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JOACHIM ISIDORE PIERRE
Contributions to Organic and Inorganic Chemistry

Jaime Wisniak [a,*] **(0000-0002-0265-4193).**

[a] **Department of Chemical Engineering, Ben-Gurion University of the Negev,Beer-Sheva, Israel 84105**

* wisniak@exchange.bgu.ac.il

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ABSTRACT

Joachim Isidore Pierre (1791-1862), a French chemist and physicist, to whom we owe a detailed study of the products and derivatives of the fermentation of beet juice, of azeotropism and steam distillation, the synthesis of many organic derivatives, of the hydrates of sulfuric acid and sulfur dioxide, and of silicon chlorosulfide.

Keywords: alcohols; azeotropism; organic acids; silicon derivatives, steam distillation; sulfur derivatives.

RESUMEN

Joachim Isidore Pierre (1791-1862), fue un químico y físico francés al que le debemos un estudio detallado de los productos y derivados de la fermentación del jugo de betarraga, del azeotropismo y la destilación por vapor, la síntesis de un gran número derivados orgánicos, de los hidratos del ácido sulfúrico y del dióxido de azufre, y del cloro sulfuro de silicio.

Palabras claves: ácidos orgánicos; alcoholes; azeotropismo; derivados del azufre; derivados del silicio; destilación al vapor.

INTRODUCTION

Life and career (Anonymous, 1891)

Joachim Isidore Pierre was born in Buno-Bonnevaux (Essonne, France) on November 14, 1812, the son of Jean Isidore Pierre, a farmer, and Marie Catherine Sophie Courier. Pierre spent his infancy at a farm and then entered the college de Fontainebleau. He then served as assistant at the Institution Barbet, a private secondary education school in Paris, while completing his education at the college Henri IV. Between 1833 and 1835 he was admitted to the École Polytechnic as an external student, from where he received his degree of Licencié ès sciences mathématiques et ès sciences physiques (1836). From May 1837 to March 1839, he served as assistant to the physics course given at the college Henri IV. Health problems forced him to stop working during 1839-1840. In 1840 he was appointed adjunct assistant to the course given by Victor Regnault (1810-1878) at the College de France and under his guidance he began to study the expansion of liquids, a task the led to his doctorate in physical sciences awarded by the Faculté des Sciences de Paris, after successfully defending two theses, one about certain zinc salts and their specific volumes, and another about the expansion of liquids (Pierre, 1845ab). From here on he began a rapid academic career: assistant chemist at the École de Mines (1842-1846), substitute to the chemistry professor at the Faculté de Bordeaux (1846-1847) and three years later appointed full professor of general chemistry and agricultural chemistry at the Faculté des Sciences de Caen (1849); in 1850 he inaugurated at the Faculty a course on agricultural chemistry; in 1853 he was elected by unanimity to Académie des Sciences (rural economy section) replacing the botanist Matthieu Bonafous (1793-1852); and in 1867 he was elected dean of the Faculty in substitution of the naturalist and paleontologist Jacques Amand Eudes Deslongchamps (1794 -1867), a position he kept until his retirement in 1879.

On May 9, 1843, Pierre married Amélie Marguerite Edouard; five children were born of this union.

Pierre passed away in Caen, on November 11, 1881.

SCIENTIFIC CONTRIBUTION

Pierre wrote more than 100 papers and books (e.g., Pierre, 1851b, 1856, 1862, 1865, 1867, 1874, 1878) about inorganic, industrial, and organic chemistry, agriculture (Pierre. 186-1864), fertilizers, rural economy, etc. In addition to the subjects described below he discovered a series of double salts formed by the oxides of the magnesium group (Pierre, 1845c); a new chlorinated derivative of the Dutch liquor (ethylene dichloride) (Pierre, 1847a) and a new crystalline hydrate of HCl (Pierre, 1876); he made a detailed study of the expansion of liquids (Pierre, 1845ad, 1846); studied the combinations of silicon (Pierre, 1848a); the presence of ammonia in the atmosphere (Pierre, 1853); the development and composition of colza (Pierre, 1860, 1863); and thermometry (Pierre, 1842, 1848c, 1849, 1851b, 1878); etc.

Attention must be taken to the fact that in all their equations and formulas Pierre and E. Puchot assumed the atomic masses C = 6 and H = 1.

Beet juice fermentation

In an initial paper on the subject Pierre and his assistant Ed. Puchot wrote that the first products passing during the ordinary distillation of the fermented juice had an offensive, penetrating, suffocating and long-lasting odor. These products were also susceptible of becoming colored instantaneously and attaching to the fractions passing afterwards; Pierre and Puchot believed that they were composed mainly of acetaldehyde and its derivatives. Towards the end of the distillation the main products were butanol, propanol, and amyl alcohol (Pierre and Puchot, 1868). Pierre and Puchot separated these alcohols as their iodides and acetates and reported their boiling point and relative density. Thus, for example, butanol boiled at 107.5 °C (they did not indicate the pressure) and had a relative density of 0.820 at 0 °C; its iodide and acetate boiled at 104.5 °C and 105 °C, respectively (they were probably a mixture of the pertinent isomers). The properties of both acetates were like those of the butyrates and were isomeric with them. Their composition did not allow determining their degree of purity because a mixture of methanol and propanol had the same centesimal composition of ordinary alcohol, a mixture of ethanol and butanol the composition of propanol, etc. (Pierre and Puchot, 1868):

$$C_2H_4O_2 + C_6H_8O_2 = 2C_4H_6O_2$$
$$C_4H_6O_2 + C_8H_{10}O_2 = 2C_6H_8O_2$$

In a following paper Pierre and Puchot reported numerical values of the relative density and vapor pressure (between 0° and 98 °C) of the normal propanol they had separated from the fermentation product of beet juice; for example, at room pressure this substance boiled at 98 °C and had a relative density of 0.820 at 0° C (Pierre and Puchot, 1869a). They also added that theoretically, propanol was derived directly from the fermentation of beet sugar by simple fixation of water and elimination of CO_2:

$$nC_{12}H_{12}O_{12} = 4C_{2n}H_{2n}O_2 + 4nCO_2 + 4(n - 2)HO$$

with $n = 3$. The same equation could be used to explain the formation of other alcohols, such as ethanol and butanol (Pierre and Puchot, 1869a).

In 1871 Pierre and Puchot published a long memoir (130 pages) describing in detail all the work that they had conducted on the question of the products of the fermentation of beet juice (Pierre and Puchot, 1871a).

Reactions of the normal alcohols

Pierre and Puchot wrote that a common procedure for oxidizing organic materials was the use of a mixture of potassium dichromate and sulfuric acid. This reaction was very lively, and the resulting products depended on the raw material, the relative proportion of the reagents, and the conditions under which it was conducted. In the case of a normal alcohol, the three most important products were the normal acid, the aldehyde, and the ether. In this particular paper they reported the results of their experiments with propyl, butyl, and amyl alcohol (Pierre and Puchot, 1869b).

Their results indicated that the ether was generally more stable than the aldehyde and easier to separate than the corresponding acid. Pierre and Puchot wrote that their main object was to find the conditions under which the greatest possible quantity of the compound ether was formed. This goal was better achieved by working at the lower temperature possible and the less complex the formula and the lower the molecular weight of the alcohol employed. The conversion of an alcohol into ether could be expressed by the following general equation:

$$2C_{2n}H_{2n+2}O_2 + (4/3)(Cr_2O_6,KO) + (16/3)\ SO_3 = 4HO + C_{2n}H_{2n-1}O_3, C_{2n}H_{2n+1}O + (4/3)[3SO_3, Cr_2O_3,SO_3,KO]$$

applicable successively to amyl ($n = 5$), butyl ($n = 4$), and propyl ($n = 3$) alcohol. The complete transformation of the normal alcohol into the monohydrate of the acid required the intervention of double the amount of oxygen, that is, double the amount of potassium dichromate and sulfuric acid (Pierre and Puchot, 1869b).

Pierre and Puchot went on to describe the preparation of amyl valerate, butyl butyrate, and propyl propionate, by the oxidation of the corresponding alcohol (amyl, butyl, and propyl).

The reaction between amyl alcohol and the chromic mixture was very exothermic and required cooling to increase the yield of amyl valerate. Thus, 540 g of amyl alcohol were mixed with 825—850 g of sulfuric acid, previously diluted with its own volume (about 400 g) of water and cooled; the whole was poured into a wide-mouthed vessel of 4-5 L capacity, furnished with a stirrer, and after addition of about 250 g of water, 675 g of finely powdered potassium dichromate were gradually introduced in small quantities at a time, under constant agitation and cooling. At the end of the reaction, the supernatant layer was removed and fractionally distilled. This layer represented from 84 to 85% of the weight of alcohol employed and consisted chiefly of amyl valerate, together with amyl aldehyde and a small quantity of unreacted alcohol. The pure amyl valerate thus obtained was a limpid, colorless liquid, of an agreeable fruity odor, boiling constantly at 190 °C. Pierre and Puchot provided a table giving the values of the relative density of the ester between 0° (0.874) and 190 °C (0.700). The ester was reacted with KOH to yield potassium valerate, which was then used to prepare several valeric acid esters (Pierre and Puchot, 1869b).

A similar process prepared butyl butyrate and propyl propionate. Butyl butyrate appeared as a limpid, colorless liquid, having an agreeable fruity odor, and boiling at 149.53 °C at 758 mmHg. Pierre and Puchot provided a table giving the values of the relative density of the ester between 0° (0.872) and 149.5 °C (0.721). Propyl propionate was a colorless limpid liquid, slightly piquant, having a fruity smell and boiling at 124.3 °C at atmospheric pressure. This ester had the same properties as the one prepared by the direct reaction between propanol and concentrated sulfuric acid. Pierre and Puchot provided a table giving the values of the relative density of the ester between 0° (0.903) and 124.75 °C (0.7625) (Pierre and Puchot, 1869b).

Esters of n-propanol

In a following publication Pierre and Puchot described the preparation and properties of propyl iodide and a series of esters of propanol (valerate, butyrate, acetate, and formiate) and propionic acid (butyl and ethyl) (Pierre and Puchot, 1869c). Propyl iodide was prepared by reacting propanol with iodine in the presence of phosphorus added in small portions. The final liquor was colorless and composed of two phases; the lower one was the most abundant and consisted mainly of propyl iodide. It was separated by means of a funnel and washed with a small quantity of water, followed by washes with a diluted solution of sodium carbonate. After drying with calcium chloride, it was rectified several times until the propyl iodide was pure enough. Pure propyl iodide was a colorless liquid boiling at 104.25º-104.5 ºC at atmospheric pressure and becoming colored on contact with air due to decomposition of a small of propyl iodide into iodine. Pierre and Puchot provided a table describing the relative density of the ester between 0° (1.784) and 104.5 °C (1.576). Propyl valerate was prepared by mixing one part of propanol with 2.5 parts of dry potassium valerate and slowly adding 1.5 parts of ordinary sulfuric acid, to avoid overheating. The upper liquid layer was then separated and distilled to yield unreacted propanol, propyl valerate, and a small amount of a mixture of propyl valerate and valeric acid. The propyl valerate was a limpid colorless liquid boiling at 157 ºC (761 mmHg). Pierre and Puchot provided a table giving the values of the relative density of the ester between 0° (0.887) and 157 °C (0.7255). Propyl butyrate was prepared in a similar manner; it was a limpid colorless liquid, with a slight fruity smell, and boiling at 137.25 ºC (765 mmHg). Pierre and Puchot provided a table giving the values of the relative density of the ester between 0° (0.888) and 137.25 °C (0.7445). Similar information was provided for the esters propyl propionate, propyl acetate, propyl formiate, butyl propionate, and ethyl propionate (Pierre and Puchot, 1869c).

Chemical stability of the alcohols

In a following publication Pierre and Puchot studied the chemical stability of *n*-propanol, *n*-butanol, and *n*-pentanol under the different conditions of their preparation: (1) alcohol obtained directly from the raw fermentation product by successive distillations, followed by dehydration; (2) alcohol remaining from the partial oxidation of alcohol #1; and (3) alcohol obtained regenerated from de ester. To do so they measured and compared the values of a series of properties: (a) boiling temperature, (b) relative density at a series of temperatures varying from 0 ºC to the boiling point; (c) refractive index at 9 ⁰C, with respect to an orange medium and angle of the prism 52⁰22'; and (d) deviation of the plane of polarized light (Pierre and Puchot, 1870a).

The experimental results indicated that under the three clearly distinct conditions, the three alcohols (a) behaved like one and only one species; (b) the identity of the pertinent properties was an index to their purity, and (c) only amyl alcohol acted upon the plane of the polarized light (Pierre and Puchot, 1870a).

Aldehydes of the alcohols

The three aldehydes (propyl, butyl, and amyl) were separated from the product of the reaction of the pertinent alcohol with the chromic mixture by successive fractionation (Pierre and Puchot. 1870b). Propionaldehyde was a perfectly limpid liquid, having a suffocating odor like acetaldehyde and promptly oxidizing in contact with air (even faster in the presence of platinum sponge). It boiled at 46 ºC at atmospheric pressure and it easily reduced silver nitrate producing a gleaming deposit. Pierre and Puchot provided a table describing the relative density of the aldehyde between 0° (0.8327) and 46 °C (0.7730). According to Pierre and Puchot the separation of propionaldehyde from the accompanying acetaldehyde was very difficult, for this reason they recommended preparing propionaldehyde by the direct oxidation of the alcohol. Butyraldehyde was a limpid colorless liquid having a suffocating odor, less penetrating than that of acetaldehyde and propionaldehyde, and boiling at 62 °C at room pressure; it oxidized easily in contact with air, yielding butyric acid, and reduced the salts of silver. Pierre and Puchot provided a table describing the relative density of the aldehyde between 0° (0.8226) and 62 °C (0.7481). Amyl aldehyde (*n*-valeraldehyde) boiled at 92.5 °C (atmospheric pressure) and converting easily into valeric acid. Pierre and Puchot provided a table describing the relative density of the aldehyde between 0° (0.822) and 92.5 °C (0.7251) (Pierre and Puchot, 1870b).

Alkyl bromides and chlorides

Pierre and Puchot prepared propyl bromide by slowly adding, alternatively, to 100 parts of pure propanol 15 parts of phosphorus and 140-145 parts of bromine, under agitation. This process had to be conducted very carefully to avoid the inflammation of the phosphorus. The original liquid became slowly colorless and towards the end of the addition it disengaged abundant vapors of HBr (Pierre and Puchot, 1871b). The product was distilled and the fraction boiling below 110 °C was washed with cold water. The crude propyl bromide collected at the bottom and was separated with a funnel. It was purified by repeated distillation up to 110 °C and then dried with calcium chloride. The purified product was a mobile limpid and colorless liquid, having a very pleasant ethereal odor, and boiling at 72 °C under atmospheric pressure. In contact with air, particularly humid air, it slowly became colored. Pierre and Puchot provided a table of the numerical values of its relative density between 0° (1.3497) and 92 °C (1.2256). Butyl bromide was prepared and purified by a similar procedure. It also was a limpid colorless liquid, having a pleasant ethereal smell, boiling at 90.5 °C under atmospheric pressure, and slowly decomposing when in contact with air. Its relative density at 0°, 40.2°, and 73.5 °C was 1.249, 1.191, and 1.1408, respectively (Pierre and Puchot, 1871b).

Pierre and Puchot (Pierre and Puchot, 1871c) prepared propyl and butyl chloride by two methods: (a) by passing a stream of HCl gas through propanol and distilling the acid mixture, and (b) by slowly adding phosphorus pentachloride to pure propanol, under strong cooling. The final product was washed repeatedly with water followed by drying with calcium chloride, and purification by fractional distillation. Pure propyl chloride was a limpid colorless liquid, having a slight alliaceous smell and boiling at 46.5 °C. Pierre and Puchot provided a table of the numerical values of its relative density between 0° (0.9156) and 46.5 °C (0.8572). They reported that the distillation of the reaction product yielded at the end, a flammable gas like the Dutch oil (ethylene dichloride). Butyl chloride was prepared by distilling a supersaturated solution of HCl in butanol and by treating butanol with phosphorus pentachloride and separating the resulting liquor by fractional distillation. Butyl chloride was a very mobile limpid liquid, having a pleasant ethereal odor, and boiling at 69 °C under atmospheric pressure Pierre and Puchot provided a table of the numerical values of the relative density between 0° (0.8953) and 69 °C (0.8159) (Pierre and Puchot, 1871c).

Distillation of mixtures of alcohols and water

In 1871 Pierre and Puchot referred to a phenomenon they had casually observed during the distillation of the products of the alcoholic fermentation of beet just (Pierre and Puchot, 1871d, 1872a). They mentioned that during the distillation of a mixture of amyl alcohol and water the temperature would rapidly increase until it reached about 96 °C, the liquid would begin to boil while the temperature remained constant. A turbid mixture of amyl alcohol and water would pass over, which promptly separated into two phases, an upper one composed of amyl alcohol, and another that was only water. Sampling this stream at different times showed that during the time the temperature remained constant at 96 °C the ratio of the volumes of the two phases separated remained constant at the 2:3. This situation remained constant until one of the two components became exhausted. If the exhausted component were amyl alcohol, the boiling temperature would brusquely increase to 100 °C; if the exhausted component were water, the temperature would promptly increase to 136 °C. The same phenomenon occurred when distilling a mixture of butanol and water. If both components were present, the boiling would take place at the constant temperature of 90.5 °C, until the complete disappearance of butanol in the presence an excess of water. The distillate would always be composed of 5 volumes of alcohol and 1 of water. At the appropriate time, the temperature would increase to 100 °C, if the water was predominant, or to 108 °C if it were butanol (Pierre and Puchot are describing the phenomenon of steam distillation under the internal steam generation mode, leading to a significant decrease in the boiling point of the components. This process is equivalent to distillation under vacuum) (Pierre and Puchot, 1871d, 1872a).

These results led Pierre and Puchot to study the distillation of a mixture of the three substances, water, amyl alcohol, and butanol. In this case the phenomenon was different, the boiling temperature increased constantly from the beginning to the end of the process, but it *was always between* 90.5° and 90.8 °C. The higher values corresponded to mixtures containing a large percentage of amyl alcohol. The proportion of water that passed over increased with increased distillation temperature. These results seemed to indicate that the distillation of the ternary mixture yielded a product increasingly poorer in butanol and increasingly richer in amyl alcohol, and that the separation of the two alcohols progressed in the same manner than the distillation of a binary mixture of butanol and amyl alcohol. In other words, during distillation of a ternary mixture of water, butanol, and amyl alcohol the boiling temperature did not remain constant, it changed according to the relative proportion of the two alcohols but remained always at a value *below* the boiling point of the most volatile component of the mixture and *between* the boiling point of the binary aqueous mixtures (Pierre and Puchot, 1871d, 1872a).

In a following paper Pierre reported that the same phenomenon was observed when distilling a mixture of water and butyl iodide (specific gravity 1.6, boiling point 122.5 °C) (Pierre. 1872). In this situation the iodide constituted the lower layer. Upon heating, the temperature of the mixture increased to 95-96 °C and remained constant while the distillation advanced regularly, and the two liquids were present. The rose color of the iodide allowed visualizing the process: large drops of the iodide disengaged from the bottom, traversed the water layer and then fell to the bottom. The condensed distillate separated into two liquid phases, in the volumetric ratio water: iodide = 21:79. Pierre added that a mixture of water and ethyl iodide presented the same behavior (Pierre, 1872).

Azeotrope n-propanol+water

According to Pierre and Puchot, some scientists believed the existence of a stable monohydrate of *n*-propanol, boiling at about 85 °C without splitting (Pierre and Puchot, 1872b). They decided to investigate this possibility in detail since their studies about the products of the fermentation of better juice allowed them to prepare the pure alcohol in large quantities. First, they reported that *n*-propanol mixed with distilled water in all proportions but was sparingly soluble in water saturated with NaCl. The saline solution absorbed a large amount of water and floated on top of water and precipitated part of the salt. Their results indicated that this hydrate, if it existed and could be prepared by a simple mixture of the components, could not be distilled without decomposition. In addition, during distillation of an aqueous solution of *n*-propanol of any composition, the boiling temperature of the mixture was always less than that of the more volatile liquid, but it never achieved a value below 88.3 °C. At the beginning of the distillation, a fraction composed of 1 alcohol and 2.18 of water passed over passed over, boiling at about 88.5 °C and having relative density 0.854. A starting mixture having this composition distilled completely, without decomposition, at the constant temperature of 88.3 °C (today we know that the mixture *n*-propanol+ water presents an azeotropic point 87.7 °C, 760 mmHg, relative density 0.866 at 25 °C, and containing 71.7% water by weight). Distillation of a starting mixture containing a larger percentage of water, left in the retort water totally deprived of alcohol. If the initial mixture contained less water than the critical one, then the residue would be dry propanol (Pierre and Puchot, 1872b).

Propionic acid

Pierre and Puchot prepared this acid (also known as *metacetonic* acid) by oxidizing propyl alcohol with an aqueous mixture of potassium dichromate and sulfuric acid. The chromic mixture was added slowly and under cooling (12°-13 °C) in order to avoid the formation of propionaldehyde (Pierre and Puchot, 1872c, 1873a). At the end of the reaction the solution appeared as two phases; the upper layer was composed mainly of propyl propionate, mixed with a little of propanal and unreacted alcohol. This liquid was distilled at about 102 °C; on cooling, the passing fraction separated into two phases. The lower phase, which was very acid, but exempt of sulfuric acid, was composed of propionic acid very diluted in water. The acid was propionate was converted into potassium propionate by means of KOH. This propionate was later used to prepare ethyl and propyl propionate (Pierre and Puchot, 1872c, 1873a).

An alternative process consisted in oxidizing the propyl alcohol with a larger quantity of chromic mixture in order to transform the alcohol, as much as possible, into free propionic acid. The resulting liquid consisted of two phases, a saline deposit colored violet green and a supernatant liquid consisting of propionic acid. The saline deposit was washed with water and all the accumulated liquid was distilled until the residue n the retort had turned into a syrupy mixture. The passing propionic acid was neutralized with potassium or barium hydroxide to form the pertinent salt (Pierre and Puchot, 1872c, 1873a).

In every case the potassium propionate was converted into propionic acid by means of sulfuric acid and the free acid purified by successive distillations. The pure acid boiled at 141.5 °C under a pressure of 760 mmHg and had a piquant odor. Pierre and Puchot determined the relative density of the acid at several temperatures between 0 °C (1.0143) and 141.5 °C (0.8608). They also described the preparation and properties of the propionates of barium and silver (Pierre and Puchot, 1872c, 1873a).

In another paper Pierre and Puchot added additional information about the preparation of this acid (Pierre and Puchot, 1873d). The separation of the acid from its potassium salt was carried on by treating the salt with sulfuric acid containing a little of water, in the ratio of 44 to 88 parts of sulfuric acid per 100 of potassium propionate. The sulfuric acid was slowly added to avoid an excessive increase in the temperature with the corresponding loss of propionic acid by volatilization. Analysis of the purified acid indicated a composition corresponding to the formula $C_6H_5O_3$,HO, showing that the acid contained 11.9% by weight, of water. In other words, this compound was a monohydrate of propionic acid. The barium propionate contained one equivalent of water per equivalent of the salt. This propionate was very useful for preparing other propionates by double decomposition. For example, the silver propionate was easily prepared by heating a mixture of barium propionate and silver sulfate, in the proportion of their equivalents. Silver propionate was an anhydrous salt having the formula $C_8H_5O_3$,AgO (Pierre and Puchot, 1873d).

Butyric acid and derivatives

In 1873 Pierre and Puchot reported the results of their experiments on butyric acid and its derivatives (Pierre and Puchot, 1872e, 1873c). The acid was prepared by converting butanol into butyl butyrate and changing the latter into potassium butyrate. For these purposes they mixed 300 g of butanol with 540 g of sulfuric acid and slowly added 400 g of powdered potassium dichromate, keeping the system under cooling and agitation. The resulting upper layer was composed mainly of butyl butyrate mixed with a small amount of butanal and unreacted butanol. The butyl butyrate was separated by fractional distillation and then reacted with potassium, in the ratio 55 parts per 100 of butyrate. The butyric acid was separated by reacting the butyrate with sulfuric acid, taking care of keeping the temperature below 50 °C. The resulting liquid split into two phases, a lower one containing potassium sulfate, and an upper yellow phase containing most of the butyric acid. The upper phase was then distilled to deposit the dissolved saline matter and sulfuric acid (Pierre and Puchot, 1872e, 1873c).

According to Pierre and Puchot, the butyric acid prepared by the oxidation of the butanol obtained from fermented beet juice, boiled at 155.5 °C and 760 mmHg. This acid had no action upon the plane of the polarized light. Pierre and Puchot reported the values of the relative density of this ester at 16 temperatures between 0° (0.909) and 155.5 °C (0.805), and the preparation and properties of the barium butyrates (C_8H_7O3, BaO), silver butyrate (C_8H_7O3, AgO), and ethyl and methyl butyrate (Pierre and Puchot, 1872e, 1873c).

Valeric acid and derivatives

Pierre and Puchot prepared this acid by the partial oxidation of amyl alcohol with the chromic mixture properly diluted (Pierre and Puchot, 1872d, 1873b). They represented the reaction as follows

$$6C_{10}H_{12}O_2 + 4(Cr_2O_6,KO) + 16SO_3 = 12HO + 3(C_{10}H_9O_3,C_{10}H_{11}O) + 4(3SO_3,Cr_2O_3,SO_3,KO)$$

Which appeared to be a simple subtraction of hydrogen (one equivalent for one equivalent of alcohol)? This reaction was always accompanied by the formation of amyl aldehyde, even when conducted at a low temperature. The final product was composed of two liquid phases; the upper one contained mainly amyl valerate mixed with unreacted alcohol, and a small amount of amyl aldehyde and valeric acid. This layer was separated and distilled; the fraction passing between 175° and 192 °C was composed of very pure amyl valerate. The fraction passing under 175 °C was mostly composed of unreacted amyl alcohol mixed with a little of amyl aldehyde, valerate, and traces of valeric acid. The amyl valerate was reacted with KOH to yield potassium valerate, and amyl alcohol. The latter was eliminated by distillation and the remaining salt decomposed with sulfuric acid (Pierre and Puchot, 1872d, 1873b).

Valeric acid, concentrated as much as possible, boiled at 178 °C under 760 mmHg and had a relative density varying between 0.947 at 0 °C and 0.7809 at 178 °C. It contained the acid and one equivalent of water, which could be eliminated by distillation. In the presence of an excess of water it boiled at between 99.8° and 100 °C, forming vapors, which, by their condensation, yielded two distinct layers of liquid; the lower layer was an aqueous solution of the acid, and the upper one was a hydrate of the acid. Valeric acid deviated the plane of polarization of light in the same direction as crystallized sugar, while anhydrous amyl alcohol did the reverse. Amyl valerate deviated the plane of light with the same intensity as a 6.6% weight aqueous solution of sugar (Pierre and Puchot, 1872d, 1873b).

In another paper Pierre and Puchot added additional information about the preparation of this acid (Pierre and Puchot, 1873d) The separation of valeric acid from its potassium salt was carried on by treating the salt with sulfuric acid containing a little of water, in the ratio of 65 parts of sulfuric acid per 100 of potassium propionate. The sulfuric acid was slowly added to avoid an excessive increase in the temperature with the corresponding loss of propionic acid by volatilization. The resulting liquid separated into two phases; the upper one contained raw valeric acid. This phase was distilled. Analysis of the purified acid indicated a composition corresponding to the formula $C_6H_5O_3$, HO, showing that the acid contained 11.9% by weight, of water. In other words, this compound was a monohydrate of propionic acid. The barium propionate contained one equivalent of water per equivalent of the salt. This propionate was very useful for preparing other propionates by double decomposition. For example, the silver propionate was easily prepared by heating a mixture of barium propionate and silver sulfate, in the proportion of their equivalents. Silver propionate was an anhydrous salt having the formula $C_8H_5O_3$, AgO (Pierre and Puchot, 1873d).

An interesting phenomenon occurred when heating mixtures of valeric acid saturated with water or water saturated with valeric acid. The temperature increased to 99.8°-99.9 °C and remained constant for a long time; both liquids distilled simultaneously and after condensation separated into two liquids phases, one saturated with water, the other with acid. The volume ratio of both layers (about 25: 75) remained constant if the boiling temperature remained constant. Eventually the temperature began to increase and the liquid in the retort to become less turbid; when the temperature reached 100.75 °C the liquid became practically limpid. The temperature now begun to increase rapidly and only one liquid seemed to be present in the retort. Analysis of the same showed that it was valeric acid saturated with water. The similar phenomenon was observed when the distillation was started with water saturated with valeric acid; now the distillation started at 99.7 °C and increased to 100 °C; at this stage the liquid in retort contained water with a small amount of valeric acid (Pierre and Puchot, 1873d).

Boiling points of homologous organic compounds

According to Pierre and Puchot, it was commonly accepted that the boiling points of homologous organic compounds differed by a constant value for each additional C_2H_2 (today, $-CH_2$) group. Some claimed that the difference was 22 °C, others that it was 19°, 20-21 °C, etc. This rule had been used more than once for predicting the boiling point of substances yet to be isolated or little known. Pierre had already claimed in one his chemistry theses that this law seemed to have so many exceptions that it should better be considered a doubtful approximation (Pierre, 1845b). Pierre and Puchot decided to put to test the practical validity of this law using the information about the many compounds they had used or prepared from the products of the fermentation of beet juice (Pierre and Puchot, 1872f).

For example, for the linear alcohol series methanol, ethanol, *n*-propanol, n-butanol, and n-amyl alcohol they found that at atmospheric pressure the difference between the boiling points of consecutive members varied between 10° to 22 °C. For the series alkyl chlorides (ethyl, propyl, butyl, and amyl) the difference varied between 22.5° and 35.5 °C. The same conclusions were inferred for the series alkyl bromides, alkyl iodides, alkyl acetates, alkyl propionates, alkyl butyrates, alkyl valerates, alkyl aldehydes, and the acids propionic, butyric, and valeric. The conclusion was very clear: the law was invalid for all the series mentioned above (Pierre and Puchot, 1872f).

Isomerization of fermentation alcohols

According to Pierre and Puchot the components of the series of normal monatomic alcohols were able to provide, by chemical derivation, numerous groups of isomeric compounds. For example, the aldehyde $C_{2n}H_{2n}O_2$, derived of the alcohol $C_{2n}H_{2n+2}O_2$ by elimination of two equivalents of hydrogen, was isomeric with the normal ether $C_{2n}H_{2n-1}O_2$ $C_{2n}H_{2n+1}O$, which could be considered the result of the union of the simple ether of the same alcohol, $C_{2n}H_{2n+1}O$ with the corresponding acid $C_{2n}H_{2n-1}O_3$; in practice (Pierre and Puchot, 1872g):

$$nC_{2n}H_{2n}O_2 = C_{2n}H_{2n-1}O_3, C_{2n}H_{2n+1}O_2$$

This aldehyde was equally isomeric with the monohydrate derived from the alcohol. $C_{4n}H_{4n+2}O_2$ since

$$2C_{2n}H_{2n+1}O = C_{4n}H_{4n+2}O_2.$$

This phenomenon was well represented by ethyl ether and butanol, and by methyl ether and ethanol. The equality was only present in the global formula; the physical properties of the isomers were substantially different. For this reason, Pierre and Puchot suggested calling them *simple, accidental*, or *centesimal isomers.*

Pierre and Puchot added several other examples. For instance, from the union of a simple ester derived from a normal monatomic alcohol with the acid derived of another normal monoatomic alcohol it was possible to obtain two very different compounds depending on if the simple ester derived from the first alcohol and the second acid, or from the second alcohol and the first acid. These compounds could appropriately be named *reciprocal isomers* (Pierre and Puchot, 1872g).

Action of derivatives of amyl alcohol upon polarized light

According to Pierre and Puchot, amyl alcohol acted upon polarized light in the same manner as a 4% aqueous sugar solution but in an inverse direction (Pierre and Puchot, 1873e). They remarked that in their experiments they had never found the second optical form of amyl alcohol reported by Louis Pasteur (1822-1895) (Pasteur, 1855) (probably because they separated the alcohol by distillation) [1]. Pierre and Puchot wrote that the optical activity of amyl alcohol presented a singular characteristic: it varied with the amount of water it contained. For example, in increased by about one-third by the addition of about 6% of water, by weight (from -8.5° to -11⁰). In addition, the alcohol recuperated from its esters or obtained as the residue of an incomplete oxidation, did not appear to have undergone any appreciable modification either in the direction or the intensity of its action upon polarized light. This was not the case with its ethers or with the oxidized compounds produced by the chromic mixture: thus, amyl aldehyde turned the plane of polarization in an opposite direction; in the same, way as would be produced by crystallized sugar. With the pure aldehyde the deviation was identical as that produced by a 1% aqueous solution of crystallized sugar. The degree of purity of the aldehyde had a great influence on the extent of deviation. For example, crude aldehyde, saturated with water, gave a deviation three times greater (+18°) than did the pure substance (+6°). The second product of oxidation, amyl valerate, deviated light in the same direction, but seven times greater and equal to that of a 6.6% aqueous solution of crystalline sugar (Pierre and Puchot, 1873e).[47]

Pierre and Puchot reported the deviation of the plane of polarized light produced by nine different compounds of amyl alcohol, for example, amyl valerate (+40°), amyl butyrate (+8.5°), propyl valerate (+9°), and anhydrous valeric acid (-8.5°). The reported values showed no relation with the value of the relative density or the boiling point of the compound (Pierre and Puchot, 1873e).

Sulfur derivatives

The hydrate of sulfur dioxide could not be obtained by a wet procedure. Nevertheless, the experimental evidence indicated that bubbling SO_2, previously washed, through a concentrated solution of the gas maintained at about 0 °C, resulted in the formation of a crystalline deposit that increased in amount as the streaming continued. The same deposit appeared as limpid crystals upon leaving a highly concentrated of solution of SO_2 in a fresh place at -1° or -2 °C. The crystals of SO_2 hydrate contained about 28%, by weight, of SO_2, against the 20% reported by August de la Rive (1801-1873) for the hydrate prepared by the dry procedure (De la Rive, 1829). The composition of the hydrate seemed to correspond to the formula SO_2,9HO (nonahydrate), which was about four times more than the SO_2 contained in a concentrated solution of the gas at room temperature and pressure. The crystals appeared as oblique rhomboidal prisms, heavier than water and very soluble in water. Exposure of the hydrate to a temperature higher than +4 °C resulted in the fusion of the crystals and the loss of part of the acid. Well-drained crystals resisted the action of atmospheric oxygen better than the solution of the acid (Pierre, 1848b).

In another publication Pierre reported that the boiling point of liquid SO_2 was about -8 °C (the actual value is -10 °C) (Pierre, 1873).

As stated by Pierre and Puchot, it was common knowledge that sulfuric acid dihydrate, SO_3,2HO, could be easily obtained in crystalline form; nevertheless, little was known about the best conditions for the preparation of the crystals, as well as their properties. Having observed the formation of a considerable amount of the hydrate in a large flask of ordinary sulfuric acid, left alone for some time they decided to study the phenomenon in more detail (Pierre and Puchot, 1874).

Pierre and Puchot found that putting sulfuric acid dihydrate in a bath maintained at -5° to -6 °C, the acid temperature decreased to 7.5 °C and deposited crystals more and more abundant. As long as the liquid was not completely solidified, the temperature of the interior remained stationary, while the external temperature of the bath gradually rose. The temperature of the acid remained constant, for a longtime, even when the external temperature increased above +10 °C. According to Pierre and Puchot the solidification of the acid was exothermal enough to maintain the temperature of the acid, if it had not completely solidified. They were able to keep 500 to 600 g of the acid at the temperature of melting ice without any trace of crystallization. The temperature 7.5 °C should then be considered to be the fusion temperature of the hydrate. Pierre and Puchot reported that SO_3,2HO crystallized as oblique rhomboidal prisms (Pierre and Puchot, 1874).

It was well known that the fusion of hydrate crystalline substances was an endothermic process and that a mixture of sulfuric acid and an excess of snow or crushed ice constituted a refrigerant mixture. This led Pierre and Puchot to assume that a mixture of the crystals of sulfuric acid dihydrate with ice

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[1] In 1855 Pasteur reported that the raw amyl alcohol sold commercially was a mixture of two isomers, one optically active and the second showing no action upon polarized light (Pasteur, 1855).

would constitute even a stronger refrigerant mixture than the acid alone. Their experiments proved this assumption to be correct: a mixture of 800 g of crushed ice with 200, 300, and 375 g of acid crystals reached a temperature of -25°, -26.25°, and 26 °C, respectively. The best results were obtained with mixture of 3 parts of acid with 8 of ice. Pierre and Puchot also found that by sufficiently cooling diluted sulfuric acid containing less than 2 equivalents of water would split it into the crystalline dihydrate and into a more concentrated acid (Pierre and Puchot, 1874).

Pierre found that passing a mixture of hydrogen sulfide and silicon chloride through a porcelain tube heated red resulted in the formation of abundant HCl, which accompanied the excess of hydrogen sulfide and the unreacted silicon chloride. Passing the product of the reaction through a U tube submerged in cold water resulted in the condensation of a fuming liquid, having a fetid and piquant odor. The resulting liquid was somewhat milky due to the suspended sulfur that accompanied it. Left alone in a closed tube for about 48 hours, it deposited the sulfur as well as lemon yellow limpid crystals of sulfur. Distillation of the liquid separated limpid colorless liquor, fuming on air, having specific gravity 1.45 at 15 °C, boiling above 100 °C, and containing, by weight, about 65.80% chlorine, 15.01% sulfur, and 19.54% silicon, corresponding to the formula $SiCl_2S$, a chlorosulfide of silicon (Pierre, 1847b).

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