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REVISION BIBLIOGRAFICA

HENRI FRANÇOIS GAL

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ABSTRACT

Henri François Gal (1839-1897), a French chemist who studied in detail the chemical reactions of acid anhydrides, acetyl bromide and chloride, ethers, organic cyanates, organometallic compounds, strychnine and other natural extracts. He also developed analytical methods to distinguish between amines and phosphines, and mono and diamides.

Keywords: acetyl halides; acids; acid anhydrides; natural extracts; organic cyanates; organometallic compounds; strychnine

RESUMEN

Henri François Gal (1839-1897), químico francés que investigó en detalle las reacciones químicas de los anhídridos carboxílicos, el bromuro y cloruro de acetilo, los éteres, los cianatos orgánicos, compuestos organometalicos, la estricnina, y otros extractos naturales. También desarrolló métodos analíticos para distinguir entre aminas y fosfinas y entre mono y diamidas.

Palabras claves: ácidos; anhídridos carboxílicos; cianatos orgánicos; compuestos organometalicos; extractos naturales; estricnina, haluros de acetilo.

INTRODUCTION

Life and career (Azzola, 2023)

Henri François Gal was born in Marseille, on July 15, 1839, the son of Marie Jean Baptiste Gabriel Gal and Marie Joséphine Augustine Armand. In 1859, after finishing his basic education, he entered the École Polytechnique from where he graduated in 1860 as licencié ès sciences, ranking 64 in a graduating class of 128. He then began advanced studies at the Faculté des Sciences de Paris and received his degree of docteur ès sciences in 1865 after successfully defending a thesis about acid anhydrides and ethers (Gal, 1865). During this period, he also served as préparateur of the chemistry course given by Victor Regnault (1810-1878) at the École Polytechnique. In 1866 he was appointed répétiteur auxiliaire (without payment) until 1871 when he was promoted to répétiteur adjoint (with salary), a position he occupied until 1872. In 1884 he was appointed professor of chemistry at the École, replacing Edmond Frémy (1814-1894), a position he occupied until his death (1897).

Gal married Emile de Laugharie on September 10, 1870.

Gal served as inspector of exams at the École and as warrant director of the French Mint. In 1872 the French Academy of Sciences awarded him the Jecker Prize for his work about the bromine and chlorine derivatives of acid anhydrides and of acetyl chloride and acetyl bromide. In 1881 he was appointed chevalier of the Légion d'Honneur and promoted to officier in 1866.

Scientific contribution

Gal wrote about 30 papers on organic chemistry, organometallic compounds, and natural products. In addition to the subjects described below he also studied the reactions of trichloroacetic acid with phosphorus chlorides, bromides, and iodides (Gal, 1873a); the diffusion of alcoholic solutions through a bladder (Gal, 1882, 1883a); the use of zinc ethyl to characterize the nature of amines and phosphines (Gal, 1883b); he development of a procedure for distinguishing mono and diamides (Gal, 1883c); etc.

In what follows, attention should be paid to the fact that Gal was using in all his chemical reactions and formulas the old values of the atomic masses, i.e., C = 6, O = 8, H = 1, Cl = 35.5, P = 31, and Pt = 98.7.

Organometallic derivatives of phosphorus, arsenic, and antimony

Auguste Cahours (1813-1891) and Gal wrote that previous researchers had found that animal and vegetable matter contained small amounts of choline, a basic substance capable of forming crystalline derivatives. Afterwards, Charles-Adolph Würtz (1817-1884), August Wilhelm Hofmann (1818-1892), and Oskar Mathias Liebreich (1839-1908) had synthesized this compound by different pathways using trimethylamine, trimethylphosphine, and other ammonia compounds as starting material. This led Cahours and Gal to try to reproduce in the phosphine series combinations like the ones present in the series of ammonium bases. For this purpose, they treated mixtures of triethylphosphine with an excess of monochloroacetic acid or monochloroacetic ether, in closed tubes heated in a water bath. A lively reaction took place, which changed the mixture into a crystalline mass. The excess reagent was then eliminated, and the resulting product treated with an aqueous solution of platinum dichloride (Cahours & Gal, 1870a).

Cahours and Gal reported that the product of the reaction of monochloroacetic ether were beautiful yellow orange flakes, little soluble in water, practically insoluble in alcohol and ether, which could well be considered the result of a coupling of both reagents. The product of the reaction of monochloroacetic acid were fine yellow orange needles, which boiled for a few minutes in the presence of the solution of platinum dichloride yielded a very stable product, which was found to contain platinum. Cahours and Gal speculated that this substance could be product of the reaction between triethylphosphine and platinum dichloride, and for this reason they carried out a new experiment in which they boiled the aqueous solution of platinum dichloride with a slight excess of triethylphosphine. Concentration of the resulting liquid by boiling resulted in the precipitation of pale-yellow crystals, which were separated and boiled in alcohol until saturation. Cooling of the alcoholic solution resulted in the precipitation of beautiful and very fragile sulfur yellow prismatic crystals. Chemical analysis indicated that they contained, by weight, 28.63% carbon, 5.96% hydrogen, 12.33% phosphorus, 14.11% chlorine, and 38.97% platinum, corresponding to the formula $P(C_4H_5)_3$. PtCl, and resulting from the following equation (Cahours & Gal, 1870a):

$$3[P(C_4H_5)_3] + 2PtCl_2 = P(C_4H_5)_3Cl_2 + 2P(C_4H_5)_3.PtCl$$

Cahours and Gal wrote that their new salt should be considered the equivalent of the green salt of Magnus in the ammonia series, NH_3, PtCl (The correct formula is $[Pt(NH_3)_4][PtCl_4]$), where triethylphosphine had replaced ammonia. An alcoholic solution of this salt, heated to 100 °C for several hours in sealed tubes, yielded crystals of an isomeric white salt. Cahours and Gal described the different crystalline compounds formed by the white and yellow salts with potassium bromide, iodide, acetate, and sulfide, and ammonia (Cahours & Gal, 1870a).

A following publication added more details about the new compound (Cahours & Gal, 1870b). Cahours and Gal repeated that this complex crystallized from its alcoholic solutions as sulfur yellow, long, and opaque prisms and from an ethereal one, as voluminous transparent prisms of yellow amber color. Its relative density at 15 °C was 1.50; it melted at 150 ^{0}C and could be heated to 250 ^{0}C without alteration. An alcoholic solution of this salt, heated to 100 ^{0}C for several hours in sealed tubes, changed completely into brilliant crystals of an isomeric white salt. The yellow crystals were insoluble in cold water. The yellow salt, boiled with water and triethylphosphine, formed colorless prismatic crystals having the composition $[P(C_4H_5)_3]_2$,(PtCl), which corresponded to the phosphorus analog of the salt of Reiset, [$(NH3)_2$, PtCl]. This new salt lost an equivalent of triethylphosphine when long kept and left the white modification of the chloride first described. Cahours and Gal added that this modification occurred rapidly when the combination was held at 100 ^{0}C, the same phenomenon experimented by the salt of Reiset, which decomposed into ammonia and an isomer of Magnus salt. A solution of the salt precipitated silver salts (sulfate, nitrate, acetate, etc.) yielding the pertinent silver salts. With silver oxide and water, it yielded strongly alkaline liquor, with gold chloride and platinum well defined salts. Palladium chloride formed a yellow compound like the one formed by platinum dichloride; insoluble in water, soluble in boiling alcohol, and in water loaded with triethylphosphine. When triethylphosphine is added to an alcoholic solution of gold chloride, $AuCl_3$, a colorless crystalline salt was obtained which had the formula [$P(C_4H_5)_3$, AuCl] (Cahours & Gal, 1870b).

In a third publication Cahours and Gal reported the results of similar experiments using trimethylphosphine instead of triethylphosphine, and on the action of the chlorides of platinum, palladium and gold on phosphines and arsines (Cahours & Gal, 1870c). Trimethylphosphine was found to produce the same results as triethylphosphine; that is, white and yellow compounds with platinum dichloride having formula $[P(C_2H_3)_3$; PtCl]. These could be easily separated using the fact that the white one was completely insoluble in ether. As before, the reaction of an alcoholic solution of aqueous platinum dichloride with triethylarsine was exothermic; after cooling the final solution precipitated sulfur yellow crystals, which ether separated into the two substances mentioned above. Chemical analysis indicated that formulas of the soluble and insoluble compounds, were $[As(C_4H_5)_3$, PtCl] and $[As(C_4H_5)_3]_2$, (PtCl), respectively. Similar results were obtained with palladium chloride and gold chloride, and with triethylstibine (Cahours & Gal, 1870c).

Organic chemistry

Amide cyanates

In 1870 Cahours and Gal reported the synthesis of new compounds produced by the reaction between hydrogen cyanide and different cyanide esters, with the esters of amides of the aromatic series (Cahours & Gal, 1870d). In the introduction to their memoir, they indicated that Peter Griess (1829-1888) had reported that the reaction between benzamide and cyanogen generated a very complex substance that under the action of HCl split into many different products, where the most important was a combination of benzamide with cyanic acid. Griess wrote that this particular compound could also be prepared by heating benzamide with urea because this reaction was accompanied by release of ammonia (Griess, 1868). Cahours and Gal also wrote that in 1858 Cahours had reported the preparation of several amides (benzamide, anisamide, and cuminamide) and shown that their basic properties were enhanced when converted into their esters (Cahours, 1858). For these reasons, Cahours and Gal thought that these compounds should also be able to combine with cyanic acid to form well-defined compounds, which, under the influence of ammonia, would split into alcohol and aromatic creatines, as illustrated by the following reaction (Cahours & Gal, 1870d):

$$C_{14}H_6(C_4H_5)NO_4,\ C_2HNO_2 + NH_3 = C_4H_6O_2 + C_{16}H_9N_3O_4$$

benzamide ester cyanic acid alcohol benzoic creatine

In practice, this reaction did not provide the expected products but allowed the synthesis of a very large number of compounds resulting from the association of cyanic acid (or cyanic esters) with the esters of acid amides of the aromatic series, such as N-methyl benzamide, N-methylcuminamide, and N-methyl

benzamide. All these compounds could be prepared by very simple methods. For example, to prepare a combination of cyanic acid with the ester of an acid amide it was enough to mix an aqueous solution of potassium cyanate with the sulfate of the amide. Upon heating, the solution separated immediately an oily phase that on cooling precipitated as a crystalline powder. After filtration and drying the powder was dissolved in concentrated alcohol to separate it from the alkaline sulfate. Evaporation of the alcohol left a very pure final product.

Cahours and Gal memoir provided a long list of the new materials synthesized by their procedure (Cahours & Gal, 1870d).

Homologs of tartaric and malic acids

According to Gay-Lussac, no substance had been found in vegetables that was combined with the tartaric or malic groups, although these acids had been prepared artificially (Gal & Gay-Lussac, 1870). For example, William Henry Perkin (1838-1907) and Baldwin Francis Duppa (1828-1873) had prepared malic and tartaric acids by reacting KOH with monobromosuccinic acid or dibromosuccinic acid, respectively (Duppa & Perkin, 1860). Gal and Gay-Lussac used the same procedure for preparing the higher homologues of tartaric and malic acids, which they named adipomalic, adipotartaric, suberomalic, and suberotartaric acids. In their paper they reported the experimental procedure and properties of each of these new acids. Dibromotartaric acid was prepared by heating in a sealed tube one equivalent of adipic acid with four equivalents of bromine. The reaction took place promptly at 170 °C, yielding abundant HBr gas and a yellow pulverulent residue smelling like camphor, which was found to be dibromoadipic acid, having the formula $C_{12}H_8Br_2O_8$. Dibromoadipic acid was unstable, easily soluble in water but decomposing. The solution was heated for several hours at 150 °C and then evaporated to dryness. Analysis of the resulting colorless crystalline residue indicated it contained, by weight, 39.7 to 40.2% carbon, 5.8 to 6.0% hydrogen, and 53.9 to 54.2% oxygen, corresponding to adipotartaric acid. This acid tasted like acid fruits, was very soluble in alcohol and ether and more soluble in boiling than in cold water. Its crystals did not deviate polarized light, the same as synthetic tartaric acid (Gal & Gay-Lussac, 1870).

The same reaction carried with two (instead of four) equivalents of bromine, yielded monobromoadipic acid, which treated with KOH decomposed into potassium bromide and potassium adipomalate. The bromo derivatives of suberic acid were prepared in a similar manner (Gal & Gay-Lussac, 1870).

Acid anhydrides

The discovery of chlorinated derivatives of glacial acetic acid and the action of KOH on these derivatives led Gal to investigate the action of chlorine on acetic anhydride (Gal, 1862a). For this purpose, he bubbled a stream of very dry chlorine through acetic anhydride contained in a retort provided with a receiver and heated in a water bath to 100 °C. No disengagement of HCl was observed; the gas stream led part of the liquid to distill and to transform the residue into a mass of crystals melting at 45 °C and boiling at about 185 °C. Chemical analysis indicated that the formula C_4H_2Cl could represent their composition. Distillation of the liquid phase showed that about three quarters of it, boiling at 55 °C, passed into the receiver and had the characteristics of acetyl chloride; water decomposed it into HCl and acetic acid. The remaining liquid, boiling at 137 °C, proved to be acetic acid. According to Gal, the results of this experience suggested that acetic anhydride, under the influence of chlorine at 100 °C, split into monochloroacetic acid and acetyl chloride, according to the reaction (Gal, 1862a):

$$C_8H_6O_6 + 2Cl = C_4H_3ClO_2 + C_4H_3ClO_4$$

Gal remarked that this reaction provided an excellent method for preparing monochloroacetic acid because acetic anhydride was prepared easily by reacting sodium acetate with phosphorus pentachloride.

More details about these findings were given in two following publications (Gal, 1862b). Cold bromine was found to produce the same results. The mixture, left to it, began to heat, and became colorless within a few minutes. Heating a mixture of two equivalents of dry bromine and one of acetic anhydride to 100 °C in sealed tubes resulted in an almost immediate reaction. When distilled over a water bath under a stream of CO_2, a liquid fraction passed at 81 °C having all the properties of acetyl bromide while the residue left in the retort, left to cool crystallized; analysis showed it was monobromoacetic acid. Hence, bromine acted in the same manner as chlorine, in splitting acetic

anhydride into acetyl bromide and bromoacetic acid and suggesting that these halogens would split in the same manner all the acids of the same series (Gal, 1862b).

Additional experiments using dry HCl showed that this acid split acetic anhydride into glacial acetic acid and acetyl chloride. Distillation of the product showed that boiling began at 55^0 and increased regularly to 120 °C, where it remained constant. The acetyl chloride could be easily separated from the first fraction. The fraction boiling at 120 °C was found to be glacial acetic acid, solidifying in contact with ice. Gal believed that these results gave weight to Charles-Frédéric Gerhardt (1816-1856) ideas that chlorine should be considered *chlorine chloride* (Gal, 1862b).

Gal also mentioned that iodine did not present the same behavior: no reaction occurred when heating acetic anhydride with iodine at a temperature below 200 °C. Higher temperatures resulted in the formation of HI and carbon (Gal, 1862b).

In a following paper Gal reported his discovery of a new procedure for preparing anhydrides of monobasic acids, based on the reaction between a metallic oxide (such as the oxides of calcium, lead, and barium) and an acid chloride (e.g., acetyl or benzoyl chlorides) (Gal, 1863a). He heated over a water bath a sealed tube containing a mixture of one equivalent of acetyl chloride with one of barium oxide and noted that the reaction ended after a few hours. Distillation of the product showed that the temperature increased rapidly to 137 °C and then remained stationary. The liquid passing over had all the characteristic of acetyl anhydride. Similar results were obtained on heating to 140° - 150 °C a mixture of one equivalent of benzoyl chloride and one of barium oxide. The resulting mixture contained barium chloride and benzoic anhydride (Gal, 1863a).

In 1867 Gal published a long memoir proving that hydracids acted on esters in the same manner as they did on acid anhydrides (Gal, 1867). This publication summarized a series of memoirs he had read to the Académie des Sciences, and which later would be the subject of his doctoral thesis (Gal, 1864b, 1865abc, 1866a). It was well known that esters, under the action of heat and alkalis, decomposed into the corresponding alcohol and acid (alkaline hydrolysis). Gal was intent in exploring the possibility that the same splitting took place when the reaction was carried on with an acid instead of an alkali (acid hydrolysis). It was known that the reaction of an acid chloride with an alcohol yielded an ester and HCl, according to the following reaction:

$$\mathbf{ACl + BO_2H = BAO_2 + HCl}$$

where A is an acid radical and B al alcohol radical. The bromides and iodides of the same radicals behaved in a similar manner, generating HBr or HI and a composite ester. Gal went on to study the possibility of the opposite reaction: that an acid, such as HBr, split an ester in the same manner that is

$$\mathbf{BAO_2 + HBr = BBr + AO_2H}$$

and not

$$\mathbf{BAO_2 + HBr = BHO_2 + ABr}$$

Gal preferred to use HBr instead of HCl or HI because it was more stable than HI and less than HCl.

In the first stage of his work, he studied the action of HBr on the esters formed by the acids of the fatty series $C_{2m}H_{2m}O_4$ (Gal, 1864b). For this purpose, he put a certain amount of methyl formate in a tube and bubbled through a stream of HBr dry until saturation of the liquid. Afterwards the tube was sealed and heated in a water bath for 24 hours. Upon opening of the tube, a clear smell of methyl bromide was felt. The remaining liquid was found to be acid, to boil at 100 °C, and being totally soluble in water and KOH. Chemical analysis indicated that it contained, by weight, 25.8% carbon, 4.5% hydrogen and 69.7% oxygen, corresponding very closely to the composition of formic acid, $C_2H_2O_4$, and indicating that under the action of HBr methyl formate decomposed into methyl bromide and formic acid. Gal repeated the experience using the methyl and ethyl esters of a series of fatty acids (e.g., acetic, butyric, valeric, and heptanoic acid) and every case he got the same kind of splitting (Gal, 1867).

In the next series of experiments, he studied the action of HBr on esters formed by the aromatic acid series $C_{2m}H_{2m-8}O_4$ (methyl and ethyl benzoate) (Gal, 1864b). The experimental procedure was the same as before. The resulting esters were methyl (or ethyl) bromide and benzoic acid. In other words, HBr acted in the same manner over the esters formed by fatty or aromatic acids (Gal, 1867).

The third series of experiments studied the reaction between HBr and the esters of the oxalic acid series, $C_{2m}H_{2m-2}O_8$, limited to ethyl oxalate, and methyl and ethyl succinate, and suberate. The same experimental procedure as before showed that these compounds decomposed into the corresponding acid and ethyl or methyl bromides (Gal, 1864b, 1867).

The last series corresponded the action of HBr on the acids of the series carbonic, $C_{2m}H_{2m}O_6$, having that the compound $C_2H_2O_6$ had never been prepared on the free state. Gal wrote that heating in a water

bath sealed tubes containing the carbonic acid saturated with HBr, resulted in the formation of two liquid phases. Upon breaking the tubes, occasioned the release of a slightly acid gas soluble in KOH and precipitating a solution of calcium hydroxide. This was CO_2. The lower colorless liquid phase, dried over calcium chloride, proved to be ethyl bromide; the upper one, boiling between 100° and 120 °C, was strongly acid and precipitated silver nitrate. After neutralization, the liquid, boiling at 100 °C, proved to be the water that contained the HBr used in excess. Once again, the carbonic ester behaved in the same manner as the other esters studied. The only difference was that the acid $C_2H_2O_6$ decomposed immediately into water and CO_2 (Gal, 1864b, 1867).

The following section of the paper reported the action of HBr on alkyl nitrates, of hydracids on alcohols, on alkyl sulfates, alkyl sulfides and mercaptans, the action of HCl and HBr on cyanic ester, and the action of hydracids on cyanic ester obtained by François Stanislaus Cloëz (1817-1883) by reacting cyanogen and sodium ethylate (Gal, 1865ab, 1866ab). For example, Gal wrote that when HBr vapor was bubbled through ethyl nitrate, the liquid became hot and acquired a red color, arising from the separation of nitric peroxide; on distilling the liquid ethyl bromide passed over. Alcohols could be considered as ethers where the acid radical had been replaced by a hydrogen atom (Gal wrote molecule because at that time hydrogen was considered to be monatomic). Hence, HBr was expected to split alcohol in the same way it split double ether:

$$C_4H_5HO_2 + HBr = C_4H_5Br + H_2O_2$$

$$C_4H_5(C_4H_5O_2)O_2 + HBr = C_4H_5Br + H(C_4H_5O_2)O_2$$

Ethers containing two atoms of alcohol radical, such as diethyl ether, were converted by HBr, not in excess, into an alcohol and a bromide of the alcohol radical; but if the HBr was in excess, the alcohol was further transformed into an alcoholic bromide and water; thus

$$(C_2H_5)_2O + HBr = C_2H_5Br + C_2H_5OH$$

$$C_2H_5HO + HBr = C_2H_5Br + H_2O$$

Hydrogen chloride and hydrogen iodide exhibited similar reactions (Gal, 1867).

Gal found that HBr dissolved in ethyl cyanate with evolution of heat, yielding a pure and simple combination which, when purified by distillation, boiled between 108° and 112 °C. Chemical analysis indicated that it contained, by weight, 23.5% carbon, 4.1% hydrogen, 52.8% bromine, 10.6% oxygen, and 9.0% nitrogen, and corresponding to the formula $C_4H_5OC_2NOHBr$. This compound, in contact with a small quantity of water, or by exposure to moist air, decomposed into CO_2 and into a white crystalline mass of ethylamine bromohydrate. Heated with KOH it released a gas smelling like ammonia. Hydrogen chloride reacted in a similar manner. The bromohydrate or chlorhydrate of cyanic ether, heated in a closed tube to 100 °C decomposed complete into the hydracid and cyanic ether (Gal, 1865a, 1867).

Gal and Alexandre Leon Étard (1852-1910) wrote that all the intents to prepare acid anhydrides directly from their monoacids had completely failed (Gal & Étard, 1876). Phosphorus pentoxide had been shown to be unable to eliminate water from acids belonging to the fatty and aromatic series. This had led Charles-Frédéric Gerhardt (1816-1856) to claim that these acids did not contain water and hence it was necessary to duplicate their formulas (Gerhardt, 1853). Gal and Étard observed that dripping glacial acetic over phosphorus pentoxide resulted in the immediate carbonization of the acid, but performing the inverse operation, that, is adding the pentoxide to the acid, did not result in a reaction but only in a small temperature increase if care was taken to submerge immediately the pieces of the pentoxide in the acid. Otherwise, the liquid absorbed by capillarity would carbonize instantly.

Distillation of the mixture yielded acetic anhydride, although in very small yield (Gal & Étard, 1876).

Gal and Étard recommended that the procedure be carried as follows: Sixty grams of glacial acetic acid, boiling at 120 °C, are introduced in a large retort. Thirty grams of phosphorus pentoxide are added rapidly into the flask, which is being rotated speedily enough to assure instant mixture of the reagents. The pentoxide does not seem to react, although it browns a little. The mixing process can be speeded by heating the contents somewhat. The final mixture is rapidly distilled; the first material passing over is acetic anhydride mixed with a large amount of acetic acid. This fraction is distilled again; the anhydride is contained in the fraction boiling over between 136° to 137 °C, weighing about 3 g. Gal and Étard wrote that the same procedure was applicable to produce the anhydride of fatty acids, but also that of benzoic acid (benzoic anhydride) (Gal & Étard, 1876).

Acid chlorides

According to Gal, acetyl bromide was usually prepared by reacting phosphorus pentabromide with glacial acetic acid, a reaction that occurred according to (Gal, 1863b):

$$C_4H_4O_4 + PBr_5 = PO_2Br_3 + HBr + C_4H_3O_2Br$$

This procedure had several shortcomings: As shown by the equation, only one of the five equivalents of bromine available was used to produce the required substance. In addition, the preparation of phosphorus pentabromide was arduous and the separation of acetyl bromide was always incomplete. After many trials, Gal was able to develop a much more efficient procedure for preparing acetyl bromide: A mixture of three equivalents of glacial acetic acid and two equivalents was put in a retort and reacted with six equivalents of bromine, added dropwise. The ensuing reaction was very lively, and each drop of bromine decolorized immediately. The products of the reaction were acetyl bromide, phosphorus trioxide, and HBr gas, as shown by the following equation (Gal, 1863b):

$$3C_4H_4O_4 + 2\,PBr_2 = 3C_4H_3O_2Br + 2PO_3 + 3HBr$$

The acetyl bromide was easily separated by distillation. The above equation showed that 50% of the available bromine appeared in the desired product.

Gal also reported the preparation of the monobromo acetyl bromide by heating to 50^0-60 ^{0}C a mixture of 6 g acetyl bromide and 8 g of bromine in a sealed tube. Once the mixture became colorless it was transferred to a retort and distilled. Most of the liquid passed between 151^o and 153 ^{o}C. Brominated acetyl bromide was a yellowish liquid, fuming in humid air, heavier than water, and slowly dissolving in water and decomposing into HBr and bromoacetic acid. Dibromo and tribromo acetyl bromide could also be prepared by a similar procedure. The dibromo derivative was obtained by heating to 150 ^{o}C, in a sealed tube, a mixture of one equivalent of monobromo acetyl bromide and two equivalents of bromine. This was a colorless compound, fuming in air, heavier than water, and reacting violently with KOH and alcohol. Gal wrote that dibromo acetyl bromide was an isomer of bromal (tribromoacetaldehyde). Tribromoacetic acid was obtained by contacting tribromo acetyl bromide with water or with humid air. This acid melted at 135 ^{o}C and boiled at 250 ^{o}C (Gal, 1863b).

Gal developed another procedure for preparing dibromo acetic anhydride, based on the reaction between monobromo acetyl bromide and finely ground sodium acetate (Gal, 1870). The mixture of both reagents was heated and distilled, and the passing liquid redistilled. The latter began boiling at 137 ^{o}C and continued doing so up to 245 ^{o}C, where it remained stationary. At this temperature a colorless liquid began to pass; chemical analysis indicated it contained, by weight, 18.0% carbon, 1.8% hydrogen, and 61.3% bromine, corresponding to dibromo acetic anhydride, $C_8H_4Br_2O_6$. Gal believed that the reaction proceeded as follows: the first stage generated monobromo acetic anhydride, which by the action of heat, decomposed into acetic anhydride and dibromo acetic anhydride (Gal, 1870).

Dibromo acetic anhydride was a liquid heavier than water that did not solidify even when cooled to 0 ^{o}C. Dropped into water it settled in the bottom and slowly transformed into monobromoacetic acid (Gal, 1870).

Years later Gal developed a better method for preparing tribromoacetic acid in large quantities. This method was based in the oxidation of bromal hydrate by fuming nitric acid. He observed that the dissolution of bromal hydrate in fuming nitric acid was highly endothermic. At the end of the dissolution, the mixture was heated carefully until the release of nitrous vapors stopped. Upon cooling, the liquid turned into a crystalline mass, which was put in a funnel and left until it stopped dripping. The resulting crystals were redissolved in cold water and the solution left to evaporate naturally. The precipitated crystals were pure tribromoacetic acid. These crystals were not deliquescent and could be kept in contact with air, without change. Tribromoacetic acid could be esterified very easily; it was enough to heat it with alcohol to obtain the corresponding ethyl ester. It yielded crystallizable salts (Gal, 1873d).

In a following publication Gal reported the synthesis of monochloro acetyl chloride, monobromo acetyl chloride, and monochloro acetyl bromide (Gal, 1864a). Monochloro acetyl chloride was prepared by reacting monochloroacetic acid with phosphorus trichloride; the byproducts were HCl and phosphorus trioxide. This compound was identical with glycolil chloride; it yielded glycolic acid (hydroxyacetic acid) when treated with a boiling KOH. Monobromo acetyl chloride was prepared by heating at 100 ^{o}C a mixture of one equivalent of acetyl chloride with 2 equivalents of bromine, or by reacting in a retort three equivalents of monobromoacetic acid with two equivalents of phosphorus

trichloride. Monobromo acetyl chloride boiled between 135° to 135 °C, it fumed heavily in contact with humid air decomposing into HCl and monobromoacetic acid. Monochloro acetyl bromide was prepared by adding dropwise six equivalents of bromine to a mixture of three equivalents of monochloroacetic acid and two equivalents of red phosphorus (Gal 1864b).

A next paper gave a more detailed description of the synthesis of monobromo, dibromo, and tribromo acetyl bromide, monochloro acetyl bromide, monochloro and dichloro acetyl chloride, and tribromoacetic acid (Gal, 1866c).

As shown above, Gal found that glycolic acid was produced by the reaction between monobromoacetic acid and KOH. That is, glycolic acid could be seen originating from acetic acid by substitution of one equivalent of hydrogen by the group HO_2. Under this supposition it could well be that substituting the base by certain potassium salts would yield more complex acid where one equivalent of hydrogen had been replaced by an alkyl group (methyl, ethyl, etc.). This hypothesis turned out to be true and allowed Gal to prepare monoethyl ethyl glycolate, monobutyl ethyl acetate, and monobutyl ethylbutyllactate, as well as determine some of their properties (Gal, 1866b).

The first compound was prepared by heating at 100 °C, in a sealed tube, an alcoholic mixture of ethyl monobromoacetate and potassium acetate. At the end of the reaction the contents were mixed with water and the resulting oily phase was washed with water and dried over calcium chloride. Analysis of the dry product indicated that it could be represented by the formula $C_{12}H_{10}O_8$, indicating that the new compound was an isomer of succinic acid, although its properties were quite different. For example, heating it with alcoholic KOH yielded a mixture of potassium acetate and potassium glycolate. The second material, with formula $C_{16}H_{14}O_8$, was prepared by reacting ethyl monobromoacetate with potassium butyrate. Distillation of this new substance over fragments of wet KOH decomposed it into ethyl butyrate and potassium glycolate (Gal, 1866b).

Action of cyanide chloride on zinc diethyl

Gal wrote that hydrogen cyanide in the presence of KOH decomposed according to the reaction:

$$C_2HN + 4OH = C_2H_2O_4 + NH_3$$

(Formic acid)

but from this reaction it was not possible to decide which of the two products contained the hydrogen of the acid. Gal thought the question could be perhaps answered by replacing the hydrogen of the acid by an alcoholic radical (e.g., C_4H_5). Unfortunately, this reaction produced two isomers, one boiling at 98 °C (Leblanc, Dumas & Malaguti, 1847):

$$C_4H_5NC_2N + 4OH = C_6H_6O_4 + NH_3$$

and the other, boiling at 82 °C (Hofmann, 1860):

$$C_4H_5NC_2N + 4OH = C_2H_2O_4 + C_4H_5NH_2$$

The first reaction indicated that C_4H_5 had replaced one equivalent of hydrogen in formic acid so that the hydrogen of the hydracid came from formic acid. The second equation provided the opposite answer: the hydrogen of HCN came from the ammonia. Now, the compound $C_4H_5NC_2N$ was prepared by reacting ethyl iodide with silver cyanide, according to

$$C_4H_5I + AgC_2N = C_4H_5NC_2N + AgI$$

This reaction suggested that this ether originated from the replacement of the silver in the cyanide by C_4H_5, hence from the hydrogen of HCN.

Consequently, Gal reacted cyanide chloride gas with zinc ethyl and obtained a liquid boiling at 98 °C, identical with the previous cyanhydric ether (Gal, 1868):

$$C_2NCl + C_4H_5Zn = C_4H_5C_2N + ZnCl$$

(chlorine was also considered to be a monatomic gas).

Gal concluded that in spite of all the research done about HCN, it was still impossible to determine the real composition of this acid (Gal, 1868).

Strychnine

Gal and Étard tried to determine the composition of strychnine by reacting it with a variety of chemicals. In their report they indicated that the best results had been obtained with an aqueous solution of barium hydroxide (Gal & Étard, 1878). They filled a tube with enough of a mixture of finely divided strychnine and about ten times its volume of a saturated solution of barium hydroxide to leave the minimum volume of air; the tube was then sealed and heated for 40 hours at a temperature between 135° and 140 °C. The contents of the tube were then emptied on two volumes of distilled water, treated with a stream of CO_2 to eliminate the excess of barium, and the solid separated by filtration. The filtrate was evaporated under vacuum while heated over a water bath. The resulting white crystalline solid was separated by filtration and purified by crystallization from boiling water. This material was found to be sparingly soluble in water and most solvents, but very soluble in aqueous HCl, from which it separated as a deliquescent salt, hard to crystallize. With tartaric acid it formed an acid salt, little soluble in cold water and more in boiling water, from which it separated as brilliant prisms.

Analysis of solid basic product of the original reaction was found correspond to the formula

$$C_{21}H_{22}N_2O_2 + 2H_2O = C_{21}H_{26}N_2O_4$$
(strychnine)

Gal and Étard named this new compound *dihdrostrichnine*.

Evaporation of the mother liquor resulted in the separation of a brown deposit, which was purified by crystallization from boiling water, taking care of avoiding all contact with air. The resulting yellow crystals corresponded to the formula

$$C_{21}H_{22}N_2O_2 + 3H_2O = C_{21}H_{28}N_2O_5$$
(strychnine)

Gal and Étard name this new compound *trihydrostrichnine*.

Gal and Étard reported that both bases were very stable in the dry state, but very unstable when in solution. They reduced hot silver nitrate forming a metallic mirror, and the chlorides of gold and platinum yielding a violet-red solution. The mixture of sulfuric acid and potassium dichromate did not generate the reaction characteristic of strychnine. Under certain circumstances the two bases behaved as aldehydes, particularly in their reaction with silver salts and sodium sulfide. Gal and Étard believed that the two new compounds, despite their basic character, were very similar to the two bases oxistrychnine and dioxystrychnine, described by Paul Schützenberger (1829-1897) (Gal & Étard, 1878; Schützenberger, 1858).

Vegetable essences

Patchouli

In 1869 Gal reported that patchouli essence, which is obtained from the leaves of *Pogostemon patchouly*, left alone, deposited a crystalline substance, which was ill defined but seemed to be an isomer of the oil itself. His experiments showed that the crystallization process was significantly improved if the essence was previously dried over calcium chloride (Gal, 1869). The relative density of its vapors, 8.00 at 324 °C, suggested that patchouli oil was a homologue of Borneo camphor (Borneol), having the formula was $C_{30}H_{28}O_2$ (today, $C_{10}H_{28}O$). Gal described patchouli camphor as a solid substance, melting between 54^0 and 55 °C, boiling at 296 ^{0}C, and having relative 1.051 at 4.5 °C. It was insoluble in water readily soluble in alcohol and ether and depositing from a solution in these solvents as voluminous hexagonal prisms, ending in a six-face pyramid. While Borneo camphor is a right-handed rotatory substance, the patchouli camphor is left-handed. Distilled over zinc chloride it yielded a hydrogen carbide, boiling between 248° and 252 °C, and having a composition corresponding to the formula $C_{30}H_{26}$ (Gal, 1869).

Alan-gilan (*Unona odoratissima*)

According to Gal, the natural essence Alna-gilan had a very pleasant odor and was used in perfumes, despite his high price (2,500 francs/kg). The essence was obtained by distillation of the flowers of a tree

of the Annoncées family, named *Unona odoratissima*, growing particularly in Antilles and Jamaica. The essence had a relative density of 0.980 (0.15 °C), was levorotatory (-14°), and distilled entirely between 160° and 300 °C without leaving a carbonaceous residue. It was insoluble in water, partially soluble in alcohol and completely soluble in ether. It was strongly attacked by nitric acid, not attacked by sodium sulfite, seemingly saponified by KOH, and found to contain benzoic acid (Gal, 1873c).

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This article does not present a conflict of interest