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ALEXANDRE-LÉON ÉTARD
Contribution to Chemistry

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ABSTRACT

Alexandre-Léon Étard (1852-1919) was a French chemist who discovered the synthesis of aldehydes by the oxidation of organic compounds with chlorochromic acid (Étard reaction), studied the synthesis and properties of cupro-cupric sulfites, the ferricyanides, determined the solubility of a large number or inorganic and organic salts, carried on the synthesis of many new organic compounds, and determined the composition of strychnine.

Keywords: aldehydes, chlorochromic acid, chrome derivatives, cupro-cupric sulfites. Étard reaction, Étard salt, solubility, strychnine

RESUMEN

Alexandre-León Étard (1852-1919) fue un químico francés que descubrió la síntesis de aldehídos mediante la oxidación de substancias orgánicas con el ácido clorocrómico (reacción de Étard), estudió la síntesis y propiedades de los sulfitos cupro-cúpricos, los ferrocianuros, determinó la solubilidad de un gran número de sales inorgánicas y orgánicas, realizó la síntesis de muchos compuestos orgánicos nuevos, y determinó la composición de la estricnina.

Palabras claves: ácido clorocrómico. aldehídos, derivados del cromo, estricnina, reacción de Étard, sal de Étard, solubilidad, sulfitos cupro-cúpricos

INTRODUCTION

A previous publication described the life and career of Alexandre-Léon Étard (1852-1919) and his contributions to biochemistry, particularly in the areas of nicotine, chlorophyll, putrefaction, and proteins (Wisniak, 2019). Here we explain his main contributions in the areas of inorganic and physical chemistry.

Scientific contribution

Étard wrote about 80 papers and books on the subjects of inorganic, organic, mineral, and physical chemistry, and physiology. In addition to the subjects described below, he studied the alkaloids in general and nicotine in particular (Cahours and Étard, 1880ab, 1881); chlorophyll and its derivatives (Étard, 1898, 1906); the phenomenon of putrefaction (Gautier and Étard, 1882ab); the hydrolysis of animal tissues (Étard, 1900, 1901; Étard and Vila, 1903, 1908); the preparation of hydrogen selenide and hydrogen bromide (Moissan and Étard, 1880); and of the carbides of yttrium and thorium and of cast thorium (Étard, 1904; Moissan and Étard, 1894, 1897); etc.

Chromium derivatives

According to Étard, no reactions were known which transformed instantly and at will the salts of chromic oxide (Cr_2O_3) from one derivative to another (Étard, 1875). Green salts were known to turn violet only under the influence of nitric acid and after a relatively long time. Certain reagents produced an immediate effect. For example, (1) the green salts turned carmine violet when mixed in the cold with a little amount of potassium nitrite; this tint gradually changed to the blue-violet typical of chromium alum for its type; (2) potassium sulfocyanide of potassium produced the same effect, although more slowly; (3) addition of KOH to a green solutions of chromium precipitated a hydrate insoluble in ammonia. Dissolution of this hydrate in acetic acid yielded a carmine violet color liquid, which did not turn violet-blue with time; (4) under the influence of arseniates or free arsenic acid the violet salts became a bright green in a few seconds in the cold and could be returned to violet by the nitrites; and (5) silver nitrate did not precipitate the arsenic acid of these salts (Étard, 1875).

Étard mentioned that Henri Loewel (1795-1856) had found four modifications of chromium hydrate, two green, one violet-carmine, and one violet-blue (Loewel, 1845). The colors and properties of their salts, modified by nitrites and arseniates, changed specifically with different reagents: The violet-carmine salt obtained with a nitrite yielded with KOH a grey precipitate insoluble in ammonia, which distinguished this salt from the common violet-blue salt. The light green salt obtained with the arseniates produced with KOH a precipitate insoluble in acetic acid and soluble in ammonia with a violet-blue tint, a reaction exactly opposite to that of the ordinary deep green salts (Étard, 1875).

According to Étard, only one crystalline chromium sulfate was known and to which Anton Schrötter (1802-1875) had assigned the formula $Cr_2(SO_4)_3,15H_2O$ (Schrötter, 1841). This violet salt differed by only three molecules of water from the hydrated aluminum sulfate, $Al_2(SO_4)_3,18H_2O$, a somewhat surprising result considering the isomerism of the salts formed by the trioxides of aluminum and chromium (Étard, 1877e). This fact led Étard to search the possible existence of a chromium sulfate containing 18 moles of water, which should be considered the normal salt. He found that this synthesis was very easy: it was enough to react ether vapors with a solution containing 100 part of CrO_3, 150 of sulfuric acid, and 225 of water. After a certain time, the mixture became a thick mass of crystals, which were then squeezed over a porous plate and washed with ether. The resulting chromium sulfate was violet, unaffected by air, and crystallizing in small flakes of formula $Cr_2(SO_4)_3,18H_2O$. Upon heating it lost part of its crystallization water becoming the hexa hydrate $Cr_2(SO_4)_3,6H_2O$. The latter was deliquescent and heated red-hot became the anhydrous sulfate $Cr_2(SO_4)_3$. These results led Étard to assign to the violet sulfate the formula $[Cr_2(SO_4)_3,6H_2O]$,12 Aq. It seemed then that the violet sulfate was simply a super hydrated form of the hexa hydrate (Étard, 1877e).

Étard reported that the pulverized violet sulfate turned green in contact with a small excess of dehydrating liquids such as fuming nitric acid, sulfuric acid, and phosphorus trichloride. Independently of dissolution, the change would take place in about 24 hours. The result with fuming nitric acid was interesting because ordinary nitric acid transformed green salts into violet ones. Étard also found that the violet chromium phosphate, $Cr_2(PO_4)_2,12H_2O$, heated to 100 ^{0}C, lost 7 molecules of water and become a green phosphate of formula $Cr_2(PO_4)_2,5H_2O$, hence the primitive formula could also be written $[Cr_2(PO_4)_3,5H_2O]$,7Aq, again a case of super hydration (Étard, 1877e).

Chromium alum was another interesting salt. The anhydrous salt $Cr_2(SO_4)_4K_2$ gave place to the crystalline alum $Cr_2(SO_4)_6K_6$ or $[Cr_2O_3.3SO_3, 3KOSO_3]$. This salt was very stable, representing a molecule of chromium sesquichloride, Cr_2Cl_6, where 6 residues of potassium bisulfate had replaced the chlorine, $Cr_2(SO_4K)_6$; with the potassium bisulfate behaving like a true monobasic acid. Étard suggested naming this new double salt *chromium kalisulfate*. This salt was easily prepared by adding a small portion of the anhydrous chloride Cr_2Cl_6 to melted potassium bisulfate and then heating to red during several minutes. Replacing potassium bisulfate by sodium bisulfate led to the formation of *chromium natrisulfate* (Étard, 1877e).

Another publication discussed the reactions of chromates (Étard, 1877f). For example, the reaction at 100 ^{0}C of one molecule of aqueous neutral potassium chromate with one molecule of ammonium sulfate or chloride resulted in the release of abundant ammonia vapors, while the liquid became more and more acid. Total elimination of the ammonia resulted in a liquid containing potassium dichromate and potassium sulfate (or potassium chloride). The fact that the ammonia was gradually eliminated by the boiling, led Étard to assume that the reaction was not simply represented by the equation

$$\mathbf{2\ K_2CrO_4 + 2NH_4Cl = 2KCl + 2NH_3 + H_2O + K_2Cr_2O_7}$$

For this reason, he decided to study in more detail the reaction between ammonium chloride and potassium chromate by examining the composition of the solution at increasing time periods and before the end of the release of ammonia. Cooling of the pertinent liquids led to the formation of an abundant amount of long brilliant yellow needles. Analysis of the relevant salt, well drained and dried in air, indicated that its composition corresponded to the formula

$$CrO_2\left\{\begin{matrix}OK\\ ONH_4 + H_2O\end{matrix}\right.$$

That is, a mixture of potassium chromate and ammonia, corresponding to the first reaction

$$CrO_2\left\{\begin{matrix}OK\\ OK\end{matrix}\right. + NH_4Cl = KCl + CrO_2\left\{\begin{matrix}OK\\ ONH_4\end{matrix}\right.$$

Which on boiling with water advanced to

$$\left[CrO_2\left\{\begin{matrix}OK\\ ONH_4\end{matrix}\right.\right]_2 = NH_3 + H_2O + K_2Cr_2O_7$$

Étard confirmed the latter property of the mixed chromate by preparing the salt directly by means of potassium dichromate dissolved in cold ammonium:

$$K_2Cr_2O_7 + 2NH_3 + H_2O + = 2CrO_2\left\{\begin{matrix}OK\\ ONH_4\end{matrix}\right.$$

As seen, the volatility of the base led to the formation or decomposition of the salt, depending only on the temperature (Étard, 1877f).

Independently of the method used, the double chromate of potassium and ammonia crystallized as long and very flat orthorhombic needles containing one molecule of water. Étard also described the synthesis of the corresponding double salt of magnesium sulfate and potassium chromate,

$(MgSO4)_2.K_2CrO_4,4H_2O$, 5Aq

(Étard, 1877f).

The most important part of this research was related to the action of *chlorochromic acid* (chromyl chloride) on organic compounds (Étard, 1877abc, 1880, 1881a, 1883), a compound discovered by Thomas Thomson (1773-1852) in 1827 (and not by Berzelius, as claimed by Étard) (Thomson, 1827; Étard, 1881a). The first paper reported the action of chlorochromic acid on toluene, hexane, and acetic acid (Étard, 1877a). Toluene reacted lively with the acid and for this reason it was necessary to add it in large excess and under cooling to avoid explosion. Thus 200 g of toluene reacted slowly with 50 g of chlorochromic acid to yield a muddy mass, which treated with water separated into chromium chloride and oil. Distillation of the oil passed a fraction boiling between 176^0 and 180 ^{0}C, composed of a mixture of the essence of bitter almond, characterized by its transformation into benzaldehyde-bisulfite (from sodium bisulfite) and benzyl chloride, which in the presence of ammonia became tribenzylamine chlorhydrate. The benzyl chloride originated from an impurity present in toluene. Étard found that the basic reaction passed through an intermediate complex of formula C_6H_5-CH_3,$2CrO_2Cl_2$. This organochromic derivative absorbed slowly the humidity of air (or rapidly in the presence of larger amounts of water) and released the smell of benzaldehyde. The benzaldehyde-bisulfite compound was decomposed with sodium carbonate and steam distilled to colorless, refrangible oil, boiling at 180 ^{0}C and presenting all the organoleptic properties of benzaldehyde (Étard, 1877a).

The reaction of hexane with chlorochromic acid generated an acid presenting all the properties of a high fatty acid and an aromatic oil, lighter than water, boiling at 145^0-150 ^{0}C, and containing by weight, 53.6% carbon, 8.6% hydrogen, 26.0 % chlorine, and 11.8% oxygen, corresponding to the formula $C_6H_{11}OCl$ (probable a ketone). Acetic acid reacted with chlorochromic acid in a closed vessel, to yield a salt green by reflection and yellow green by transparency, and containing chromium in an acid and a basic form. According to Étard, this salt was probably a chromium acetochromate hydrate, of formula

$$\mathbf{Cr_2O_7[Cr_2(C_2H_3O_2)_5].8H_2O}$$

(Étard, 1877a).

In the next series of experiments Étard reacted three parts of benzene with one of chlorochromic acid in a reflux distiller until no more HCl was disengaged, and then separated from the product a yellow liquid containing quinone dissolved in benzene, which was easily isolated as hydroquinone ($C_6H_4O_2$) by means of sulfur dioxide (Étard, 1877b). Treating nitrobenzene by the same procedure yielded nitroquinone, which crystallized as brilliant yellow flakes, soluble in alcohol, chloroform, and hot water. Nitroquinone fused at 232 ^{0}C and then sublimed. Étard found that chlorochromic acid attacked phenol violently and for this reason it was preferably to carry the reaction with phenol dissolved in carbon disulfide. The product of this reaction was a whitish, pulverulent, and non-crystallizable material containing, by weight, 70.9% carbon, 5.3% hydrogen, and 23.8% oxygen, corresponding to the formula $C_{12}H_{10}O_3$, that is, to dihydroquinone ether. Étard also found that the oxidation of chloroform with chlorochromic acid yielded phosgene ($COCl_2$), ethyl acetate, acetic acid, and acetaldehyde (Étard, 1877b).

Étard wrote that all his results indicated that chlorochromic acid acted by decomposing as follows:

$$\mathbf{4CrO_2Cl_2 = Cr_2Cl_6 + 2CrO_3 + O_2 + Cl_2}$$

That is, in addition to the formation of oxygen and chlorine the acid generated chromium (III) chloride and chromic acid [chromium(VI) oxide, chromium trioxide].

The latter contributed by its own to the oxidation of the organic reagent (Étard, 1877b).

Étard also studied the oxidation of nitrotoluene and *p*-dibromobenzene by chlorochromic acid (Étard, 1877c). The reaction with nitrotoluene was carried at 200 ^{0}C using a large excess of the chemical and adding the acid drop-wise, under agitation. At the end, the excess of nitrotoluene was eliminated by abundant water washes; the supernatant liquid contained, among others, chromium(III) chloride and the nitrotoluquinone formed. No chromic acid was formed, indicating that the oxidation was complete. After purification, nitrotoluquinone appeared as large yellow brown flaky crystals, melting at 237 ^{0}C and subliming afterwards (Étard, 1877c).

The oxidation of *p*-dibromobenzene was carried out by a similar procedure. The purified chloroanilic acid appeared as red needles *(*Étard, 1877c).

In 1908 Law and Perkin reported the results of their study of the oxidation of very pure nitrotoluenes and chlorotoluenes with chromyl dichloride (Law and Perkin, 1908). These compounds were hard to oxidize because of the presence of a negative group, although most oxidizing agents converted easily the methyl group into the carboxylic group. On the basis of their results, Law and Perkin stated that they did not believe that Étard had used the pure nitro compounds but a *mixture* of *o*- and *p*-nitrotoluene obtained by nitrating commercial toluene. Their findings indicated that *p*- and *m*-nitrotoluene produced the corresponding aldehydes in good yields while *o*-nitrotoluene rendered a mixture of chlorinated compounds. The latter result was probably due to the close proximity of the nitro group to the methyl group. Law and Perkin were convinced that the actual product obtained by Étard was *p-nitrobenzoic acid* (melting point, 237 ^{0}C, see above) derived from the oxidation of the aldehyde first formed (Law and Perkin, 1908).

Étard wrote that his results indicated that the oxidation of organic compounds by means of chlorochromic acid followed different paths according to the nature of the substances attacked and the substitution groups present. The reaction allowed the formation of ketones or quinones, with accompanying release of HCl or chlorine. In the case of hydrocarbons, no gases were released and the combination formed was direct and total. In order to complete this picture, he proceeded to determine the possible additional effects produced by certain substitution groups. For this purpose, he selected bromotoluene, anethole (anise camphor), and cymene (*p*-cymene) (Étard, 1878b). The bromotoluene employed contained the three isomers (*o*-, *m*-, and *p*-). The results indicated that only *p*-bromotoluene was attacked by chlorochromic acid. The reaction with anethole dissolved in carbon disulfide showed the formation of anisic aldehyde, $CHO\text{-}C_6H_4\text{-}OCH_3$. Cymene was also oxidized in solution with carbon disulfide, yielding isocuminic aldehyde monohydrate, melting at 80 ^{0}C and then losing its hydration water (Étard, 1878b). The synthesis of cumene was afterwards added as another example of the preparation of aromatic aldehydes (Étard, 1880). Once again, conducting it with the reagent dissolved in carbon disulfide controlled the rate of the reaction. Heating a mixture of one mole of cymene with two of chlorochromic acid produced a green precipitate, slightly crystalline, colored brown chocolate and containing $C_{10}H_{14},2CrO_2Cl_2$. After decomposition with water and purification, the complex left a yellow oily liquid boiling at 223 ^{0}C and having all the properties of cuminic aldehyde extracted from ordinary cumin essence. The complex was purified further by converting it into its crystalline bisulfite derivative, and regenerated with sodium carbonate (Étard, 1880).

Étard's doctoral thesis contained a more detailed description of all the syntheses described above plus that of some additional compounds (Étard, 1881a). The first part was an historical review of the discovery of chlorochromic acid its synthesis, and properties. Étard wrote that the original purpose of his project was based on the apparently equally large chemical activity of the chlorine and oxygen present in this reagent, and the idea that it would act simultaneously as an oxidizing and chlorinating agent. The activity of the two electronegative elements of the acid was related to the action of water on it, as represented by the equation

$$\mathbf{CrO_2Cl_2 + H_2O = CrO_3 + 2HCl}$$

This equation showed that the chlorine could attack the water and withdraw its hydrogen and turn oxygen into an active oxidation of organic substances, under the form of chromic acid (Étard, 1881a).

Chlorochromic acid was usually prepared by distilling a mixture of 4 moles of NaCl and 1 of potassium dichromate and double their weigh of concentrated sulfuric acid. Unfortunately, this procedure was very inefficient. The maximum yield obtainable could be derived from the following reaction

$$\mathbf{K_2Cr_2O_7 + 4NaCl + 3SO_3 = K_2SO_4 + 2Na_2SO_4 + 2CrO_2Cl_2}$$

No water was present which could interfere with the course of this reaction, except that present in any excess of sulfuric acid added. Étard mentioned that for this reason it was more convenient to use fuming sulfuric acid, instead of common acid. Assuming that fuming sulfuric acid was $SO_3 + H_2SO_4$, the above reaction became

$$\mathbf{K_2Cr_2O_7 + 4NaCl + 3H_2S_2O7 = 2CrO_2Cl_2 + K_2SO_4 + 2Na_2SO_4 + 3H_2SO_4}$$

This procedure allowed preparing easily large amounts of the reagent. Thus, 4 kg of the reacting mixture produced 750 g of chlorochromic acid per kilo of dichromate employed, that is, a yield 70% of the theoretical one. The acid thus prepared was limpid when fresh but promptly decomposing, even in closed recipients, into chromium dioxide and chlorine:

$$\mathbf{CrO_2Cl_2 = CrO_2 + Cl_2}$$

The acid was irritant and provoked strong hiccups.

Étard mentioned that he tested many solvents for conducting his reaction and rejected all, except carbon disulfide, because they reacted with the acid and/or were too expensive (chloroform, for example). In addition, due to the vigor of the reaction, it was recommendable to add the acid drop-wise to keep it under control.

The thesis described also the reaction of chlorochromic acid with benzyl chloride, xylene, ethylbenzene, propylbenzene, diethylbenzene, turpentine, pentane, and phenol.

Étard wrote that his results indicated that chlorochromic acid (a) transformed the methyl groups attached to an aromatic nucleus into the pertinent aldehyde and allowed the synthesis of aldehydes directly from a hydrocarbon; (b) the attack of an aromatic ring yielded quinones; (c) generated a new series of substituted derivatives represented by the general formula $X,2CrO_2Cl_2$; and (d) water decomposed this complex into aldehydes or quinones (Étard, 1881a).

This reaction is known today as *Étard's reaction*.

Copper sulfites

In 1878 Étard proved that sulfates were able to intermix to generate complex acid or neutral salts presenting certain stability and coloration properties quite different from those of the simple salts from which they derived (Étard, 1878c). He wrote that while trying to produce the same phenomenon with sulfites, he became quite interested in the cupro-cupric sulfite dihydrate, $CuSO_3.Cu_2SO_3{\cdot}2H_2O$, discovered by Michael Chevreul (1786-1889) in 1812 (Chevreul, 1812). According to Étard this salt could be prepared by rapidly passing a stream of SO_2 through a cold saturated solution of cupric acetate (Étard 1881d). This resulted in the flocculent precipitation of $CuSO_3.Cu_2SO_3{\cdot}2H_2O$. The bubbling was stopped when no more precipitate was seen forming. The pertinent chemical reaction was

$$4[Cu(C_2H_3O_2)_2]+3SO_2+6H_2O=8C_2H_4O_2+CuSO_4+\left\{\begin{matrix} Cu_2SO_3,CuSO_3 \\ 2H_2O \end{matrix}\right.$$

In this reaction, an immediate double decomposition generated the unstable cupric sulfite, which oxidized the SO_2 to yield cuprous sulfide and a sulfate. Afterwards, the cuprous sulfide reacted with the remaining cupric sulfite to yield a stable double sulfite. According to Étard, Chevreul's salt heated to 180 ^{0}C in a closed flask with sodium sulfite, with an aqueous solution of SO_2, or with distilled water, decomposed into 2 moles of sulfuric acid and 3 of metallic crystalline copper. Heated to the same temperature with a stream of SO_2, CO_2, or CO, it lost all its hydration water, leaving a solid basic residue of $Cu_2SO_3.CuO$. At the same temperature, and under the action of hydrogen sulfide, it transformed into Cu_2S_2 and other compounds of sulfur (Étard, 1881d).

Sodium bisulfite, in the absence of contact with air, did not affect Chevreul's salt, but a concentrated solution, in contact with air, resulted in the oxidation of the cuprous sulfite and fixation of sodium bisulfite (Étard, 1882a). The resulting chrome yellow crystals, of formula $Cu_{12}Na_8S_{14}O_{43} + 18H_2O$, were insoluble in water. Étard named this salt *cupro-cupric acid octasulfide.* Treated with SO_2 it transformed back into Chevreul's salt. Étard developed two processes for preparing this new salt in large quantities: (1) Agitation of pulverized anhydrous cupric sulfate with a solution of sodium bisulfite of relative density 1.26, in a closed flask, with the accompanying release of a large amount of SO_2; and (2) mixing a solution of cupric acetate with an excess cold sodium sulfite. In both cases, the resulting precipitate was filtered, washed first with water and then with alcohol and ether, and then dehydrated in contact with air (Étard, 1882a).

Étard mentioned that treatment of the chrome yellow crystals with cold sodium bisulfite, in contact with air, produced a brown red salt, which after washes with water, alcohol, and ether, had composition corresponding to the formula $Cu_4Na_8S_8O_{23}+9H_2O$ where the copper was present as cuprous oxide. (Étard, 1882a).

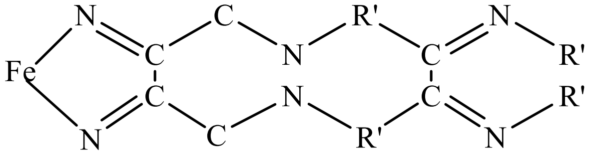
In 1854 Léon Péan de Saint-Gilles (1832-1863) reported the synthesis of cupro-cupric sulfite pentahydrate, $Cu_2SO_3.CuSO_3.5H_2O$, by reacting an insufficient amount of sodium bisulfite with a solution of cupric acetate (Péan's salt) (Péan de Saint-Gilles, 1854). According to Étard, this yellow salt did not transform into Chevreul's salt by simple desiccation but did it promptly when treated with an excess of SO_2 cold. Thus behavior was identical with that of cupro-cupric acid octasulfide, which did not transform into Chevreul's salt by desiccation but did it after a long digestion with SO_2. An interesting result was that treatment of Péan's salt with an excess of sodium bisulfite of relative density 1.16 transformed in into the yellow cupro-cupric acid octasulfide. Hence, Péan's salt could be considered a generator of both Chevreul's salt and cupro-cupric acid octasulfide (Étard, 1882b).

In a following publication (Étard, 1882c) Étard repeated his findings that the action of SO_2 on a solution of cupric acetate yielded at first the salt S_8O_{32} $Cu'_2Cu''_{10}H_{10}.21H_2O$ described by Péan de Saint-Gilles. If a current of the same gas was passed through a solution of cupric acetate at 85 ^{0}C, a granular, yellow precipitate of the composition S_8O_{32} $Cu'_4Cu''14CuO.5H_2O$ was formed. Further action of the gas converted it into the compound $Cu_2SO_3.CuSO_3 + 2H_2O$ described by Chevreul. According to Étard, varying the temperature and relative proportions of the acetic acid and water allowed obtaining a series of basic salts varying in colors from light brown to deep violet. Eventually the salt formed would contain Cu_2O, for example, the violet crystals of composition $Cu_2SO_3.9Cu_2O$ (Étard, 1882c).

Passing a stream of SO_2 through a solution of crystallized basic copper acetate in acetic acid turned it deep blue accompanied by the precipitation of heavy white pearly plates. This precipitate was filtered and washed, as before, with water, alcohol, and ether, and found to be composed of cuprous sulfide monohydrate of composition $Cu_2SO_3 + H_2O$. This new salt crystallized as colorless or slightly amber hexagonal tables, optically active, and having specific gravity 3.83 at 15 ^{0}C. Étard found the continuous digestion of cuprous-ammonium sulfite, $Cu_2SO_3,(NH_4)_2SO_3$, with a great excess of SO_2 converted it into brick red prismatic salts, optically active, having the empirical composition $Cu_2SO_3 + H_2O$ and specific gravity 4.46 at 15 ^{0}C. This new compound could also be readily obtained by the action of SO_2 on the sodium salt $Cu_2SO_3,Na_2SO_3 + 2\ H_2O$, which turned immediately from white to red. This finding indicated that cupric sulfite existed in two isomeric forms: one white of relative density 3.83, and one red of relative density 4.46 (both at 15 ^{0}C) (Étard, 1882c). A further publication described the properties and reactions of these two isomers (Étard, 1882d).

Ferricyanides

According to Étard and George Bémont, Gay-Lussac had assumed that ferrocyanic acid was a compound radical formed of one equivalent of iron and three of cyanogen, united to two equivalents of hydrogen, which he named *ferrocyanogen* (Gay-Lussac, 1815). Hence, the ferrocyanic acid should then be properly named, *hydroferrocyanic acid*. Consequently, Étard believed that the stability of ferricyanides could then be explained with a hexagonal formula (Étard and Bémont, 1884a):



The use of this formula, representing a tetrabasic unsaturated acid, allowed the preparation of numerous substances having formulae diverging from the ones assumed regularly.

In 1842 Louis Posselt (1817-1880) reported that ferrocyanic acid could be prepared by treating a concentrated solution of potassium ferricyanide, $Fe(CN)_6K_4$, with HCl and precipitating the resulting acid with ether (Posselt, 1842). The excessive amount of ether required led Étard and Bémont to suspect that the precipitate formed was not ferrocyanic acid but an ether combination of formula $Fe(CN)_6K_4,2[(C_2H_5)_2O]$. This supposition was tested by reacting dry ether with dry crystals of $Fe(CN)_6K_4$ and finding that the product was the same as that obtained during the synthesis of the acid by Posselt's method. Analysis of the ether derivative showed that it contained 15.2% iron (theoretical: 15.3%). Prolonged exposure to air caused decomposition of the complex into pure ferrocyanic acid (Étard and Bémont, 1884a).

Étard reported that ferrocyanic acid heated to 440 ^{0}C, lost 46.0% of its weight as HCN, leaving a light yellow-tan crystalline body containing, by weight, 24.1% carbon, 29.2% nitrogen, 46.1% iron, and 0.8% hydrogen, corresponding to hydroferrous pentacyanide, $Fe(CN)_5FeH$:

$$\mathbf{2Fe(CN)_6H_4 = [Fe(CN)_2]_2HCN + 7HCN}$$

The pentacyanide turned blue in contact with air, fixing oxygen and water.

Ammonium ferricyanide heated to 440 ^{0}C, lost 62.4% of its weight as water and ammonium cyanide, leaving an insoluble residue of formula $Fe(CN)_5$, which on further heating turned into the black iron carbide $Fe''C_2$. According to Étard, to these two salts corresponded the ferroso-ferric cyanide $Fe_4(CN)_{10}$, the salt $Fe(CN)_5FeK$, and the nitroferric cyanide $Fe(CN)_5Fe(NO)$ (Étard and Bémont, 1884a).

Étard and Bémont wrote that ferrocyanic acid heated with water, in the absence of air, decomposed rapidly into HCN and a lemon-colored crystalline substance. Elemental analysis of the latter indicated a composition corresponding to the formula $Fe(CN)_6FeH_2.2H_2O$, that is, the acid from where Williamson's salt, $Fe(CN)_6FeK_2$, was derived. Boiling ferrocyanic acid with water in the presence of air was supposed to generate Prussian blue. Upon performing this reaction, Étard and Bémont found that it produced a different substance of formula $(FeC_2N_2H_2O)^n$, containing the maximum amount of iron, as shown by its reaction with KOH. This substance was found to be a ferroso-ferric ferrocyanide hydrate. Oxidation of this hydrate in the presence of humid air generated a crystalline substance containing Prussian blue (Étard and Bémont, 1884b).

Étard and Bémont heated sodium nitroprussiate (sodium nitrosopentacyanoferrate) to 440 ^{0}C and obtained ferroso-sodium tetracyanide, $Fe(CN)_4N_2$, a yellow-tan crystalline substance, slightly unstable at dark red, stable to water, and insoluble in this liquid (Étard and Bémont, 1884b).

In another work, Étard and Bémont found that heating dry potassium ferricyanide transformed it into potassium cyanide and Williamson's salt. The latter was a crystalline substance, insoluble in water, and decomposing at the temperature of dark red, into potassium cyanide, cyanogene, and metallic iron (Étard and Bémont, 1885a). They also reported that the reaction of ammonium chloride with ferricyanides yielded a variety of products having a composition that depended on the medium, the temperature, and the time of reaction. For example, a solution of potassium ferricyanide added drop-wise to a boiling solution of ammonium chloride, reacted according the following equation:

$$\mathbf{2Fe(CN)_6K_4 + 6NH_4Cl = Fe(CN)_6Fe^{(3)}K_2 + 6NH_4CN + 6KCl}$$

Ammonium (or sodium) ferricyanide treated with ammonium chloride yielded Bunsen's salt, $Fe(CN)_6(NH)_2,2NH_4Cl$ (Étard and Bémont, 1885a).

The last publication discussed the green ferrocyanides or glauco ferrocyanides (Étard and Bémont, 1885b).

Solubility of salts

This subject was thoroughly studied by Étard (Étard, 1884abc, 1887, 1889ab, 1892b, 1894c). In his first paper (Étard, 1884a) he mentioned that although the solubility of a salt was usually expressed as the amount of solute dissolved in 100 part of water, he preferred to state it as the amount of anhydrous salt present in 100 parts of solution. In this manner all the results were included between 0 and 100, and the pertinent solubility curves were easier to compare. Gay-Lussac had shown that the solubility of salts (for example, Gay-Lussac, 1819) could be represented by straight or by curved lines. Étard mentioned that after months of work he had determined the variation of the solubility with temperature of the bromides, chlorides, and iodides of barium, calcium, cadmium, cobalt, iron, magnesium, manganese, nickel, strontium, and zinc, taking all the precautions to avoid supersaturation, and if necessary, in the absence of contact with air. The solubility had been determined by titration with silver nitrate, between the freezing point of the saturated solution and about 180 ^{0}C. In general, this implied a temperature range of about 200 ^{0}C. The results indicated that independently of the nature of the salt (anhydrous or hydrated), and within a certain temperature range a straight line making a large angle with the axis, represented the solubility. At higher temperatures the straight line became curved. The solubility curve of salts forming hydrates presented one or more inflexion points, as illustrated by sodium sulfate (Étard, 1884a).

According to Étard, the changes from linear to curved behavior were due to a state of dissociation of the combinations of the solute with the solvent (Étard, 1884b). In order to express the solubility (S) with enough significant figures, it was appropriate to use the formula $S = a + bt$ accompanied by an indication of the perturbation points. The lower point of solubility was determined using methyl chloride (freezing point -20 ^{0}C) as the refrigerant. The upper limit was determined by introducing in a Faraday (double) bottle a mixture of an excess of crystalline salt and a solution saturated at low temperature. The mixture was heated in a thermostated oil bath, under agitation, and decanting the saturated liquid to the second chamber. Proper precautions were taking to avoid condensation of the vapor phase (Étard, 1884b).

The solubility of sodium chloride, in grams/100 g of solution, between 0^0 and up to 160 ^{0}C could be expressed by the straight line $S = 26.4 + 0.0248t$, where 26.4 was the solubility at 0 ^{0}C. Étard mentioned that since the literature reported the formation of the hydrate $NaCl.2H_2O$ below 0 ^{0}C, which lost its water of crystallization below -10 ^{0}C, the straight line should bend below this temperature. The results of his measurements at -5^0, -10^0, -15^0, and -22 ^{0}C confirmed this supposition $^{(1)}$ (Étard, 1884b).

The following papers reported the solubility in water of NaBr, NaI, KCl, KI, $CaCl_2$, and $CuSO_4$, the pertinent algebraic equation, and its variation for the hydrates present (Étard, 1884c, 1887). For example, for NaI the solubility between 0^0 and 80 ^{0}C was expressed by $S = 61.3 + 0.1712t$, corresponding to the hydrates $NaI.5H_2O$ and $NaI.3H_2O$. Between 80^0 and 160 ^{0}C it was $S = 75 + 0.0258t$, corresponding to the hydrates $NaI.3H_2O$ and $NaI.2H_2O$ (Étard, 1884c). The solubility measurements allowed Étard discovering a new hydrate of cupric sulfate, CuSO4.3H_2O. This compound was slightly less blue than the common sulfate and crystallized as orthorhombic octahedrons (Étard, 1887).

In the next publications Étard provided high temperature solubility data for silver nitrate, potassium nitrate, sodium nitrate, and potassium chlorate, and claimed that his results indicated that their solubility increased up to the point of fusion of the anhydrous salt, in same the manner that the freezing point of the anhydrous salt signaled the *lower limit* of the phenomenon (Étard, 1889a, 1892).

Étard also determined the simultaneous solubility of potassium chloride and sodium chloride, two salts known not to react. He found that between -20^0 and 180 ^{0}C the sum of the amounts of salt dissolved could be represented by the single straight line $S = 27.0 + 0.0962t$. This line had no relation with those of the individual salts; in other words, the solubility in a mixture was not the same when in the presence of another solute (Étard, 1889b).

Étard summarized his results in two long papers (85 pages), divided into the following sections; (1) Experimental equipment and analytical procedures, in detail, (2) representation of the data, (3) aqueous saline solutions, (4) solubility of organic substances, (5) solubility in

The solubility data for aqueous solutions included a very large number of salts not reported in previous publications; the pertinent section was divided according to the anion, i.e. nitrates and chlorates, chlorides, bromides, iodides, and ferrocyanides, sulfates, and selenites and chromates. The section on solubility in non-aqueous solvents included the solubility of mercuric chloride in water, methanol, ethanol, propanol, isopropanol, allyl alcohol, acetone, butanol, isobutanol, pentanol, diethyl ether, ethyl formiate, ethyl acetate, acetic acid, and formic acid, and the solubility of cupric chloride in several alcohols. The section on the solubility of organic compounds included the solubility of naphthalene, triphenylmethane, diphenylamine, phthalic anhydride, and sulfur in carbon disulfide, hexane, and chloroform. The section of solubility of various solutes in water also contained information about the couples KBr + KI, KCl + KI, KCl + KBr, KNO_3 + NaCl, KNO_3 + KCl, KNO_3 + $AgNO_3$, $Ba(NO_3)_2$ + $BaCl_2$, and the triple mixture KCl + KBr + KI (Étard, 1894).

Miscellaneous

Acid anhydrides

In 1876 Henri François Gal (1839-1897) and Étard wrote that addition of glacial acetic acid to anhydrous phosphorus pentoxide turned the acid into a carbonaceous matter. This result led them to develop a fast method for preparing the anhydrides of organic acids based on the opposite operation: addition of the pentoxide to the acid (Gal and Étard, 1876). To 60 g of glacial crystal acid (boiling at 120 ^{0}C), stored in a large flask, they added 30 g of phosphorus pentoxide rapidly and under strong agitation. The pentoxide, which seemed not to react, became slightly brown. The mixture was distilled immediately thereafter, avoiding the pass over of the swollen contents. The first distillation yielded acetic anhydride mixed with acetic acid. Redistillation of this mixture yielded the anhydride as the fraction passing over at 136^0 to 138 ^{0}C (Gal and Étard, 1876).

Monochlorinated acetones

As mentioned above, the reaction of hexane with chlorochromic acid generated an acid presenting all the properties of a higher fatty acid, mixed with an aromatic oil, lighter than water, boiling at 145^0-150 ^{0}C, and composition corresponding to the formula $C_6H_{11}OCl$ (probable a ketone) (Étard, 1877ad). This assumption was confirmed by the study of the same reaction with 1-chloropentane. By its properties and composition, the substance $C_6H_{11}OCl$ behaved like a higher homologue of butylacetone monochloride. The latter was easily prepared by slowly adding chlorochromic acid to an excess of amyl chloride maintained at normal temperature by cooling. The product of the reaction was mixed with a large volume of water to dissolve the acid and separate the ketone as an oily phase, mixed with amyl chloride. The oil was fractionated by distillation, the ketone passing at 120 ^{0}C (Étard, 1877d).

Butylacetone monochloride was a slightly amber liquid, of formula CH_2Cl-CO-CH(CH3)$_2$, without optical activity, having a particular aromatic odor and burning taste, insoluble in water and KOH, and vapors irritating the eyes. According to Étard, his results indicated that chlorochromic acid transformed the hydrocarbons of the series C^2H_{2n+2} directly into chloroacetones (Étard, 1877d).

Amylene

Étard wrote that Russian scientists believed that commercial amylene (pentene, 2-methylbut-2-ene) contained four isomers, two soluble in diluted sulfuric acid (ethyl methyl ethylene and trimethylethylene) and two insoluble in the acid (isopropyl ethylene and normal amylene). The isomers were distinguishable by their boiling points (Étard, 1878a). Amyl alcohol, obtained by fermentation, was a mixture of active amyl alcohol (ethyl methyl ethanol) and inactive alcohol (isopropyl ethanol). Étard prepared amylene by melting 500 g of zinc chloride in a large vessel provided with a condenser, and then adding amyl alcohol (containing small amounts of isopropanol and butanol). The product of the reaction was dried with potassium carbonate. Amylene corresponded to the fraction passing a 35 to 38 ^{0}C. The next fractions were propanol, boiling at 95-96 ^{0}C, butanol, boiling at 108-109 ^{0}C, ethyl methyl ethanol, boiling at 128-129 ^{0}C, diamylene, boiling at 165 ^{0}C, and higher polymers (Étard, 1878a).

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 and Étard, 1878). The alkaloid was mixed with at least 10 times its volume of an aqueous solution of barium hydroxide and heated for 40 hours at 135^0 to 140 ^{0}C in a closed tube. The contents of the tube were then mixed with two volumes of distilled water, treated with a fast 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, forming a deliquescent salt, hard to crystallize. With tartaric acid it formed an acid salt, slightly 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) (dihydrostrychnine)

Gal and Étard named this new compound *dihdrostrychnine*.

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 prismatic 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 *trihydrostrychnine*.

The two 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, chiefly in their reaction with silver salts and sodium sulfide. Gal and Étard believed that the two new compounds, in spite of their basic character, were very similar to the two bases oxistrychnine and dioxystrychnine, described by Paul Schützenberger (1829-1897) (Gal and Étard, 1878; Schützenberger, 1858).

Glycerin derivatives

According to Étard, ammonium chloride reacted upon glycerin as a reductor eliminating the hydroxy groups as water. The product of the reaction was an oxygenated alkaloid containing the group C_6H_9NO, which Étard named *hydroxypicoline* (Étard, 1881b). Hydroxypicoline was prepared by slowly distilling a mixture of 50 g of ammonium chloride and 300 g of industrial glycerin not dried. Treatment of the product with concentrated NaOH yielded 40 g of yellow oil, containing the alkaloid in almost pure form. The purified oil, of relative density 1.008 at 13 ^{0}C, boiled at 155 ^{0}C without decomposition, had a repellent odor and acrid taste, and dissolved completely in water, alcohol, and ether. It was a strong base, bluing litmus, and releasing white fumes in the presence of HCl (Étard, 1881b).

Additional work on the subject proved that the correct formula of the oil was $C_6H_{10}N_2$ and not C_6H_9NO. Étard named the new product *glycoline* and prepared its chlorhydrate and iodoethyl derivative [$C_6H_{10}N_2(C_2H_5I)$]. Étard mentioned that glycoline seemed to have a structure similar to 2-methylpiperizine (Étard, 1881c).

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