat, straw, kidney, blood, flesh, ox bile, human muscle, human spleen, eggs, cheese, etc. For several of these substances they provided quantitative information about their copper content. Their analytical procedure consisted in burning the organic substance to ash, followed by solution in HCl, precipitation with KOH, solution of the precipitate in HCl, and electrolyzing the resultant solution with zinc and platinum. The existence of copper was corroborated with ammonia and potassium ferrocyanide (Oldling& Dupré, 1858).

After a large number of experiments, Odling and Dupré reached the following conclusions: (1) tissues, particularly of the liver and kidney, usually contained large amounts of copper; these could be extracted sometimes from liver by boiling water or with diluted HCl; (2) the element was present in blood in minute amounts; and (c) that in the cases were copper was readily detected in the fully incinerated ashes, it was not to be extracted by HCl from the black ash, even after its exposure to red heat. In this situation it was necessary to burn to the black ashes again to white ashes, and then extract them with the acid (Odling & Dupré, 1858).

In a following publication Odling analyzed in detail the problems of using potassium ferrocyanide for the determination of the presence of copper. He remarked that the formation of a gelatinous chocolate red precipitate to an acid or neutral liquid was the critical step in the analytical procedure. The resulting precipitate was a mixture having a composition varying between Cu4Fe2(CN)6 and K2Cu2Fe2(CN)6, and the experimental evidence indicated that although the conditions of solubility of this precipitate in ammonia were somewhat complex, the process could be carried out by mixing the precipitate, washed or unwashed, with a little KOH, so as to convert it into the opaque pale blue or blue white hydrate of copper. Treating the latter with a weak of strong solution of ammonia solubilized it completely yielded a purple blue liquid (Odling, 1862).

As a following step, Oldling decided to determine if the copper was present in the tissues as crystalloid or as a colloid, where the former was able of dialyzing or diffusing through a moist membrane. For this purpose he treated pieces of sheep kidneys with a weak solution of HCl and let the solution diffuse into distilled water. The results indicated that while most of the mineral components of the tissue passed through the dialyzer, the copper compound was left completely behind. Repeated experiments showed that dialysis of the finely divided tissue moistened with HCl resulted in most of the mineral part diffusing away without carrying any trace of copper (Odling, 1862).

Aluminum alkyls

The actual formula of aluminum chloride had been the subject of much discussion; some believed it to be AlCl3, others Al2Cl3, depending if the decision was based on the specific heat of the element or on the dissociation of its chloride. According to George Bowdler Buckton (1818-1905) and Odling, the available experimental information was insufficient for making a definite decision. They believed that an examination of the alkyl derivatives of aluminum would provide a more solid base to determine not only the correct formula of its chloride but also the location of aluminum within the classification of the elements (Buckton & Hodling, 1865). The actual preparation of these organo compounds derivatives was not new and had been discussed in detail by Auguste Cahours (1813-1891) (Cahours, 1860). In the particular case of aluminum Cahours had reported that it did not react with ethyl iodide at room temperature, but did completely at 130 °C. The resulting crude liquid was colorless and had a penetrating disagreeable odor, similar to that of decomposed turpentine. It strongly fumed in contact with air and reacted explosively with water generating aluminum oxide and hydrogen iodide. It reacted strongly with ethyl zinc forming zinc iodide and a very flammable liquid, which was probably ethyl aluminum. The reaction of aluminum with methyl iodide was very similar (Cahours, 1860).

Buckton and Odling reported that they had been able to prepare pure methyl aluminum and ethyl aluminum by reacting the metal with methyl and ethyl mercury at 100 ºC, following a process suggested by Frankland and Baldwin Francis Duppa (1828-1873) (Frankland & Duppa, 1864). Ethyl aluminum was synthesized by heating an excess of aluminum clippings with mercuric iodide in a sealed tube; it was a colorless mobile liquid boiling at 194 ºC, which did not solidify at -18ºC, and was completely decomposed by water with explosive violence. It contained (by weight) 61.4 % of carbon, 12.9 % of hydrogen, and 24.0% of aluminum, corresponding quite well with the formulas Al(C2H5)3 or Al2(C2H5)6. The density of its vapor at 234 ºC was 4.5, compared with the theoretical value of 3.9 for the formula Al(C2H5)3. Buckton and Odling believed that the difference between the experimental number 4.5 and the theoretical number 3.9 was a result of the high oxidizability of the compound (Buckton & Odling, 1865).

Methyl aluminum was prepared in a similar manner. It was a colorless mobile liquid, boiling at 1300, solidifying a few degrees above 0 ºC into a beautiful transparent crystalline mass, and containing, by weight, 48.4 % of carbon, 12-3 % hydrogen, and 38.2 % aluminum, numbers which corresponded well with the formula Al(CH3)3, or Al2(CH3)6. The density of its vapor at 240 ºC, 220 ºC, and 220 ºC, was 2.80, 2.80, and 2.81 respectively, which agreed closely with the theoretical number 2.5 calculated for the formula Al(CH3)3. The density increased as the temperature was decreased, suggesting the possibility that Al(CH3)3 existed in two molecular states of condensation or that the density procedure was inadequate for determining its formula (Buckton & Odling, 1865).

In a following paper, Odling described his use of the specific heat and the atomic proportion (mass) of aluminum (as known then), to determine the formula of aluminum chloride. The experimental evidence indicated that the different proportions had exactly the same specific heat, that is, for example, 7 parts (today, 6.941) of lithium, 65 (65.39) of zinc, 108 (107.87) of silver, and 210 (208.98) of bismuth, absorbed the same amount of heat when going through the same change in temperature. Hence, taking silver as a standard, the atomic mass of any other metal could be defined as that quantity of the metal having the same specific heat as 108 parts of silver (Odling, 1866a).

Many of the metals combined with halogens and with the radicals methyl or ethyl to form gaseous compounds in which the nonmetal and the metal were in the same proportion, so that their molecule could be considered formed by two volumes. Consequently, the quantity of the metal that had the same specific heat as 108 of silver was also the quantity of the metal contained in two volumes of its chloride, methyl, ethyl, etc. derivative. Now, it was known that the quantity of aluminum that had the same specific heat as 108 of silver, was 27.5 (26.98) parts, and that this quantity of aluminum combined with three times 35.5 parts (35.45) of chlorine. Hence, the atomic proportion of aluminum was 27.5 and its chloride would have the formula AlCl3. Unfortunately, Henry Sainte-Claire Deville (1818-1881) and Louis Joseph Troost (1825-1911) had determined that the quantity of aluminum contained in two volumes of aluminum chloride was 55.5 instead of 27.5, while the quantity of chlorine was 6 times 35.5 instead of 3 times 35.5 (Deville & Troost, 1857). In other words, the two-volume theory indicated that the atomic weight of alumina should be 55 and the formula of its chloride AlCl6, a conclusion that negated the equality of specific heats. Odling now indicated that he and Stockton had found that two gaseous volumes of ethyl aluminum and methyl aluminum contained 27.5 parts of aluminum combined with 3 atomic proportions of methyl and ethyl (Stockton & Odling, 1865). The discrepancy between the two procedures could be straightened out by the fact that the density of aluminum chloride was known to be anomalous: at temperatures of 220 ºC and above, two volumes of methyl aluminum contained 27.5 parts of aluminum and 3 times 15 parts of methyl, while at 1300C the corresponding figures 55 parts of aluminum and 6 times 15 parts of methyl. Hence, the correct formula of methyl aluminum was $AlCl_3$ (Odling, 1866a).

Ammonia and its platinum compounds

In a paper published in 1879 Odling described in detail the information available on ammonia, its salts, and in particular, the compounds it formed with platinum (Odling, 1870a). Ammonia was particularly characterized by its property of combining directly with HCl to form ammonium chloride, a solid salt. This compound could be considered the chloride of a composite metal ammonium, the same, as KCl was the chloride of the simple metal potassium. During the electrolysis of potassium chloride, potassium hydroxide instead of potassium deposited at the negative pole, but if the latter was a drop of mercury, then potassium remained dissolved in the mercury as an amalgam. If the electrolyte was ammonium chloride, then the negative pole produced an amalgam of ammonium, which as soon as the current was interrupted broke down into ammonia, hydrogen, and mercury (Odling, 1870a).

Odling remarked that ammonia was also characterized by its high solubility in water; this solution had many of the properties of aqueous KOH. Thus the solution could very well be regarded as a solution of ammonia hydrate (ammonium hydroxide), but only in theory. All attempts to separate it from the solution decomposed it into ammonia gas and water. Ammonia´s most interesting property was that it could be considered a type from which it was possible to derive a variety of different compounds by substitution of its hydrogen atoms (e.g. ethylamine, diethylamine, triethylamine, and their hydrochlorides, ethylenediamine, etc.). The principal developments had resulted from the reactions of ammonia with certain metallic salts, particularly those of platinum. Platinum was known to form two well-defined chlorides, $PtCl_2$ and $PtCl_4$. In 1828 Gustav Magnus (1802-1870) streamed ammonia through an aqueous solution of platinum dichloride and obtained a dull green crystalline precipitate containing ammonia, chlorine, and platinum (green salt of Magnus) (Magnus, 1828). Afterwards, a number of researchers treated the salt of Magnus with nitric acid and other reagents and obtained a large variety of new compounds of ammonia and platinum, but no one had been able to develop a general compositional scheme of all these new compounds (e.g. Gros, 1838; Reiset, 1840; Rawesky, 1846, Peyrone; 1849).

In 1870 Odling announced that he had been able to differentiate the simplest of the salts of platinum-ammonia from several related and isomeric compounds with which they had been confounded, as well as preparing the corresponding hydrated bases of the series. He remarked that his scheme was based on the following two propositions: (1) the different platinum-ammonia compounds were prepared from platinum dichloride, as the starting material. In the same manner that this chloride could take two more atoms of chlorine to become $PtCl_4$, its ammonia derivatives were also able to take up two atoms of chlorine or its equivalent of another negative radical. Hence, Odling´s division into compounds having two or four substituents, (2) the radical (amidogen) NH_2, which was able to become the ammon-amidogen N_2H_5 just as the radical CH_2 was able to become the methylene-methyl radical C_2H_5. The group of platinum-ammonia compounds was thus divisible into the two classes of platinous and platinic, and each of these divided again into the two classes of amic and ammon-amic compounds (Odling, 1870a).

Odling provided a large list of platinum-ammonia compounds classified as indicated above, for example, the compounds derived from platisamine [Pt(NH2)2.2HCl, Pt(NH2)2.2H(OH), and Pt(NH2)2.2H(NO3)], from amo-platisamine [Pt(N2H5)2.2HCl, Pt(N2H5)2.2H(OH), and Pt(N2H5)2.2H(NO3)]; from platinamine [Cl2Pt(NH2)2.2HCl, (OH)2Pt(NH2)2.2H(OH), and (NO3)2Pt(NH2)2.2H(NO3)], and from amo-platinamide [Cl2Pt(N2H5)2.2HCl, (OH)2Pt(N2H5)2.2H(NO3), and (NO3)2Pt(N2H5)2.2H(NO3)], corresponding respectively to the chloride, hydrate, and nitrate. He also described in detail the preparation and properties of all these compounds (Odling, 1870a).

The formula of water

The question of the correct formula of water had occupied the minds of scientists for a long time. In the words of Odling, ¨whether and atom of water contains the same quantity, or double the quantity of hydrogen that is contained in an atom of hydrochloric acid, and whether the atomic weight of oxygen is 8 or 16, are concrete examples of many of the disputed questions, which lie at the very basis of scientific chemistry¨ (Odling, 1859b).

He then went on to repeat the principles behind the law of definite proportions. There we about 60 different elements, and these were known to combine one with the other in fixed or definite proportions to form a very large number of compound bodies. Thus, for example, one part of hydrogen was known to combine with 35.5 parts of chlorine to form the chlorhydric acid, and 35.5 parts of chlorine combined with 23 parts of sodium to form sodium chloride. The numbers 1, 35.5, and 23 represented the smallest proportion of the element that united with one part of hydrogen. The combining proportion of hydrogen was the smallest of all know elements and thus was given the value 1; from there on it was possible to assign a particular value to each other element. These values were mere results of experiments independent of theoretical considerations; they were the least quantity of the element that could combine with or replace 1 part of hydrogen. Odling indicated that this simple idea was soon modified. It was known that the smallest quantity of nitrogen that united with hydrogen was 4.7 but the combing proportion of nitrogen was fixed not at 4.7 but three times that quantity (14). Odling then asked: why we not express the compound body HN the same as we express the compound body chlorhydric acid by HCl? The answer laid in facts such as: (a) a given bulk of gaseous ammonia contained three times as much hydrogen as the same bulk of HCl; (b) a given bulk of nitrogen combined with three times as much hydrogen as did the same bulk of chlorine, and (c) that the relative weights of equal bulks of nitrogen, chlorine and hydrogen were as 14:35.5:1, etc. etc. This type of arguments had been accepted for the elements phosphorus, arsenic, antimony, and bismuth (the concept of valence was yet to be developed). Odling went on and remarked that although the determination of the smallest proportion of an element that could unit with or replace one part of hydrogen was purely experimental, the determination of its atomic weight was a question of judgment, ¨which could only be decided by an intimate knowledge of many circumstances connected with the body¨ (Odling, 1859b).

Most English chemists represented the atomic weight of carbon, oxygen and sulfur by 6, 8, and 16 respectively. Since Odling believed that the correct numbers were twice those numbers, was the atom of water OH = 9 or H2O = 18? He argued that if the atom of HCl consisted of 1 part of hydrogen united with 35.5 of chlorine, and if the atom of ammonia contained 3 parts of hydrogen united to 14 parts of nitrogen, then the atom of water had to consist of 2 parts of hydrogen united with 16 of oxygen. All this was based on the facts that a given bulk of gaseous water contained twice as much as the same bulk of HCl, that the relative weights of equal bulks of oxygen and chlorine were in the ratio 16:35.5, and that ¨in

99 % of the cases the quantity of water, which is the agent or is resultant of a reaction, must contain H2, or some multiple of H2, and consequently 16, or some multiple 16 parts of oxygen¨ (Odling, 1859b).

Odling went on to justify the last statement with examples taken from a wide variety of compounds, among them, formation of ammonia from ammonium chloride and cyanogen from ammonium oxalate, formation of triethylamine, of CO from formic acid, the action of an acid upon a hydrocarbon, decomposition of hippuric acid, etc. etc. (Hodling, 1859b, 1863).

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