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PHILIPPE HENRI ARNOUT DE CLERMONT
Organophosphates, ethers, phenols, and other organic subjects

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ABSTRACT

Philippe de Clermont (1831–1921) was a French organic chemist, known particularly for his synthesis of tetraethyl pyrophosphate, the first organophosphate cholinesterase inhibitor. This achievement was part of an extensive research about phosphoric ethers using Wurtz's procedure. This type of synthesis was found to be also appropriate for the preparation of carbonic ethers. Another important consequence was that the reaction between ammonia and an ether composed of a mineral oxacid resulted in the formation of an alcoholic alkali. Clermont also carried extensive research about octene and its derivatives that culminated in the synthesis of a large number of new derivatives, among them octylene oxide acetate, caprylene halides and alcohol, octyl glycol, octyl glycol chlorhydrin, etc. Clermont determined the composition of persulfonic acid, synthesized sulfophenylurea, and a variety of thioureas. He also studied a variety of reactions of pyruvic acid, the composition of pyrogallic acid, synthesized purpurogallin, and a variety of metallic sulfides, in particularly the flesh and green sulfides of manganese and the decomposition reaction of ammonium chloride with metallic sulfides. Likewise, he showed that the production of aurin required the presence of nascent CO_2.

Keywords: aurin, metal sulfides, phenols, phosphorous ethers, pyrogallic acid, tetraethyl pyrophosphate.

RESUMEN

Philippe de Clermont (1831–1921) fue in químico francés, conocido particularmente por su síntesis del tetra etilo pirofosfato, el primer inhibidor del orgánofosfato colinesterasa. Este logro fue parte de un programa extenso acerca éteres fosfóricos usando el procedimiento de Würtz. Este tipo de síntesis probó ser también apropiado para la preparación de éteres carbónicos. Otro resultado importante indicó que la reacción entre el amoníaco y un éter formado por un oxácido mineral daba lugar a la formación de un álcali alcohólico. Clermont también llevó a cabo un extenso programa de investigación acerca del octeno y sus derivados que culminó con la síntesis de un gran número de nuevos derivados, entre ellos, el acetato del óxido de buteno, los haluros y el alcohol caprílico, el octil glicol, la clorhidrina del octil glicol, etc. Clermont determinó la composición del ácido persulfónico, sintetizó la sulfofenil urea y una variedad de tioureas. Estudió una variedad de reacciones del ácido pirúvico, la composición del ácido pirogálico y sintetizó purpúrogalina, y una variedad de sulfuros metálicos, en particular los sulfuros verdes y rosados del manganeso, y la reacción de descomposición del cloruro de amonio con sulfuros metálicos. Asimismo, demostró que la producción de aurina requería la presencia de CO_2 naciente.

Palabras claves: ácido pirogálico, aurina, éteres fosfóricos, fenoles, sulfuros metálicos, tetra etil pirofosfato.

INTRODUCTION

Life and career (Meunier, 1924; Fauque, 2007; Anonymous, 2022)

Philippe Henri Arnout de Clermont (Figure 1) was born in Paris on January 18, 1831, the son of Auguste de Clermont (1797-1841), a businessman, and Frederique Christine Helmine Hessler (1801-1867). After finishing his basic classical studies, he enrolled at the Sorbonne from where he received his diploma of baccalauréat ès-lettres in 1848.

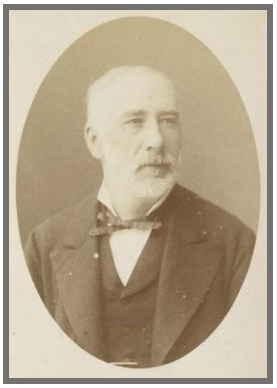

***Fig. 1**. Philippe de Clermont (1831- 1921)*

He then made a short trip to Germany and England to pursue additional studies. In 1853 he joined the chemistry laboratory of Adolf Würtz (1817-1884) at the Faculté de Médecine and begun an academic and research career. In 1874 he tried and failed to get a position of répétiteur at the École Polytechnique and in 1876 he replaced Emil Jungfleish (1839-1916) as curator of the chemical and mineralogy collections of the École Polytechnique. Between 1875 and 1878 he served as professor of chemistry at the École Normale de Lavoisier (1875-1878). He was also honorary sub-director of the chemistry teaching laboratory at the Faculté de Sciences de Paris (1868), and sub-director of the laboratory of Henri Sainte-Claire Deville (1818-1881) at the Sorbonne (1870). In parallel with these many positions, he pursued his doctoral studies at the Faculty of Sciences in Paris from where he graduated docteur ès-sciences physiques in January 1870, after successfully defending a thesis about octylic derivatives (Clermont, 1870). The jury was composed of Paul Quentin Desains (1817-1885), Henry Sainte-Claire Deville (1818-1881), and Louis Joseph Troost (1825-1911). In 1900 he resigned his positions at the École Polytechnique and the Faculté des Sciences and was appointed honorary professor at both of institutions.

Clermont was one of the founding members of the Société Chimique de France and of its scientific journal, *Repertoire de Chimie Pure et Appliquée*, which in time became *Bulletin de la Société Chimique*. Between 1875 and 1992 he served as Secretary of the Society and in 1886, as its President. Following the 1870 Franco-Prussian war he collaborated with Charles Friedel (1832-1899) in the creation of the École Alsacienne. Clermont was also a founding member of the Association Française pour l'Avancement of Sciences and President of the same in 1885, 1889, and 1895. In 1870 the French Academy of Sciences awarded him the Jecker Prize for his work on the production of phosphoric and carbonic ether, the first-time synthesis of the hydrate of octene and the corresponding glycol, and the action of iodine and cyanogene iodide on turpentine. In 1890 he was appointed Chevalier of the Legion d'Honneur and in 1912 promoted to Officier.

In 1860 Clermont married Virginie Eugénie Anna Clementine Peugeot; three children were born of this union. Clermont passed away in Paris, on January 12, 1921.

Scientific contribution

Clermont wrote about 40 papers and books (i.e., Clermont, 1890) on the subjects of inorganic and organic chemistry, and toxicology. Clermont wrote a booklet describing his research and achievements, as customary for candidates to the Académie des Sciences, (Clermont, 1881). He also contributed several chapters to the dictionary of pure applied chemistry edited by Adolphe Würtz (Würtz, 1869-1908). In addition to the subjects described below, he developed with J. Frommel a new method for separating arsenic from other metals (Clermont & Frommel, 1878a) and the value of magnesia as an antidote for arsenious acid (Clermont & Frommel 1878c); he studied synthesis of volatile fatty acids by the reaction between phosgene and octanol (Clermont & Fontaine, 1870) and the reaction between citric acid and glycerin (Clermont & Chautard, 1887); etc.

Preparation of ethers

Clermont wrote that after Würtz requested from him to study the reaction of ethyl iodide with different silver salts and he obtained the following results (Clermont, 1854): the reaction between dry ethyl iodide and dry silver pyrophosphate was highly exothermic; the mass heated up and turned yellow and compact. To carry the reaction, it was necessary to heat the mixture in a water bath and use an excess of pyrophosphate to avoid the decomposition of ethyl iodide and conversion of the mass into an acid product impregnated with iodine. The resulting product was extracted with ether pure and then filtrated to eliminate the silver iodide. The ether was eliminated by evaporation in a water bath and the resulting viscous liquid dried by means of a stream of dry air at 130 ^{0}C. Further heating to 140 ^{0}C under vacuum eliminated the remaining ethyl iodide and ether. Elemental analysis of the resulting pyrophosphoric ether indicated that it contained, by weight, 33.70% carbon, 6.71 % hydrogen, and 49.30% pyrophosphoric acid, corresponding to the formula $(2C_4H_5O)PO_5$ (Clermont is using the old values of atomic mass, C = 6, ethyl = C_4H_5) (Clermont, 1854, 1855). This result indicated that the reaction leading to the pyrophosphoric ether was a neat double decomposition, similar to the one taking place between two metal salts: Two molecules of ethyl iodide reacted with one of silver pyrophosphate to yield two molecules of silver iodide and one of ethyl pyrophosphate:

$2AgO.PO_5 + 2C_4H_5I = 2AgI + (2C_4H_5O)PO_5$

Clermont described pyrophosphoric ether as a viscous liquid, having a burning taste, relative density 1.172 at 17 ^{o}C, soluble in water, alcohol, and ether, and becoming promptly acid in contact with humid air. Exposed to the alcohol flame it burned with a whitish flame and releasing white vapors. Heated to about 200^o-210 ^{o}C it carbonized and became acid while at the same time it distilled a colorless liquid having the composition of the phosphoric ether $(3C_4H_5O)PO_5$. The ether dissolved a small quantity of silver iodide, which after a long time precipitated as small crystals. KOH turned it acid, forming a crystalline deliquescent salt, probably of potassium ethylpyrophosphate $PO_5.2C_4H_5O.KO$. Clermont mentioned that Wladimir Petrovich Moschnin, another student of Würtz, had also previously prepared the same ether (Clermont, 1854, 1855).

Clermont added that ethyl iodide reacted in a similar manner with trisilver phosphate (silver phosphate, silver orthophosphate, Ag_3PO_4). This reaction was slow at room temperature but could be completed when conducted in a water bath. The best proportion was 3 equivalents of ethyl iodide for 1 of silver phosphate. The product was treated with ether and the solvent eliminated by distillation. The resulting liquid was heated at 160 ^{o}C in an oil bath and distilled under vacuum. The fraction passing at 140 ^{o}C was the phosphoric ether, containing, by weight, 39.14% carbon and 8.39% of hydrogen, corresponding to the formula $(3C_4H_5O)PO_5$. According to Clermont, it was a colorless liquid with a burning taste

and becoming acid in contact with water. It did not react with ammonia at room temperature but decomposed it at higher temperatures. This reaction could be conducted by heating in a sealed tube a mixture of the phosphoric ether with a solution of ammonia in absolute alcohol. The purified product appeared as white crystals having the composition of ammonia ethyl phosphate, $(2C_4H_5O)NH_4O.PO_5$, accompanied by ethylamine (Clermont, 1854, 1855):

$$(3C_4H_5O)PO_5 + 2NH3 = (2C_4H_5O)NH_4O.PO_5 + C_4H_7N$$

The carbonic ether was obtained in a similar manner. Twelve grams of ethyl iodide were reacted with 12 g of silver carbonate; the resulting double decomposition yielded silver iodide and carbonic ether. Clermont recommended using one equivalent of ethyl iodide for one equivalent of silver carbonate; the presence of an excess of the latter resulted in its decomposition and failure of obtaining the desired result. Once the mixture became solid and pulverulent, it was distilled in an oil bath in order to separate the volatile silver iodide. The resulting liquid was purified by redistillation, separating the fraction boiling at 160 ºC. The resulting fraction was very fluid and had a burning taste and an aromatic odor. Elemental analysis indicated that it contained, by weight, 50.50% carbon and 8.55% hydrogen, corresponding to the formula $CO_2.C_4H_5O$ (Clermont, 1854, 1855).

Today we know that tetraethyl pyrophosphate is a potent organic phosphate pesticide, which acts as an inhibitor of cholinesterase, and as such it is highly toxic by all routes of exposure. As mentioned by Georgi A. Petroianu, it is surprising that Clermont tested this chemical without fatal consequences (Petroianu, 2008).

In 1859 E. Juncadella reported that the reaction between ammonia and an ether composed by a mineral oxacid resulted in the formation of the pertinent amine (Juncadella, 1859). His experiments indicated that the reaction of ammonia with methyl nitrate or ethyl nitrate occasioned the production of methylamine or ethylamine, according to the reactions:

$C_2H_3O,NO_5 + NH_3 = C_2H_5N,OH,NO_5$

$C_4H_5O,NO_5 + NH_3 = C_4H_5N,OH,NO_5$

Treatment of the product of the reaction with HCl and absolute alcohol allowed separation of pertinent chlorhydrate. According to Jucatella, the formation of these amines was so abundant that they could be used for their production, instead of the complicated processes employed for these purposes (Juncadella, 1859).

This publication brought a prompt answer from Clermont who wrote that the results of Juncadella were not new; in 1855 he had already reported that the reaction of phosphoric ether with an alcoholic solution of ammonia resulted in the formation of ethylamine, that is, the reaction between ammonia and an ether composed of a mineral oxacid resulted in the formation of an alcoholic alkali (Clermont, 1859).

Octyl derivatives

Clermont carried extensive research about octylene, its derivatives, and properties, which culminated in his doctoral thesis (Clermont, 1864, 1868, 1869ab, 1870).

Octylene glycol (caprylic glycol)

According to Clermont, the reaction between dry silver acetate and dry octyl bromide yielded octylene oxide acetate (Clermont, 1864). The best actual conditions consisted in reacting 1 equivalent of the bromide with 2 of acetate in the presence of glacial acetic acid, to allow a better mixing of the silver salt and the bromide. This mixture, heated in a flask to a temperature not exceeding 120 ºC, yielded silver bromide and octylene oxide acetate. The

acetate and the excess acetic acid were separated with ether and the ethereal solution subject to fractional distillation. Ether passed first, followed by acetic acid and water. The fractions containing the acetate, boiling at a higher temperature, were collected and fractioned again. The purified acetate boiled between 245º and 250 ºC; it appeared as a thick, oily and colorless liquid. Saponification with KOH yielded a mixture of octyl glycol and potassium acetate, which were separated by repeated distillation over an oil bath. The resulting octyl glycol was purified by fractional distillation. The purified material was an oily colorless liquid, odorless and having a piquant taste. It was insoluble in water and soluble in ether, had specific gravity 0.932 at 0 ºC and boiling point between 235º and 240 ºC. Its elemental analysis corresponded to the formula $C_8H_{10}O$. Clermont obtained the corresponding chlorohydrin reacting the glycol with concentrated HCl. The resulting substance was a mixture of several derivatives of various degree of chlorination (Clermont, 1864).

Caprylene iodides and alcohol

Clermont wrote that in 1849 Würtz showed that treating amyl iodide with wet silver oxide generated an isomer of amyl alcohol (Clermont, 1868). He also proved that a certain number of hydrocarbons treated with silver oxide produced alcohols, which he named *hydrates*. Würtz also found that treating caprylene iodide with silver oxide regenerated the hydrocarbon, accompanied by only traces of an oxygenated substance (Würtz, 1862). Clermont continued the experiments of Würtz and obtained a series of new derivatives. Caprylene iodide was prepared by heating over a water bath a closed vase containing a mixture of caprylene with a solution of hydrogen iodide saturated at 0 ºC. The resulting liquid was present in two phases, the iodide was found as an oily liquid at the bottom of the vessel. This phase was separated, washed first with water and then with a diluted solution of KOH, dried over calcium chloride, and then fractionated under vacuum. The portion passing at 120 °C was pure iodide, having specific gravity 1.33 at 0º, and 1.314 at 21 °C. Caprylene bromide was prepared by a similar procedure. Caprylene acetate was synthesized by reacting caprylene iodide with silver acetate suspended in ether. This was an exothermic reaction that generated a mixture of silver iodide, caprylene, acetic acid, and caprylene acetate. The ether was eliminated by distillation and the acetic acid by washing with a solution of sodium carbonate. The residual liquid was dried over calcium chloride and then fractionated by distillation. Caprylene passed first, followed by pure caprylene acetate. This compound was a colorless liquid, possessing a fruity odor and relative density 0.822 at 0 ºC. Caprylene hydrate was prepared by reacting caprylene acetate with an equivalent amount of KOH. The resulting liquid was a mixture of caprylene alcohol (pseudo octylic alcohol) and potassium acetate. The alcohol was purified by successive fractionations (Clermont, 1868). Clermont described 1-octanol as a transparent and colorless liquid, having aromatic odor and a burning and persistent taste. It was insoluble in water, soluble in alcohol and ether, having relative density 0.811 at 0 ºC and boiling point 174º to 178 ºC. Elemental analysis indicated that its formula was $C_8H_{12}O$. Treatment with concentrated HCl in a closed tube yielded caprylene chloride. According to Clermont, this chloride was a new isomer of similar chlorides synthesized by Jules Bouis (1822-1886) (Bouis, 1854) and by Carl Schorlemmer (1834-1892) (Schorlemmer, 1867). Caprylene iodide and bromide were prepared from the hydrate by a similar procedure (Clermont, 1868).

Oxidation of pseudo octylic alcohol

Clermont wrote that Hermann Kolbe (1818-1884) had predicted, on theoretical basis, that the octanol obtained from castor oil was a secondary alcohol that by controlled oxidation yielded methylœnanthol and caproic and acetic acids (Kolbe, 1864). Schorlemmer

confirmed this assumption (Schorlemmer, 1868). This information suggested Clermont that it would be of interest to investigate if his pseudo octylic acid behaved in the same manner (Clermont, 1869a). For this purpose, he boiled for six hours a mixture of 32 g of pseudo octylic alcohol with 128 g of potassium dichromate, 192 g of concentrated sulfuric acid and 1,280 g of water. Distillation of the product yielded an oily substance and a heavy aqueous solution. The oily phase contained the unreacted alcohol and the methylœnanthol. Addition of sodium bisulfite resulted in the partial precipitation of the methylœnanthol as a crystalline complex, which was decomposed by sodium carbonate. The separated methylœnanthol boiled at 170 ºC and reduced silver nitrate. The liquid separated from the oil was found to be acid. It was first neutralized with sodium carbonate and then evaporated to dryness and treated with sulfuric acid. The resulting liquid phase was found to be caproic acid, boiling at 198 ºC. Distillation of the liquid separated from the caproic acid yielded acetic acid. The above results showed that the pseudo alcohol produced the same decomposition products as the alcohol from castor oil, making impossible to differentiate between them (Clermont, 1869a).

Oxidation of octylene and octanol

Clermont also studied the oxidation of octylene by the same process used for the pseudo alcohol. The products of the reaction were found to be caproic and propionic acids (Clermont, 1869a).

Octyl glycol acetochlorhydrin

According to Clermont, Paul Schützenberger (1829-1897) and Gabriel Lippmann (1845-1921) had shown that ethylene and acetyl chloride reacted directly yielding glycol acetochloride (Schützenberger & Lippmann, 1865). This result led him to try the same reaction with octylene, a hydrocarbon of the same series (Clermont, 1869b). For this purpose, he put a known quantity of pure octylene in a glass balloon, submerged in a refrigerating bath, and added, drop-wise and with agitation, the corresponding of a solution of acetyl chloride in acetic anhydride and glacial acetic acid (to moderate the reaction). The resulting product was a solution of acetochlorhydrin in acetic acid. Addition of water separated the acetochlorhydrin as a second liquid phase. This phase was separated, washed with water, dried over calcium chloride, and further purified by distillation. According to Clermont, this substance appeared as a colorless liquid, having a pleasant aromatic odor and a burning taste. It was soluble in alcohol, ether, and acetic acid, and insoluble in water. It boiled at 225 ºC without decomposition, had a relative density of 1.026 at 0 ºC, and was hardly saponified by KOH or calcium carbonate. Elemental analysis indicated that it contained, by weight, 58.35% of carbon, 9.47% of hydrogen, and 17.32 of chlorine (Clermont, 1869b).

Sulfo derivatives

Persulfocyanic acid

In the second half of the nineteenth century the exact formula of persulfocyanogen (persulfocyanic acid) was still uncertain, although Auguste Laurent (1807-1835) and Charles Gerhardt (1816-1856) had proposed the formula $C_3H_2N_2S_3$ (Laurent & Gerhardt, 1847). J. Ponomareff, a colleague of Clermont, carried additional experiments with the purpose of determining the possible constitution of this compound (Ponomareff, 1874). In the first stage he studied the action of phosphorus pentachloride and ammonia upon this compound, reasoning that if the formula of Laurent and Gerhard were correct then following reaction would also be:

$C_3H_2N_2S_3 + 3PCl_5 = 2PCl_3 + S_2Cl_2 + PSCl_3 + HCl + C_3N_2Cl_3$

With formation of solid cyanogen chloride. The results confirmed this assumption.

It was known that at room temperature aqueous ammonia dissolved persulfocyanogene partially and that the acids precipitated the solute without alteration. Ponomareff found that at higher temperatures, 150^0 to 160 ^oC, the solubility was total with formation of ammonia sulfide. He diluted the product with water and then boiled it until the smell of ammonia sulfide had disappeared, with precipitation of sulfur. Upon cooling the solution deposited voluminous crystals that he separated and recrystallized twice. Elemental analysis of the crystals corresponded to the formula $C_4HN_7H_7S$, that is, it was a sulfocyanide of melamine, $C_3N_6H_6$,CHNS, as further chemical assays proved. According to Ponomareff, the formation of this particular compound proved that the reaction between ammonia and persulfocyanogen was not limited to a substitution of the sulfide (SH) and sulfur, by the residues of ammonia; apparently it was accompanied by a more profound split of the molecule, which included the formation of ammonium sulfocyanide (Ponomareff, 1874).

Clermont and Ponomareff heated a mixture of aqueous ammonia and persulfocyanic acid to 100^0-120 ^oC in a sealed glass tube and observed the formation of sulfur and ammonium sulfocyanate, and no formation of ammonium cyanate (Clermont & Ponomareff, 1875). They also found that KOH reacted strongly with persulfocyanic acid above 100 ^oC, also forming sulfur and potassium thiocyanate, without traces of potassium cyanate. These results led them to reject the formula (CS-NH)-S-(NH-CS) proposed by L. Glutz for persulfocyanic acid (Glutz, 1870; Clermont & Ponomareff, 1875).

Sulfophenylurea

Clermont stated that this compound had been so far prepared by non-practical procedures, for example, by reacting in a water-bath at 100 ^oC, one mole of phenylamine hydrochloride with one mole of ammonium sulfocyanide, according to the equation (Clermont, 1876a):

C_6H_7N,HCl + CN,NH_4S + CS,NH_2,NH,C_6H_5 + NH_4Cl

The product of the reaction was evaporated to dryness and then washed with water to eliminate the accompanying impurities and take advantage that sulfophenylurea was little soluble in water. The residue was dissolved in boiling alcohol and the crystalline sulfophenylurea precipitated by cooling. Clermont reported that the purified substance melted at 154 ^oC and was more soluble in alcohol than in water. Sulfophenylurea, heated in a closed flask at 180 ^oC, decomposed into a complex mixture that contained thiocyanic acid, ammonia, phenylamine, ammonium sulfide, and diphenyl sulfide urea. When heated with an excess of aqueous ammonia in a closed flask at 130-140 ^oC, it decomposed with the ammonia displacing the phenylamine and yielding ammonium sulfocyanide (Clermont, 1876a).

Acetyl persulfocyanic acid

Clermont prepared this compound by heating in a glass flask provided with a condenser, a mixture of acetic anhydride and persulfocyanic acid. Upon cooling, the resulting mixture deposited crystalline yellow needles, little soluble in water, more soluble in alcohol and ether, and presenting a weak acidity. Elemental analysis indicated that its formula was $C_2H(C_2H_3O)N_2S_3$, that is, acetyl persulfocyanic acid (Clermont, 1876b), the same compound that Marcel Nencki (1847-1901) and W. Leppert had prepared by reacting acetic anhydride and ammonium thiocyanide (Nencki & Leppert, 1873).

Thioureas

In 1876 Clermont and E. Wehrlin reported the synthesis of the two new thioureas, cresylthiocarbamide and naphtylthiocarbamide (Clermont & Wehrlin, 1876; Clermont, 1877). Cresylthiocarbamide was prepared by heating in a water bath a mixture of *p*-toluidine and ammonium thiocyanide, in the presence of water. After a short time, an insoluble substance precipitated, which was separated by filtration and washed with water until the water showed no color reaction with a ferric salt (indicating the absence of sulfocyanide). The solid was purified by recrystallization from boiling alcohol. Clermont and Wehrlin wrote that cresylthiocarbamide appeared as small colorless plates, transparent and brilliant, melting at 188 ºC, and composition corresponding to the formula CS,NH_2,NHC_7H_7. It had a bitter taste, and was little soluble in water and ether, cold or warm, and very soluble in boiling alcohol. KOH decomposed it regenerating the toluidine (Clermont & Wehrlin, 1876; Clermont, 1877).

Naphtylthiocarbamide was prepared in the same manner, replacing the toluidine by naphtylamine. It appeared as small prismatic crystals with rhombic base, which were colorless, transparent and bitter, and melting at 198 ºC. They browned in contact with air and were slightly soluble in water and very soluble in alcohol. KOH decomposed it regenerating naphtylamine. Treating a solution in sulfuric acid with a little of nitric acid resulted in the generation of nitrous vapors and precipitation of a flocculent yellow substance having a strong tinctorial power that dyed silk a beautiful yellow (Clermont & Wehrlin, 1876; Clermont, 1877).

Pyruvic acid

In 1868 Johannes Wislicenus (1835-1902) reported that the reaction of one molecule of dehydrated pyruvic acid with one more of bromine, in a sealed tube maintained at 0 ºC for several hours, yielded an addition crystalline derivative, highly unstable in the presence of water, humid air, alcohol, or heat, with release of HBr. The sodium amalgam transformed it into lactic acid. Elemental analysis indicated that its formula was $C_3H_4Br_2O_3$. Wislicenus believed that this substance was dibromolactic acid, $CH_2Br\text{-}C(Br)OH\text{-}COOH$ (Wislicenus, 1868).

Clermont studied some additional reactions of pyruvic acid, $CH_3\text{-}CO\text{-}COOH$ (Clermont, 1873). In the first series of experiments, he treated the melted dibromo dibromolactic with a stream of chlorine gas and observed the release of HCl vapors. When it ended, he extracted the product with water and then crystallized the solution. The resulting matter appeared as large rhomboidal crystals, colorless, melting at about 93 ºC, and efflorescing in the air and under vacuum. Chemical analysis indicated that the crystals contained bromine but not chlorine. Elemental analysis indicated that they contained, by weight, 15.38% carbon, 1.90% hydrogen, and 63.61% bromine. In spite of the small analytical differences all these data suggested that the new compound was identical with dibromopyruvic acid described by Karl Hermann Wichelhaus (1842-1927) (Wichelhaus, 1867; Clermont, 1873), according to the equation:

$$C_3H_4Br_2O_3 + Cl_2 = C_3H_2Br_2O_3 + 2HCl$$

dibromolactic acid — dibromopyruvic acid

Clermont and R. Silva left an aqueous solution of dibromolactic acid under vacuum for some time and noted the formation of abundant crystals, which they dissolved in water and recrystallized again. The purified crystals were colorless and effloresced in a dry atmosphere. They were unable to determine their composition (Clermont & Silva, 1869).

Clermont wrote that several publications had reported the formation of pyrotartaric acid at the expense of the elements of pyruvic acid and that he had found one new one (Clermont, 1873). He heated in a sealed glass tube a mixture of pyruvic acid and HCl and noticed that the pyruvic acid decomposed releasing abundant CO_2, while the mixture turned partially black and deposited a carbonized material. Evaporation of the filtrated liquid yielded crystals that after purification with animal carbon were found to contain, by weight, 45.00% carbon, 6.69% hydrogen, and 48.31% oxygen, corresponding to $C_5H_8O_4$, the formula of pyrotartaric acid.

Clermont added that he had reacted in a sealed tube a mixture of aqueous bromine with sulfopyruvic acid ($C_3H_4O_6S$) and obtained a brominated sulfopyruvic acid, appearing as a non-crystallizable syrupy liquid. The same reaction with barium sulfopyruvate yielded crystalline barium sulfopyruvate, which was soluble in water (Clermont, 1873).

Pyrogallic acid

In 1879 Aimé Girard (1831-1898) reported that the oxidation of pyrogallic acid by means of an oxidant and an alkali resulted in the formation of CO, alkaline carbonate and acetate, and a group of products highly colored and non-crystallizable (Girard, 1869). In the presence of potassium permanganate and sulfuric acid the pyrogallic acid split into a gaseous mixture of CO and CO_2 and a precipitate of crystalline flakes colored red brown. The crystals were separated by filtration, washed with a little of water, followed by dissolution in alcohol and recrystallization. Girard named this crystalline product *purpurogallin*; its elemental analysis corresponded to the formula $C_{40}H_{16}O_{18}$. According to Girard, purpurogallin appeared as garnet red needles, more colored and more brilliant than alizarin, sublimating at about 200 ^oC with slight decomposition, slightly soluble in water, more soluble in alcohol, ether, and benzene, and coloring yellow all these solvents. The solutions in other reagents were also colored, with the color usually changing with time (Girard, 1869). In 1872, Wichelhaus reacted pyrogallol with chromic acid and obtained a colored material that he identified as Girard's purpurogallin, although his elemental analysis led to a different global formula, $(C_{12}H_{14}O_9)_n$ (Wichelhaus, 1872).

These differences led Clermont and P. Chautard to conduct additional experiments to determine the composition of purpurogallin (Clermont & Chautard, 1882a). In the first stage they prepared purpurogallin by oxidation of pyrogallic acid with aqueous silver nitrate and obtained the same product described by Girard. In the second stage they prepared the salts of purpurogallin with sodium and barium and its bromo, acetyl, ethyl, and nitrate derivatives. Elemental analysis of all these derivatives indicated that the correct formula was the one reported by Girard, $C_{20}H_{16}O_9$. Afterwards, they reacted purpurogallin with hydrogen iodide, in a closed glass tube, and obtained a golden green precipitate, which dried at 100 ^0C and had a composition equivalent to $C_{18}H_{14}O_8$, identical to the product prepared by Wichelhaus by reacting a cold mixture of pyrogallol acid and quinone. Clermont and Chautard concluded that the oxidation of pyrogallic acid in an acid medium by means of silver nitrate, chromic acid, and potassium permanganate was a complex reaction where purpurogallin was the main product. The oxidation of pyrogallol with a mixture of potassium permanganate and sulfuric acid yielded purpurogallin, $C_{20}H_{16}O_9$, pyrogalloquinone, $C_{18}H_{14}O_8$, and a third body, yet unidentified (Clermont & Chautard, 1882a).

Clermont and Chautard wrote that in 1872 the physiologist Heinrich Struve had mixed aqueous solutions of Arabic gum and pyrogallic acid and noticed the formation of a red brown compound that reduced Fehling's liquor and presented all the reactions of purpurogallin (Struve, 1872, Clermont & Chautard, 1882b). Being in need of large amounts

of purpurogallin, Clermont and Chautard decided to try this reaction as a possible easy source of the chemical. For this purpose, they reacted aqueous solutions of Arabic gum of different concentrations with aqueous solutions of pyrogallic acid and in every case, they obtained a substantial crop of purpurogallin. The best procedure was to dissolve 10 g of pyrogallic in the smallest possible amount of water and mixing it with 500 cm^3 of a 10% solution of gum. The precipitation of purpurogallin was very slow; it took about 2 months to complete. The precipitate was washed with water and then with alcohol to eliminate the residue of gum. The procedure was highly efficient, yielding 67% of purpurogallin at the end of two months. Elemental analysis of the product corresponded to the formula of purpurogallin. Clermont and Chautard were unable to explain this reaction; they only warned that it had to be conducted in the presence of air (Clermont & Chautard, 1882b).

In a following paper, Clermont and Chautard stated that purpurogallin could be also prepared by contacting a solution of pyrogallol with platinum black and described some of its properties (Clermont & Chautard, 1882c): (1) sodium reacted with purpurogallin to yield sodium purpurogallate, $C_{20}H_{12}Na_4O_9$, crystallizing as prismatic needles, very deliquescent and very soluble in water. It was insoluble in alcohol and other solvents; (2) bromine and purpurogallin reacted violently, yielding the compound $C_{20}H_{12}Br_4O_9$ that crystallized easily and blackened in contact with air. It was insoluble in water and soluble in alcohol, acetic acid, benzene, and chloroform, producing solutions of different colors; (3) HCl did not attack it, and sulfuric acid dissolved it producing a beautiful purpuric color. With HI it yielded a series of hydrocarbons; and (4) with acetic anhydride it produced purpurogallin tetra acetate, crystallizing as prismatic needles, insoluble in water and very soluble in alcohol and ether; it melted at 186 ^oC and sublimed afterwards (Clermont & Chautard, 1882c).

Metal sulfides

Clermont and H. Guiot mentioned that the color transformation of manganese sulfide from flesh to green had called the attention of many chemists; and that their experiments had shown the formation of the green sulfide in many new situations (Clermont & Guiot, 1877a).

Clermont and Guiot repeated the experiences of Fritz Muck (1837-1891) on the subject (Muck, 1869) and confirmed some of his claims and disagreed on others. They recorded the following results: (a) the flesh sulfide heated with water for 48 hours showed no change in color but at 305 ^oC some green sulfide was produced; (b) the same sulfide, heated in a closed tube at 250 ^oC, also showed no changes but turned green when heated with ammonia in a closed tube at 220 ^oC. Muck did not achieve this result at 150 ^oC; (c) at 150 ^oC, a diluted solution of KOH in water or alcohol produced no changes other than oxidation. Heating the flesh sulfide with KCl in a closed tube at 200 ^oC turned it grey; (d) boiling the flesh sulfide with H_2S in an open flask produced no changes but turned it green when heated in a closed flask at 220 ^oC, contrary to the claim of Muck; (f) the flesh sulfide did not react with alkaline sulfides in the open air or when heated at high temperatures in a closed tube. Potassium hydrosulfide turned the flesh sulfide violet when heated in a closed vessel at 200 ^oC. A mixture of ammonium hydrosulfide and alkaline sulfide turned it green when heated in a closed tube; (g) Muck found that manganese carbonate could not be transformed into flesh sulfide. Clermont and Guiot were able to realize this change by boiling in the open-air manganese carbonate precipitated with ammonium hydrosulfide. Conducting this operation at 220 ^oC in a closed tube resulted in the complete conversion into flesh sulfide; (h) the conversion could also be obtained by passing dry CO_2 or dry ammonia over the flesh sulfide at the temperature of the Bunsen burner; (i) Anton Geuther (1833-1889) claimed that

freezing manganese sulfide resulted in a color change (Geuther, 1866) while Muck reported the opposite result. Clermont and Guiot repeated this experiment cooling manganese sulfide down to -15 ºC and observed no changes, but the flesh sulfide turned green when returned to atmospheric temperature (j) Muck reported that the green sulfur contained 7% of water without indicating how he obtained this result. No one had reported the constitution of the flesh sulfide. Clermont and Guiot conducted a detailed analysis of both sulfides and found that at 105 ºC the green species was anhydrous while the flesh one was a hydrate containing, by weight, 9% of water; and (k) the two sulfides presented different solubility in ammonium salts; the solubility of the green sulfide in ammonium chloride was five times larger than that of the flesh sulfide (Clermont & Guiot, 1877a).

Clermont and Guiot also found that compressing pulverized manganese sulfide resulted in a violent oxidation. The same operation conducted with other compressed and pulverized oxides resulted in different exothermal effects: iron sulfide heated gradually up to 50 ºC while simultaneously releasing water vapor; with nickel sulfide the effect was faster and more violent while with the sulfides of cobalt, copper, and zinc it was weaker (Clermont & Guiot, 1877b).

As mentioned before, ammonium chloride at room temperature dissolved manganese sulfide without reaction. Clermont and Guiot found that this was not the case with boiling ammonium chloride; a complex reaction took place accompanied by generation of ammonium sulfide, total disappearance of sulfur from the liquid phase, and formation of a soluble double salt of manganese and ammonium (Clermont & Guiot, 1877c). The liquid was filtrated and dried first at 100º and then at 120 ºC to eliminate all the crystallization water. Chemical analysis of the crystals indicated that their formula was $MnCl_2(NH_4Cl)_{16}$, H_2O. These results induced Clermont and Guiot to examine the result of the same reaction in a closed glass tube held at 200 ºC for 10 hours. Under these conditions the results were different: this time the product contained no more than 3% of manganese, compared with 5% in the open vase experiment. In addition, the liquid phase did not contain HCl or sulfuric acid. Clermont and Guiot believed that these results could be easily explained: ammonium chloride dissociated at the boiling temperature of the solution in a constant percentage. The freed HCl decomposed the manganese sulfide forming manganese chloride, while the hydrogen sulfide boiled out with the ammonia and formed ammonium sulfide. Since the products of the dissociation of ammonium chloride were eliminated incessantly, the HCl reacted with manganese sulfide while the ammonia volatilized. The system returned to the initial state and a new dissociation took place, regulating by the same laws as before. The phenomena taking place in a closed was equally explained in an easy manner. Dissociation also occurred but its products could not be eliminated; the ammonium sulfide reacted continuously with the manganese chloride, regenerating the manganese sulfide (Clermont & Guiot, 1877c).

Clermont and Guiot tested also the reaction of ammonium chloride with other metallic sulfides. For example, the results with silver sulfide were very different from those with manganese sulfide: a very small of ammonium chloride dissociated, no silver chloride was formed, and very little ammonia volatilized (Clermont & Guiot, 1877c).

In a previous publication Clermont and Guiot described the decomposition of metallic sulfide by boiling water and showed that this phenomenon consisted in a decomposition of the hydroxides with the help of heat. The first experiments were carried with a boiling aqueous suspension of manganese sulfide and showed the release of a significant amount of H_2S. The reaction was very simple and could be represented by the equation $MnS + H_2O = MnO + H_2S$. It was also shown that under the same conditions, other sulfides (i.e., iron, cobalt, nickel, silver, antimony, arsenic, and tin) behaved in a similar manner. Clermont and

Guiot published an additional paper summarizing all their work about sulfides (Clermont & Guiot, 1877d).

Clermont and J. Frommel wrote that dissociation was a phenomenon where a complex substance, under the influence of heat, decomposed into the simpler bodies that constituted it (Clermont & Frommel, 1878b). This had led to the natural supposition that sulfides in contact with water formed first sulfide hydrates and then dissociated without the water solvent playing a chemical role. This reasoning had been amply supported by experimental results. Thus, for example, when dissociating arsenic sulfide, freshly precipitated, there was a certain value for describing the rate of release of the hydrogen sulfide. If now the same process was carried using the same amount of arsenic sulfide that had been dried at 125 ºC and contacted previously with boiling water in a closed vessel for many hours, the value representing the rate of release of the hydrogen sulfide would be found to be sensibly the same as in the first experiment. These results demonstrated clearly that the sulfur hydrate produced in the first place, dissociated afterwards. Clermont and Frommel did not find numerical data for the dissociation of sulfides below and above 100 ºC, so they demonstrated their dissociation by boiling them with water, under vacuum. In this manner they found that arsenic sulfide begun to dissociate at 22 ºC, ferric sulfide at 56 ºC, silver sulfide at 89 ºC, and antimony sulfide at 95 ºC (Clermont & Frommel, 1878b).

Clermont and Frommel were also intent in proving that other sulfides also dissociated, and that before this phenomenon took place the sulfides were in the state of sulfide hydrates (Clermont & Frommel, 1879a). In order to determine the action of water on manganese sulfide, Clermont and Frommel boiled a suspension of 10 atoms of the sulfide (0.88 g) in 500 g of water, replacing the water as it evaporated. The vapors were bubbled though a titrated solution of iodine, containing 12.7 g of iodine per liter, to determine the amount of hydrogen sulfide distilled until the end of the reaction. Clermont and Frommel found that it was impossible to determine the total amount of acid released because part of it always decomposed into sulfur, inside the tubing. Similar experiments were carried with silver sulfide and arsenic trisulfide. The results of these three series of experiments showed that the ratio amount of water/amount of sulfide had no influence on the disengagement of H_2S, a first argument proving the phenomenon of dissociation. The same experiment conducted in a closed vessel ended when the atmosphere of the apparatus became saturated at the limit of the dissociation pressure (Clermont & Frommel, 1879a).

Iodacetone

Clermont and Chautard found that iodine reacted directly with acetone producing iodacetone; the iodine dissolved in the acetone with release of heat and produced a dark color (Clermont and Chautard, 1885). Bringing the mixture to boiling was enough to complete the reaction. This resulted in the total destruction of the HI produced and formation of a mass-colored dark red brown and composed mostly by a dark resinous material originating from the destruction of most of the acetone iodated by the HI. Clermont and Chautard found that the destruction of iodacetone could be avoided by conducting the reaction in the presence of iodic acid. They described iodacetone as a limpid and volatile liquid, of relative density 2.17 at 15 ºC, very corrosive and not inflammable. It was completely soluble in alcohol, ether, benzene, chloroform, and carbon disulfide, and highly soluble in agitated water. It decomposed before boiling, even under vacuum. It had a suffocating odor and strongly irritated the mucus membranes, particularly of the eyes. It did not react with diluted KOH and was soluble in concentrated KOH producing a brown solution. The halogens attacked it strongly; HCl, HBr, and sulfuric and nitric acids

dissolved it with release of heat; after a short time, the solution deposited a precipitate of symmetric di-iodacetone, CH_2I-CO-CH_2I, melting at 61.5 ºC (Clermont & Chautard, 1885).

Phenols

Aurin (rososolic acid, corallin)

In 1834 Friedlieb Ferdinand Runge (1794-1867) obtained for the first time the dye aurin by distillation of coal tar (Runge, 1834). This dye was studied by many chemists and found that it could be prepared by mixing phenol with calcium carbonate, and leaving the mixture alone for a long time, basically according to the reaction:

$CO_2 + 3C_6H_5OH = 2H_2O + C_{19}H_{14}O_3$

Clermont and Frommel decided to study this reaction in more detail to determine if it took place with CO_2 or CO (as other chemists believed) and if the gas had to be in a nascent state to effect the reaction (Clermont & Frommel, 1879b). For this purpose, they reacted under pressure and at 250 ºC, carbon monoxide (or dioxide) with phenol. The results were negative in both cases. These results indicated that in no case the CO and CO_2 (previously prepared) were actually participating in the reaction. They repeated the experiment this time using a mixture of CO and oxygen. Now the CO reacted with the oxygen and the resulting CO_2 caused in the formation of a large amount of aurin, proving that the reaction occurred only in the presence of nascent CO_2 (Clermont & Frommel, 1879b).

Quinones

Clermont and Chautard studied the combination of quinone with a series of benzoic phenols (Clermont & Chautard, 1886). In the first experiments they reacted an excess of acetyl chloride with phenoquinone and observed the release of abundant HCl accompanied by a discoloration of the liquid phase. They eliminated the excess of acetyl chloride and distilled the residue. The fraction passing at 190 ºC was found to be phenyl acetate, C_6H_5O-OC_2H_5. The residue, after being held for a long time under vacuum, became a crystalline mass, which after purification and analysis was found contain, by weight, 51.20% of carbon and 4.20% hydrogen, corresponding to monoacetylated chlorohydroquinone, $C_6H_3Cl(OH)(OC_2H_5O)$. This compound melted at 62 ºC. Similar results were found with acetyl bromide and benzoyl chloride (Clermont & Chautard, 1886).

Clermont and Frommel reacted an equimolar ethereal mixture of pyrocatechol and quinone and obtained a crystalline product containing, by weight, 65.95% carbon and 5.00% hydrogen, corresponding to pyrocatechol-quinone, $C_6H_4(OH)O$-O-$C_6H_4(OH)$, crystallizing as deep green needles, melting at 153 ºC, and sublimating with decomposition at higher temperatures. They also prepared pyrogalloquinone by the method proposed by Wichelhaus, (involving the reaction of pyrogallic acid and quinone) and found that this compound was identical with the purpurogallin prepared by oxidation of pyrogallol. For this reason, they suggested naming both compounds pyrogalloquinone (Clermont & Chautard, 1886).

Clermont and Chautard prepared phloroquinone by reacting phloroglucinol with quinone, having formula $C_6H_4O_2$-2[$C_6H_3(OH)$-O]. This substance appeared as rectangular plates, red and transparent, sublimating without decomposition, and being split by hydrogen sulfide into phloroglucinol, and hydroquinone (Clermont & Chautard, 1886).

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