Revista CENIC Ciencias Químicas
ISSN: 1015-8553
ISSN: 2221-2442
Centro Nacional de Investigaciones Científicas

Wisniak, Jaime
GUSTAVE ANDRÉ
Revista CENIC Ciencias Químicas, vol. 53, no. 2, 2022, July-December, pp. 201-215
Centro Nacional de Investigaciones Científicas

Rev. CENIC Cienc. Quím.; Vol. 53. (2): 201-215. Año. 2022. e-ISSN: 2221-2442.

REVISION BIBLIOGRAFICA

GUSTAVE ANDRÉ

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Recibido: 05 de enero de 2022; Aceptado: 26 de octubre de 2022;

ABSTRACT

Gustave André (1856-1927), a French chemist and physician who studied in detail the synthesis and properties of numerous new oxychlorides, the complexes of acetamide and salts, the azeotropic distillation of mixtures of pyridine and fatty acids, the products of blood fermentation, and the splitting of carbohydrates.

Keywords: acetamide; azeotropy; blood; halides; organo-metallic complexes; oxychlorides; pyridine; sugars.

RESUMEN

Gustave André (1856-1927), químico y médico francés que estudió en detalle la síntesis y propiedades de numerosos oxicloruros nuevos, de complejos de acetamida y sales, la destilación azeotrópica de mezclas de piridina y ácidos grasos, los productos de la fermentación de la sangre, y el desdoblamiento de los carbohidratos.

Palabras claves: acetamida; azeotropía; azúcares, complejos organo-metálicos; haluros; oxicloruros; piridina; sangre.

INTRODUCCIÓN

Life and career (André, 1884a)

There seems to be little information about the life of Gustave André. He was born in Paris, on August 17, 1856. He received his degree of bachelier ès lettres in 1873, of bachelier ès lettres in 1875, and of licencié ès sciences physiques in 1877. Between 1879 and 1881 he worked as préparateur of natural history at the École Pratique of the Faculty of Medicine of Paris while pursuing medical studies. In 1880 he was awarded the degree of docteur ès médicine after successfully defending a thesis about the phenomenon of respiration in vegetables (André, 1880). During 1881 he also worked as préparateur in the laboratory of chemistry of Marcelin Berthelot (1827-1907) at the Collège de France. In 1884 he was awarded his doctoral degree in physical sciences by the Faculty of Sciences of Paris after defending a thesis about the chemical and thermal behavior of the oxychlorides of certain metals (André, 1884a), under the direction of Berthelot. In 1885 he was appointed head of works at the station de of vegetable chemistry of Meudon. In 1895 he was appointed adjunct professor at the Faculty of Medicine of Paris and began a successful academic career, which included appointments as replacing professor at the Collège de France (1895-1896) and professor of agricultural chemistry at the French National Institute of Agronomy (1897). His research activities earned him several important prizes, among them a gold medal of the Société d'Agriculture de France (1894), the 1898 Saintour prize of the Académie des Sciences for his work on vegetable physiology and chemical analysis of soils, and the 1906 Houlleguille prize of the Académie des Sciences for his work on chemical physiology of vegetables. In 1889 Andre was nominated Officier d'Académie and also Chevalier du Mérite Agricole. In 1899 he was elected corresponding member of the Académie d'Agriculture de France and promoted to full member in 1921.

André passed away in Paris on May 14, 1927.

Scientific contribution

André was a very prolific writer; he published about 140 papers (including near 60 with Berthelot) and books (André, 1908, 1909-1913, 1921, 1923) mainly about vegetable physiology and chemistry, on new synthesis processes of organic compounds, particularly oxychlorides and complexes of acetamide and salts. As customary for candidates to the Académie, he published a booklet describing the results of his scientific research (André, 1917); unfortunately, he failed several times in his attempt to become a member of the Académie Nationale de Médicine and of the Académie des Sciences.

In addition to the subjects described below, he studied the action of ammonium metal salts (André, 1885abc, 1887ab, 1888, 1889ab, 1891a); the properties of ammonium bicarbonate (Berthelot & André, 1886) the nitrogen principles present in vegetable soils (Berthelot & André, 1887ab, 1892a; André, 1898c, 1899de, 1902); the action of ammonia and water on chloroform (André, 1886c); studied the preparation and properties of bismuthic acid (André, 1891bc); of pyrophosphoric and metaphosphoric acids (Berthelot & André, 1896a, 1897a); and of furfuryl alcohol (André, 1899f); etc. Here we describe a few of his results in the areas of organic and inorganic chemistry.

Inorganic compounds

Halides and oxyhalides

André wrote that the study of the preparation of basic salts, their constitution, and heat of formation, constituted one of most challenging subjects of mineral chemistry. It was well- known that most metals formed basic salts, which served as intermediates of two successive reactions, the sense of which was determined by their heat of reaction. As mentioned before, this subject was the topic of one of the doctoral theses of André, under the guidance of Marcelin Berthelot (1827-1907), and gave place to many publications (André, 1881ab, 1882abc, 1883abcd, 1884abcde).

Calcium oxychloride

Several researchers had reported that when a concentrated solution of calcium chloride was boiled with calcium hydroxide or calcium sulfate and then filtered and allowed to cool, it precipitated a salt in the form of long slender needle-shaped crystals (i.e. Trommsdorf; 1802, Berthollet, 1803; Rose, 1820, 1854; André, 1881a, 1884a).Claude-Louis Berthollet (1748-1822) did not report its composition but believed that it was a particular compound composed of calcium chloride and an excess of calcium hydroxide. This substance was highly unstable in the presence of water, splitting into calcium chloride and calcium hydroxide. Heinrich Rose (1795-1864) tried to purify the needles by treating them with small quantities of water or of alcohol; he observed that both reagents, as well as CO_2, decomposed it easily. The salt decomposed in contact with air and the calcium hydroxide dissolved in nitric acid with release of gas. In a further publication (1854) Rose proposed that the formula of the new compound was $CaCl,2CaO,15H_2O$. Alfred Ditte (1843-1908) observed that the compound was relatively stable in a solution of calcium chloride and proposed that its formula was $CaCl,3CaO,16H_2O$. He observed that upon pouring water on the salt, it decomposed into calcium chloride that dissolved in the water and a precipitate of calcium hydroxide. An interesting result was that this splitting did not take place when the concentration of calcium chloride reached 85 g/L (Ditte, 1880; André, 1881a, 1884a).

André prepared large amounts of calcium oxychloride according to the method described by Rose (Rose, 1854). He heated to boiling a solution of 500 g of crystalline calcium chloride in 1500 g of water, and then added 40 g of a solution of diluted calcium hydroxide. Afterwards the solution was filtered and left to cool alone. After several hours, long needle shaped crystals deposited with a poor yield. These were dried over paper in a glass bell containing as little as possible CO_2. Analysis of the same indicated that its approximate formula was $CaCl,3CaO,16H_2O$. The crystals, left under vacuum, lost 41% of its weight and its formula became $CaCl,3CaO,3H_2O$. André then determined that at 13 ^{0}C the heat of solution of one mole of $CaCl,3CaO,16H_2O$ in three moles of HCl (highly diluted in water) was +31.7 cal, indicating that the heats of reaction of solid calcium chloride and solid calcium hydroxide were:
CaCl + 3CaO + 16HO (liquid) released 46.003 cal
CaCl + 3CaO + 16HO (solid) released 34.563 cal
and for the lower hydrate:
CaCl + 3CaO + 3HO (liquid) released 28.83 cal
CaCl + 3CaO + 3HO (solid) released 26.6853 cal

Similar measurements with quicklime indicated that CaCl + CaO disengaged +3.652 cal and CaCl,2CaO + 2HCl disengaged +49.763 cal. These results showed that

CaCl,3CaO + 3 HO (solid) disengaged +23.6 cal, CaCl,3CaO + 16HO (solid) disengaged +30.46 cal, and CaCl,3CaO,3HO + 13HO (solid) disengaged +7.88 cal. The last result being larger than the heat of hydration of calcium chloride, explained the formation of the oxychloride in the presence of water (André, 1881a, 1884a).

André reported that as a result of his experiments he had modified the procedure for making crystalline calcium oxychloride. Now he mixed a solution of 100 g of crystalline calcium chloride in 100 g of water with 10 to 15 g of pulverized strontium hydroxide, and then heated all for several minutes to a temperature below boiling. The mixture was then filtered and left to cool for several hours. The long needle-shaped crystals of oxychloride were found to be completely exempt from strontium hydroxide (André, 1884a).

Strontium oxychloride

André prepared this new crystalline compound by boiling a saturated solution of crystalline strontium chloride and strontium hydroxide. Upon cooling, the filtered liquid precipitated pearly thin strips of strontium oxychloride, which were easily decomposed by water and alcohol. In contact with air the crystals became white and opaque. These crystals were dried on paper and found to have a composition corresponding to the formula SrCl,SrO,9HO. Upon drying the hydrate lost 34.19% of water and its formula became SrCl,SrO,HO. Measurement of the heats of formation at 22 ^{0}C led to the following results (André, 1881b, 1884a):

SrCl,SrO + 9HO (liquid) + HCl (diluted)	+8.36 cal
SrCl + SrO + 9HO (liquid)	+24.44 cal
SrCl + SrO + 9HO (solid)	+18.01 cal
SrCl + SrO + HO (liquid)	+13.14 cal
SrCl + SrO + HO (solid)	+12.425 cal
SrCl + SrO,HO = SrCl,SrO,HO	+5.24 cal

Barium oxychloride

This new crystalline compound was obtained by heating to boiling a mixture of 500 g of water, 200 g of crystalline barium chloride, and 60 of barium hydroxide. The hot filtrate was left to cool and at 50 ^{0}C it transformed into a mixture of mother liquor and crystals of barium oxychloride containing an excess of barium hydroxide, and composition corresponding to the formula BaCl, BaO,8HO + (1/10)BaO,10HO(1/10)BaO,10HO. This oxychloride was easily decomposed by cold water, alcohol and bleached by the CO_2 contained in the air. André was unable to discern if this compound was a simple mixture of one equivalent of oxychloride and one of hydroxide, or a true combination containing 10 $BaCl_2$ and 11 BaO. André measured the heat of reaction, discounted the heat of solution of (1/10) BaO,10HO, and reported the following results (André, 1881c, 1884ad):

BaCl,BaO,8HO + HCl (diluted)	+ 9.84 cal
BaCl + BaO + 8HO (liquid, released)	+18.81 cal
BaCl + BaO + 8HO (solid, released)	+13.09 cal
BaCl,2HO + BaO,10HO = BaCl,BaO,8HO + 4HO	+ 3.01 cal

André also reported similar information for the oxychlorides of magnesium (André, 1882a, 1884a), zinc (André, 1882c, 1884a), lead (André, 1883a, 1884a), ammonia (André, 1884a), and mercury (André. 1884abe).

André remarked that the study of some of the above oxychlorides required knowledge of the corresponding chlorides. The combination of zinc chloride with ammonium and ammonium chloride was important because several of these combinations were destroyed by water forming oxychloride (André, 1882b, 1884a). Edward Divers (1837-1912) had reported that passing a stream of ammonia gas through a cold solution of zinc chloride dissolved in concentrated ammonia, resulted in the precipitation of a crystalline principle. Heating the suspension until disappearance of the precipitate and waiting about 24 hours resulted in the precipitation of large octahedral crystals of formula $2ZnCl,5NH_3,2HO$ (Divers, 1868). André found that these crystals were very soluble in a small amount of water and decomposed as more water was added, with formation of a voluminous white precipitate. The precipitate was promptly decomposed by air into an opaque material, accompanied by release of ammonia. André reported that dissolution of the precipitate in diluted HCl resulted in the release of 4.9 cal, as follows:
$2ZnCl,5NH_3,2HO + 5HCl$ (diluted) +46.9 cal
with the known data that
2ZnCl (solid) + 5NH3 (gas) + 2HO (liquid) +74.67 cal
2ZnCl (solid) + 5NH3 (gas) + 2HO (solid) +73.24 cal

Robert John Kane (Kane, 1839) had reported formation of an additional compound of formula $2ZnCl,2NH_3,HO$; André repeated Kane's experiments and found that the correct formula was $4ZnCl,4NH_3,HO$. Measurement of the heat effect of the corresponding reactions gave the following results (André, 1882b, 1884a):
$4ZnCl,4NH_3,HO + 4HCl$ (diluted) +27.3.9 cal
4ZnCl (solid) + $4NH_3$ (gas) + HO (liquid) +88.08 cal
4ZnCl (solid) + $4NH_3$ (gas) + 2HO (solid) +87.37 cal

André also reported similar information for lead chlorides (André, 1883a) and the double chlorides of lead and ammonia (André, 1883c).

Oxybromides and bromides

André also prepared the oxybromides and bromides of several elements and measured the pertinent heat effects.

(a) **Zinc**

Zinc oxide was digested with a concentrated and boiling solution of ammonium bromide; the saturated liquid was then filtered and left to cool. The composition of the resulting precipitate of fine white needles was found to correspond to the formula $3ZnBr,3NH_3,HO$. This compound was easily decomposed by water, particularly hot water, leaving a residue of zinc oxide. When heated on a closed tube at 200 ^{0}C, in the presence of water, it turned into an ammoniated zinc oxybromide of formula $ZnBr, 3ZnO,NH_3,5HO$. André described other procedures that allowed him to prepare three similar compounds of formulas $ZnBr,NH_3,HO$, $3ZnBr,4NH_3,2HO$, and $3ZnBr,5NH_3,HO$, as well as the oxybromides ZnBr,4ZnO,13OH, ZnBr,6ZnO,35HO. Some of the corresponding heat effects were as follows (André, 1883b, 1884a):
$3ZnBr + 4NH_3 + 2HO$ (liquid) +77.05 cal
ZnBr + 6ZnO + 35HO (liquid) + 3.0 cal

Lead

André described the preparation of a variety of lead bromides, ammoniated lead oxybromides, lead oxybromides, etc., among them, $PbBr,3NH_3Br,HO$; $PbO,PbBr$; $2PbO,PbBr$; $3PbO,PbBr$, with their corresponding effect, for example (André, 1883d, 1884a):

$PbO + PbBr$	+2.00 cal
$2PbO + PbBr$	+3.03 cal
$3PbO + PbBr$	+4.20 cal

Mercury

André wrote that very little information was available about the preparation of the oxybromides of mercury (André, 1884ace). He obtained them by heating in a closed tube at 300 ^{0}C a mixture of a given number of equivalents (1/10, 2/10, 3/10, and 4/10) of red oxide (HgO), with 1/10 equivalents of mercuric bromide. All the resulting substances looked homogeneous, colored iron grey, and crystalline, and reacted with KOH to give the yellow oxide (HgO). Each of the products was dissolved in an excess of HBr and showed the following heat effects (André, 1884ace):

$HgO + HgBr$	+1.66 cal
$2HgO + HgBr$	+2.20 cal
$3HgO + HgBr$	+3.16 cal
$4HgO + HgBr$	+3.9 cal

Organic chemistry

Acetamide

It was known that acetamide molten in a small capsule was able to dissolve a large number of anhydrous halides. Unfortunately, the crystals formed were separated with most difficulty from the accompanying excess of acetamide. For this reason, André investigated the possibility of carrying the process using acetamide dissolved in absolute alcohol (André, 1886a).

(a) Cupric chloride

The salt was dried in a stove at 120 ^{0}C and then added to a solution of 10 g of acetamide dissolved in 40 cm^3 of absolute alcohol, while heating and avoiding exceeding 120 ^{0}C to prevent the salt from becoming basic. The solution was then filtered and evaporated under vacuum. After some hours it deposited small round pieces of a soft material, which was cleared of the accompanying liquid and then washed with absolute alcohol, crushed, pressed between papers, and dried under vacuum. Chemical analysis indicated that its chemical composition corresponded to the formula $C_4H_5NO_2,CuCl$. André found that addition of ether helped the precipitation of the crystals and that using crystalline copper chloride produced the same result as using the dried salt. The cupric complex, heated under a stream of hydrogen, changed slowly; at 100 ^{0}C it turned green as result of the sublimation of the acetamide, at 130 ^{0}C it became black while releasing an acetic odor, and at 150 ^{0}C it became a black liquid, which remained viscous and did not solidify upon cooling (André, 1886a).

(b) Cadmium chloride

This chloride was also used in a dried form. A low yield deposit was formed of fine crystals having formula $C_4H_5NO_2,CdCl$.

(c) Mercuric chloride

The same experimental procedure, in the presence of ether, generated crystals of constant composition $C_4H_5NO_2,2HgCl$. This precipitate was washed with absolute alcohol and dried under vacuum. It melted at 125 0C into a slightly yellow liquid, accompanied by sublimation of a small amount of acetamide. André reported that mercurous chloride did not combine with acetamide.

(d) Nickel and cobalt chloride

These salts reacted with an alcoholic solution of acetamide producing a green and a rose liquid, respectively. Evaporation of these solutions produced after several days a crystalline salt having the same color as the initial solution and formulas $NiCl,C_4H_5NO_2,2HO$ and $CoCl,C_4H_5NO_2,2HO$, respectively. The cobalt complex absorbed humidity easily and could be dehydrated. It melted at 62 ^{0}C and when kept for 2 hours at 110-115 ^{0}C in a slow stream of hydrogen it lost all its water and traces of acetamide (André, 1886a).

Dichloromethane

Dichloromethane, boiling at 41 ^{0}C, was destroyed easily by water only when heated in a sealed tube to at least 180 ^{0}C, mainly into HCl, formic acid, and methyl chloride. Afterwards, the methyl chloride decomposed into methanol and HCl. Opening the tube resulted in the formation of a mixture of CO_2 and CO; the latter gas originated form the partial oxidation of formic acid according to the reaction (André, 1886c):

$$2C_2H_2Cl_2 + 2H_2O_2 = 3HCl + C_2H_3Cl + C_2H_2O_4$$

According to André, addition of a small amount of KOH to the tube diminished the quantity of methanol formed.

The same results were obtained substituting water by a dilute solution of ammonia. The products of the reaction included ammonium hydroxide, ammonium chloride, and methylamine hydrochloride. No cyanide was formed. The reaction could also be carried at a lower temperature; thus 3.0844 g of dichloromethane heated at 140 ^{0}C with ammonium hydroxide yielded 95.65% of the product after reacting for four hours (André, 1886c).

Pyridine

It was known that the distillation of two miscible liquids of different boiling points separated into a series of mixtures and finally into species chemically defined. Cases were known where this separation was very difficult if not impossible and where the variation of the boiling points of the mixtures presented some interesting anomalies. André mentioned that this was the case of mixtures composed of a volatile acid and a liquid having weak basic properties such pyridine, a tertiary base. It was evident that propionic, acetic, and formic acid combined with pyridine and that the reaction was exothermic. The acidity of the mixture (as seen with litmus paper or phenolphthalein) was almost identical to the dose of acid that participated really in the combination at room temperature, although pyridine had not action of these dyeing substances. André also mentioned that these mixtures reached a constant distillation temperature and composition (azeotrope)* at certain values of the pressure and temperature (André, 1897, 1899a).

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* Several solutions boiling at constant temperature and composition were already known but the phenomenon of azeotropy and its consequences were yet to be developed. Today, the systems investigated by André are known to have an azeotropic point at the following conditions (Gmehling et al., 2004):

	t/^{0}C	P/kPa	x_1
Pyridine (1) + formic acid (2)	149	101.3	0.25

Pyridine (1) + acetic acid (2)	138.1	101.3	0.422
Pyridine (1) + propionic acid	148.6	101.3	0.314
Trimethylamine (1) + formic acid (2)	91.1	2.67	0.271
Trimethylamine (1) + acetic acid (2)	149	101.3	0.20

For example, André distilled at atmospheric pressure an equimolar mixture (153 g) of propionic acid and pyridine and after six hours recovered 51 g of a liquid boiling between 150^0 and 151.5 ^{0}C, still showing striae in its mass, and having the composition corresponding to two molecules of propionic acid and one of pyridine. André believed that it was the acid salt ammonium diacetate; it had acidity between 62.79 and 62.82 per 100 (as measured with baryta), in accordance with the previous assumption. The boiling point was 110^0 higher than that of the acid and 30^0 higher than that of pyridine, another result attesting the presence of an acid-dissociating compound. This dissociation capacity became more evident when distilling the acid at a lower pressure. This new compound now did not boil at a constant temperature and during distillation the above physical data were substantially different. The first fraction passing at 15 mmHg had a boiling temperature of 58.5^0 to 59.5 ^{0}C and an acidity of 55.63% (propionic acid), corresponding to an excess of about 25% of pyridine above the formula of the acid*. Mixtures of acetic acid and pyridine and formic acid and pyridine showed the same characteristics. For example, at atmospheric pressure, the mixture of acetic acid and pyridine began boiling at 100 ^{0}C, the boiling temperature increased continuously until it gave a portion boiling at almost constant temperature of 139^0-140 ^{0}C and having composition 3 moles acetic acid + 2 moles of pyridine* (André, 1897, 1899a).

In another publication André reported that he had also measured the density of the vapors of the above three mixtures and found that they were completely dissociated in their components. Thus, the compound $5CH_2O_2,2C_5H_5N$ (molecular mass 388) had vapor density 56.3, corresponding to 1/7 of its real molecular mass. The compound $3C_2H_4O_2,2C_5H_5N$ (molecular mass 338) had vapor density 70.7, corresponding to 1/5 of its real molecular mass (André, 1898a, 1898b).

André also measured the heat of formation of these compounds by two different procedures, and obtained the following results:

$5CH_2O_2,2C_5H_5N$ (liquid) released	15.25-15.30 cal
$3C_2H_4O_2,2C_5H_5N$ (liquid) released	5.75-5.90 cal

In addition, André examined the distillation of mixtures of formic and acetic acids with trimethylamine* (André, 1898a, 1899a). He found that at 16 mmHg the liquid corresponding to the composition $5CH_2O_2,2(CH3)_3N$ boiled at the constant temperature of 95.5 ^{0}C. The vapor of the same, (molecular mass 348) was completely dissociated, its density was 1.69, corresponding to the molecular mass 48.8, 1/7 of the real value. In the case of acetic acid, the compound $4C_2H_4)_2,(CH3)_3N$ (molecular mass 299) boiled at the constant temperature 80^0-81 ^{0}C and pressure 37 mmHg. It was completely dissociated in the vapor state. The density of its vapor, 2.08, corresponded to the molecular mass 60, that is, 1/5 of the real value. André reported that the mixture acetic acid + trimethylamine did not have a constant boiling temperature; distillation separated it neatly into the two pure components (André, 1898a, 1899a).

André studied the reaction of pyridine with sulfur dioxide and hydrogen sulfide (André, 1900). He found that saturating dry pyridine with a stream of dry SO_2 produced a deep yellow liquid, which deposited spontaneously beautiful yellow strips, highly deliquescent and unstable, of formula $C_5H_5N.SO_2$. Pure zinc pure in contact with pyridine saturated with SO_2 became promptly covered with a thick white layer, sparingly soluble in water, and very soluble in HCl, with release of SO_2 and deposition of sulfur. This layer was found to have a variable composition; André failed repeatedly trying to purify it. It contained zinc, sulfur, oxygen, and pyridine. André used the same procedure to prepare combinations of pyridine with tri-and tetrationic acids as well-defined crystalline compounds. For this purpose, he saturated dry pyridine with a dry stream of SO_2, and afterwards with a stream of dry hydrogen sulfide. Eventually all the mass became almost solid. He then dissolved it with absolute alcohol over a water bath and separated the liquid by filtration. The filtrate, upon cooling, separated into two liquid phases. The upper phase deposited white, deliquescent strips of composition corresponding to the formula $(C_5H_5N)_2S_4O_8H_2$. The lower phase became a crystalline mass that was then dissolved in absolute alcohol. Purification of the crystals yielded a substance with the same composition as the solid separated from the upper surface. According to André, all these facts pointed to the reaction

$2C_5H_5N + 3SO_2 + H_2S = (C_5H_5N)_2S_4O_6H_2$

This pyridine tetrathionate was soluble in water and alcohol and melted at about 135 ^{0}C, yielding a yellow limpid liquid that promptly decomposed releasing SO_2.

André obtained pyridine trithionate by mixing 100 g of pyridine with 100 g of water, followed by saturation with SO_2 and hydrogen sulfide. The filtrate turned crystalline after 15 hours. Purification of the solid with water yielded transparent crystals, deliquescent and composition corresponding to the formula $(C_5H_5N)_2S_3O_6H_2$. These were highly soluble in water and alcohol and melted at 106 ^{0}C with decomposition and release of SO_2 (André, 1900).

Piperidine

André prepared some new bases derived from piperidine. Ethylene dipiperidine dichlorohydrate was prepared by mixing two molecules of piperidine with one molecule of ethylene chloride. The reaction was rapid at room temperature and much rapid at 100 ^{0}C, transforming all the volume into a crystalline magma. The final addition product had formula $C_2H_4Cl_2$. $(C_5H_{11}N)_2$.

Treating this complex (or the corresponding dibromohydrate) yielded ethylene dipiperidine. This base was a colorless oil of relative density 0.9364 (0 ^{0}C), which did not solidify even when cooled down to -23 ^{0}C. André also prepared a new derivative by heating a mixture of one molecule of propylene bromide with 2 molecules of piperidine, in the presence of aqueous KOH. This new methylethylene dipiperidine, of formula $C_5H_{10}N$, $CH(CH_3)$-$CH_2.C_5H_{10}N$, was almost insoluble in water and did not solidify even in the presence of boiling methyl chloride. Trimethylene dipiperidine was prepared by heating a mixture of trimethylene bromide with piperidine in the presence of KOH. Its relative density was 0.9183 (16 ^{0}C) and did not solidify even when cooled to -23 ^{0}C. André described the preparation and properties of trimethylenol dipiperidine, $C_5H_{10}N.CH_2CH(OH)CH_2.C_5H_{10}N$, and methylolethylene dipiperidine $C_5H_{10}N.CH_2CH(CH_2OH).C_5H_{10}N$, (André, 1898b).

Blood fermentation

It was known that blood, left alone, began putrefying and transforming into a variety of products accompanied by gas release. Berthelot and André experiments on the transformation of vegetable and animal matter used in agriculture led them to study in detail the transformation of blood during its fermentation (Berthelot & André, 1892b). For this purpose, they used defibrinated beef blood collected at the slaughterhouse. The sample had relative density 1.045 (15 ^{0}C) and contained by liter, 87.0 g of carbon, 11.8

hydrogen, 26.0 g of nitrogen, and 37.6 g of oxygen (in addition to minerals and sulfur). The fermentation process was carried for 130 hours in a water bath initially at 35 ^{0}C and ending at 45 ^{0}C. The activity of the pertinent agents diminished accordingly, as the composition of the medium changed. The products formed were CO_2, ammonia, volatile fatty acids, and principles containing fixed nitrogen. During the whole process the liquid kept the brown color characteristic of modified blood (Berthelot & André, 1892b).

The gas released was found to be exempt of hydrogen and nitrogen, a surprising result; such a simple reaction was known to take place only during the alcoholic fermentation. It also contained traces of hydrogen sulfide. The results indicated that the fermentation process had transformed 2/3 of the nitrogen contained in the proteinic material into ammonia. Comparison of the equivalents of ammonia and CO_2 contents indicated that they were in the ratio 1:1, exactly the same ratio that occurred during the hydration of urea, indicating that these two substances originated from ammonium carbonate. Distilling the fermentation product in the presence of diluted sulfuric acid isolated the fatty acids. The results indicated the presence of all the acids from acetic to caproic; the average composition was located between propionic and butyric acids. The composition of the product was thus similar to the one from the butyric fermentation, except that it was not accompanied by release of hydrogen. The carbon content of all the volatile fatty acids was practically one-half of that contained in the fixed nitrogen compounds (52.9 g) (Berthelot & André, 1892b).

The nitrogen compounds were examined after separation of the fatty acids. The results were divided into four groups: (1) an insoluble compound, of humic nature, containing, by weight, 68.2% carbon, 7.6% hydrogen, 8.4% nitrogen, and 15.8% oxygen, corresponding to the empirical formula $C_{15}H_{24}N_2O_2$. André believed that this substance originated from the coloring matter of the blood, altered by the successive influences of fermentation and the diluted sulfuric acid. It was a condensed anhydride, which perhaps originated from a derivative of tyrosine and fatty acid. It contained about 5% of the total carbon contained in blood; (2) barium salts soluble and crystallizable, obtained by treating with baryta the residue of the distillation of the volatile fatty acids. This precipitate, formed of two salts, did not contain sulfur but contained about one-third of the nitrogen contained in all the fixed nitrogen derivatives. The elemental analysis indicated that they were probably highly nitrogenated acids, very oxygenated. The ratio hydrogen/carbon was approximately that of the fatty acids; (3) a compound neutral or acid, soluble in absolute alcohol, and non-crystallizable. It was purified by treatment with diluted sulfuric acid, evaporation, and alcohol extraction. Elemental analysis indicated that it contained, by weight, 47.81% carbon, 7.59% hydrogen, 9.29% nitrogen and 35.3% oxygen. André believed that it was an imide of the fatty series, derived from a very oxygenated acid, such as $C_6H_{12}O_3$; and (4) alkaline salts, insoluble in the liquids, some of them crystallizable, and containing about 5% of the carbon of the nitrogenated compounds (Berthelot & André, 1892b).

Sugar splitting

Berthelot and André wrote that their research on vegetation had led them to study acid levulinic, one of the simplest products of sugar splitting (Berthelot & André, 1896c):

$C_6H_{12}O_6 = C_5H_8O_3 + CH_2O_2 + H_2O$ (now the formula of water is written correctly)

The experiments were conducted using levulinic acid, very pure and well crystallized, obtained by distillation. This acid boiled at 239 ^{0}C, indicating that at room temperature its vapor pressure was very close to zero. This assumption was confirmed by boiling to dryness an aqueous solution of one gram of the acid in 50 of water. The amount of acid recovered was about 99% of the original mass. In another experiment, the acid was put inside a glass bell over large pieces of quicklime, and the whole submitted to very low pressure. After 14 days the weight of the acid had decreased to 91% of the initial value. The residue looked crystalline but partially deliquesced. An elemental analysis indicated that it contained, by weight, 50.77% carbon, 6.98% hydrogen, and 42.25% of oxygen (by difference), indicating that the acid had become hydrated into the acid $C_5H_{10}O_4$ (dioxivaleric acid). This was a keto acid, a group of acids well known to dehydrate partially. Hence, levulinic acid represented the first anhydride or lactone of dioxivaleric acid. Berthelot and André mentioned that their research on humic acid had shown similar results (Berthelot & André, 1896a).

The transformation of sugars into carbohydrates and CO_2 by the wet method had called attention due to its relations to animal and vegetable respiration, and with the fermentation and the actual constitution of sugar principles. These facts induced Berthelot and André to further study the production of CO_2 by the pure action of diluted acids (Berthelot & André, 1896b). They decided to study the conditions leading to the formation of the acids humic, levulinic, and formic. The experiments conducted consisted in treating ordinary glucose (dextrose), levulose, galactose, and maltose with diluted mineral acid such as HCl, sulfuric and phosphoric acids. The last acid was particularly interesting because it did not distill with water and did not exert an oxidation action like concentrated sulfuric acid. The experiments consisted in heating the reagents to 100 ^{0}C, inside a closed tube sealed under vacuum, allowing thus to study the gases and volatiles released, or inside glass balloons heated in an oil bath, and provided with a refrigerated condenser, allowing maintaining a constant composition. Some experiences were conducted under vacuum, others in the presence of air or in the presence of hydrogen. The glucose was determined by means of Fehling's liquor, the CO_2 by absorption in limewater, the CO using acid cuprous chloride (after separation of the CO_2), humic acid by means of drying at 100 ^{0}C and weighing, formic acid by neutralization with baryta water, levulinic acid by indirect means after dosification of the mineral acids, and levulinic acid by means of phenylhydrazine, by defect against the original weight (Berthelot & André, 1896b).

Berthelot and André presented a table giving the results of the experiments conducted in sealed tubes, lasting 644 hours, with samples taken at time 0, 15, 168, and 644 hours, and giving the amount % of CO_2, CO, formic, levulinic and humic acid, and unattacked glucose, as well as the amount % of carbon, hydrogen, and oxygen, and of water by defect. The final amount of water eliminated came from the simultaneous formation of humic, levulinic, and formic acids. The last two acids derived from the total decomposition of glucose, according to the equation $C_6H_{12}O_6 = C_5H_8O_3 + CH_2O_2 + H_2O$. This formula required that the amount of carbon of formic acid be equal to a fifth that of levulinic acid, a requisite not supported by the chemical analysis, indicating that one third of the formic acid was coming from another source. The production of humic acid exceeded that of formic acid, indicating that the formation of these acids was independent one from the other. This result was confirmed by experiments done in closed tubes provided with a mixture of 10 g of glucose and 50 cm^3 of different acids (HCl of 6.5 and 12.3%, sulfuric acid of 8.5%, and phosphoric acid of 9.4 and 28%). The contents showed that there was no proportionality between the amounts of humic and formic acids formed (Berthelot & André, 1896b).

In the experiments done with glass balloons, the gases were eliminated as formed in order to avoid being converted by the remaining material. These experiments were conducted with a mixture of 5 g of glucose, 61 g of phosphoric acid, and 200 g of water, heated at a temperature below 200 ^{0}C for 268 hours, under a slow stream hydrogen. Several additional experiments were done using the same amount of glucose, mixed with varying amounts of sulfuric and HCl acids instead of phosphoric acid, an air current, and rapid distillation of the product. The results indicated that CO_2 was now released in larger amounts and faster, a result that could not be attributed to oxidation, as seen by comparing the results done in the presence of hydrogen with those performed in the presence of air. Once again, there was no relation between the amounts formed of humic and formic acids. The amounts of barium salts of the volatile acids were now much different from those of the formiates, and closer to the acetates. This result proved the modification of the reaction by the conditions of the distillation (Berthelot & André, 1896b).

Berthelot and André reported that the other sugars tested behaved in the same manner as ordinary glucose. All the sugars released, more or less, the same amount of CO_2 (about 20% of the carbon of the carbohydrate) (Berthelot & André, 1896b).

A following paper reported the results done on the carbohydrate arabinose, carried on in sealed tubes or in an open glass flask, with water or diluted acids (Berthelot & Andre, 1896c).

A dilute solution of arabinose, distilled at 100 ^{0}C, showed no traces of furfuryl alcohol (tested with phenylhydrazine). The results were quite different when the solution was heated for five hours at 200 ^{0}C in a closed tube: the product was found to contain near 30% of the alcohol, 50% more or less of the theoretical amount. The next experiments were carried in sealed tubes containing an aqueous solution of arabinose acidified with HCl, heated to 100 ^{0}C for five hours. The product was a back matter containing the same amount of carbon as the original arabinose and no signs of furfuryl alcohol. In other words, arabinose behaved the same as ordinary glucose (dextrose). Berthelot and André conducted the same experiment with furfuryl alcohol to try to understand the dissimilar results obtained with the two different experimental procedures. For this purpose, they heated in a sealed tube furfuryl alcohol saturated with HCl to 100 ^{0}C, for five hours. This resulted in the complete destruction of the alcohol and the production of a substantial amount of CO_2 and CO. A mixture of furfuryl alcohol with phosphoric acid produced the same results, while heating a mixture of the alcohol with water at 200 ^{0}C resulted in the destruction of 50% of the alcohol (Berthelot & Andre, 1896c).

Glucose was known to split into alcohol under the action the action of beer yeast, a living cell, $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$, and another living cell was able to convert it into lactic acid $C_6H_{12}O_6 = 2C_3H_6O_3$. As shown above, a third split into levulinic acid, $C_6H_{12}O_6 = C_5H_8O_3 + CH_2O_2 + H_2O$, was also possible under pure chemical conditions, without the help of a living cell. Berthelot and André measured the heat effect of the different reaction in order to compare the thermochemical work attached to each of them. Their results were as follows (Berthelot & André, 1897b):

$C_6H_{12}O_6$ (dissolved) = $C_5H_8O_3$ (dissolved) + CH_2O_2 (dissolved) + H_2O released + 36.7 cal

$C_6H_{12}O_6$ (dissolved) = $2C_2H_6O$ (dissolved) + $2CO_2$ (released) " + 33.0 cal

$C_6H_{12}O_6$ (dissolved) = $2C_3H_6O_3$ (dissolved) " + 34.0 cal

According to Berthelot and André these results indicated that the splitting of glucose, performed by completely different means and into different products, had very similar heat exothermal effects, without the need of a foreign energy source (Berthelot & André, 1897b).

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