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REVIEW ARTICLE

Louis Henry: The Henry reaction and other organic syntheses

Louis Henry: La reacción de Henry y otras síntesis orgánicas

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ABSTRACT

Louis Henry (1834-1913) was a Belgian chemist having a sharp deductive reasoning in organic chemistry, which led him to synthesize hundreds of new compounds in a wide range of functionalities. He isolated pure berberine from the roots of Berberis vulgaris, determined its composition, and prepared many of its derivatives. He proved the analogy between the sulfocyanides and thiocyanates of the monatomic alcoholic radicals and synthesized a variety of new organic thiocyanates. He demonstrated that monatomic nitriles should be considered to be primary amines where a positive triatomic radical had replaced the three hydrogen atoms of the ammonia, and presented a new general method for preparing nitriles based on the fact that phosphorus pentasulfide exchanged its sulfur for oxygen. Henry studied the reaction of iodine chloride with a variety of compounds and prepared the corresponding halohydrins. He proved the identity of the four valences of the carbon atom, the isomerism of many glyceric compounds, carried on the total synthesis of glycerin and discovered dipropargyl (a linear isomer of benzene) and diallylene. He described the preparation of many derivatives allyl, diallyl, and dipropargyl and their physical and chemical properties, in particular, the reaction with hypochlorous and hypobromous acids. He proved that nitromethane was able to combine with aldehydes and ketones to form nitro alcohols conforming the general system of the alcohols; this led him to develop the nitro-aldol reaction (Henry's reaction). Henry determined that lactide was a dilactic substance represented by two molecules of lactic acid minus two molecules of water and synthesized methylene lactate by reacting 1,3,5 trioxane with lactic acid.

Keywords: berberine; glycerin derivatives; Henry's reaction; iodine chloride; nitriles; thiocyanates.

RESUMEN

Louis Henry (1834-1913) fue un químico belga dueño de un agudo poder deductivo en química orgánica que lo llevo a sintetizar cientos de compuestos nuevos en un amplio rango de funcionalidades. Sintetizó la berberina en estado puro a partir de las raíces de Berberis vulgaris, determinó su composición y preparó muchos de sus derivados. Demostró la analogía entre los sulfocianuros y tiocianatos de los radicales de los alcoholes monoatómicos y sintetizó una variedad de nuevos tiocianatos orgánicos. Demostró que los nitrilos monoatómicos podían ser considerados como aminas primarias en las que un radical triatómico positivo había reemplazado los tres átomos de hidrógeno, y propuso un nuevo método general para preparar nitrilos basado en el hecho que el pentasulfuro de fósforo intercambiaba su azufre por oxígeno. Henry estudió la reacción entre el cloruro de yodo con una variedad de compuestos y preparó las halohidrinas correspondientes. Demostró la identidad de las cuatro valencias del átomo de carbón, el isomerismo presente en muchos compuestos glicéricos, realizó la síntesis total de la glicerina y descubrió el dipropargilo (un isómero lineal del benceno) y el diallileno. Describió la preparación de un gran número de derivados del allyl, diallyl y propargilo, así como sus propiedades físicas y químicas; en particular, la reacción con los ácidos hipocloroso e hipobromoso. Demostró que el nitrometano era capaz de reaccionar con aldehidos y cetonas para formar nitro alcoholes conforme al sistema general de los alcoholes; esto lo llevó a desarrollar la reacción nitro-alcohol, (reacción de Henry); Henry determinó que el láctido era una substancia diláctica representada por dos moléculas de acid láctico menos dos moléculas de agua, y sintetizó el lactato metilénico mediante la reacción entre el 1,3,5 trioxano y el ácido láctico.

Palabras clave: Berberina; cloruro de iodo; glicerina y derivados; láctido; nitrilos; reacción de Henry; tiocianatos.

Life and career (Delacre, 1914; Bruylants, 1979)

Louis Henry (Figure 1) was born in Marche-en-Famenne, Belgium, in December 26, 1834, a son of Marie-Antoinette Dagneux Albert and Joseph Henry, a tax collector. He received his basic education in humanities at the Petit Séminaire de Bonne-Espérance (today Collège Notre-Dame de Bonne-Espérance) and then (1851) entered the University of Leuven. The following year he approved with distinction the qualifying examination and in 1853 he become a candidate to a degree in natural sciences, at the head of a class of 23. Two years later he was awarded the degree of doctor of natural sciences. Laurent-Guillaume de Koninck (1809-1897), professor of chemistry at the Liege University and one of the examiners, recommended that Louis be awarded a travel scholarship, and also recruited him to work in his private laboratory; afterwards he sent him to complete his training as experimental chemist under Heinrich Will (1812-1890), at the laboratory of Justus von Liebig (1803-1883) in Giessen. In 1857, before departing to Giessen, Louis presented to the Royal Academy of Sciences of Belgium a long memoir (42 pages) discussing the relations between certain classes of organic compounds, and also about chemical radicals in general (Henry. 1859a). As a result of his stay at Giessen Louis published another paper describing the analysis and properties of the alkaloid berberine (Henry, 1859b). In 1858 Louis joined the University of Leuven as professor of mineralogy and geology, replacing the mineralogist professor Johannes Van Oyen (1816-1858); in 1863, after the death of Martin Martens (1797-1863) he replaced him at the chair of general chemistry. In the same year he was elected corresponding member of the Académie Royale des Sciences of Belgium. In 1867 Louis published his book on elementary general chemistry (Henry, 1867b), which went through many editions. During his tenure at Leuven Henry fought and succeeded in establishing experimental chemistry as part of the curriculum. Louis Henry passed away on March 9, 1913, at Leuven, after being paralyzed for some years.

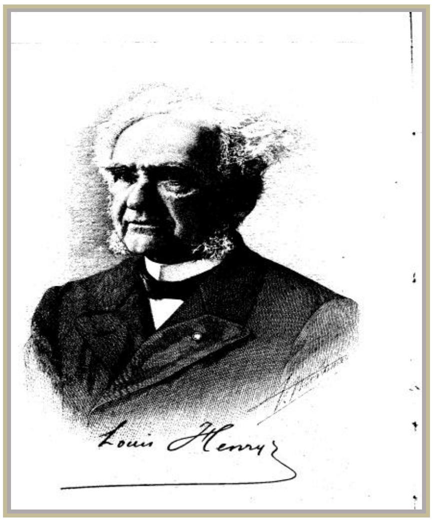


Figure 1. Louis Henry (1834-1913).

Henry received many awards for his scientific achievements. He was corresponding member of the Académie Royale des Sciences et Belles-Lettres de Bruxelles (1865) and promoted to full member in 1886; he was also corresponding member of the Institut de France (Académie des Sciences) (1905-1913) and of the scientific societies of Denmark, Portugal, and Romania. He was awarded the Grand Croix of the Papal Order of Saint Sylvester of Pius X, appointed Grand Officier of the Order of Leopold (King Leopold II) Order and of the Romanian Crown (established in 1881 by the King Carol I), as well as Commander of the Légion d'Honneur. In 1899 the Belgian government awarded him the Decennial Price of Chemistry and Physics and in 1873 he received a gold metal from the Universal Exposition of Vienna in recognition for his exposition of samples of the many organic products he had synthesized.

Scientific contribution

Henry was a very prolific writer; he published more than 300 papers and books (e.g. (e.g. Henry, 1867b, 1898, 1899, 1900) on the subjects of inorganic and organic chemistry, vegetable, principles, isomerization, etc. His most important book was titre *Précis de Chimie Générale élémentaire* (Henry, 1867b) (in 3 volumes). In addition to the subjects described below, he discussed the classification of organic acids and radicals (Henry, 1859a) studied chromium salts (Henry, 1866); reported the preparation and properties of straw wax (Henry, 1869e); studied the isomerism present in salicylic series (Henry, 1869f); the synthesis of a large number of new esters of polyfunctional alcohols and acids (Henry, 1872, 1873a); the synthesis of acetylenic hydrocarbons (Henry, 1874c); and pyruvic alcohol and derivatives (Henry, 1881);the valence of the carbon atom ; (Henry, 1886b); etc. Attention must be paid to the fact that in his initial publications Henry assumed the atomic masses C = 6, H = 1, O = 8, and N = 14.1.

Berberine

In 1835 Ludwig Andreas Büchner (1813-1897) isolated the active principle berberine from the roots of *Berberis vulgaris* and described it a very light yellow powder, composed of very thin silky prisms, having a strong bitter taste, being sparingly soluble in cold water and alcohol, very soluble in boiling water and boiling alcohol, little soluble in fatty oils and turpentine, and insoluble in ether, carbon disulfide, and petroleum ether. Sulfuric acid transformed it into ulmin and nitric acid into oxalic acid. Berberine reacted with metallic salts producing colored precipitates. Büchner believed that it contained nitrogen (Büchner, 1835). In 1846 Thomas Fleitmann demonstrated that berberine was not a neutral coloring matter but a true alkaloid and that the material isolated by Büchner was actually the hydrochloride of the true berberine. The elemental analysis of the hydrochloride corresponded to the formula $C_{42}H_{36}N_2O_9,2HCl+5H_2O$ and $C_{42}H_{36}N_2O_2$ for the free berberine. Fleitmann reported the preparation and properties of several derivatives of berberine, among them the chromate (the first organic compound containing chrome $C_{42}H_{36}N_2O_9+2Cr_2O_3$) (Fleitmann, 1846). In the following years berberine was found to be present in the root of other plants, such as *Cocculus palmatus* and *Menispermum fenestratum*.

Henry conducted a detailed study of berberine during his stay at Giessen (Henry, 1859b). He prepared berberine in a pure state following Fleitmann's procedure: Berberine chlorhydrate was first transformed into sulfate and this salt treated with barium hydroxide until de appearance of a brownish color, which indicated the full decomposition of the salt. The filtrate was treated with a stream of CO_2 to eliminate the excess of baryte, followed by boiling to precipitate any barium carbonate remaining in solution. The filtrated liquid was evaporated to dryness and berberine purified by repeated recrystallizations from alcohol. Pure berberine appeared as a powder composed of small needles or prisms, having a strong yellow color, which turned deep red on long heating at 100 °C. Berberine had no action on polarized light; combustion analysis indicated that it contained, by weight, 67% carbon and 5.54% hydrogen, corresponding to the formula $C_{42}H_{19}NO_{10}+HO$, containing one equivalent of water (Henry is assuming the atomic masses C = 6, H =1, N = 14, O = 8 and water as HO). Henry reported that an aqueous solution of berberine suffered no alteration when boiled with HCl or sulfuric acid and when treated with cupric solutions. Berberine dissolved completely in ammonia, boiling the solution with concentrated baryte resulted in the release of a strong ammoniacal odor (Henry, 1859b).

Henry described the preparation and properties of a large number of berberine derivatives (i.e. the hydrobromide, hydroiodide, ferrocyanide, ferricyanide, chloraurate, picrate, bitartrate, acid succinate, bioxalate, cyanide, thiocyanate, and nitrate), and described its reaction with chlorine, bromine, ethyl iodide, and nitric acid. For example, berberine cyanide was prepared by reacting a solution of berberine hydrochloride with potassium cyanide. The initial yellow liquid turned immediately deep red with the simultaneously formation of an abundant flocculent precipitate, which was separated by filtration, washed with cold water, and recrystallized from alcohol. According to Henry, berberine cyanide was quite different from other berberine salts. It crystallized as yellow brown rhomboidal flakes, very soluble in water but non-crystallizable, even more soluble in alcohol, particularly when hot. Its solutions released always a strong smell of HCN Henry, 1859b).

Thiocyanates

A. Habich and Heinrich Limpricht (1827-1909) showed that the thiocyanates of monoatomic alcoholic radicals combined easily with HCl and HBr (Habich and Limpricht, 1859). The analogy that existed between corresponding sulfurized and oxidized compounds suggested Henry that the sulfocyanides and thiocyanates of the same radicals would also show similar characteristics. The experimental results proved this theory to be correct (Henry, 1868).

In his first publication Henry described the reactions of the sulfocyanides of the radicals C_nH_{2n+1}, in particular, methyl, ethyl, and amyl, with HCl and HBr. The sulfocyanides were obtained by heating to 100 °C in a closed glass bottle, a mixture of the radical iodide with KCN. Henry's first results indicated that dry HCl gas did not combine with these compounds at room temperature or below it. HBr and HI showed a completely different behavior: they reacted vigorously and with such a large release of heat that it was necessary to cool the reacting mixture with a mixture of water and ice to avoid decomposition of the product. All the resulting compounds were white crystalline solids, insoluble in anhydrous ether and carbon disulfide. They remained unaltered when kept in dry or in closed vessels but decomposed rapidly in contact with humid air or water. The iodides were particularly sensitive acquiring quickly a brown color. This fact made their purification and their analysis very difficult: They had to be washed with anhydrous ether and then dried under pressure between two pieces of very fine paper. The important analytical factor was determination of the content of bromine and iodine; for this purpose, the halo derivatives were decomposed with water and the acid precipitated with silver nitrate. For example, the bromine derivative of ethyl sulfocyanide was found to contain, by weight, 63.60% of bromine, corresponding to the formula $C_2H_5CNS,2HBr$. The composition of the bromide of amyl sulfocyanide was also found to correspond to the *dihydrobromide*. The iodides of both compounds were found to be the pertinent *monohydroiodide* (Henry, 1868).

In his following publication Henry reported the action of iodine cyanide, ICN, upon ethylmercury sulfide, $(C_2H_5)_2HgS_2$, and the synthesis of allyl trisulfocyanide, $C_3H_5(CNS)_3$, benzyl thiocyanate C_6H_5-CH_2-CNS, and benzyl nitrothiocyanate, $C_7H_6(NO_2)$ (CNS) (Henry, 1869a). Iodine cyanide reacted easily with the mercury derivative. The resulting product was a colorless and limpid liquid, with a disagreeable alliaceous smell, boiling about 150 °C, and having all the properties of ethyl bisulfide, $(C_2H_5)_2S_2$. Henry prepared allyl trisulfocyanide by heating a mixture of allyl iodide and potassium sulfocyanide in a closed glass vessel, submerged in a water bath. This compound crystallized as small needles, brilliant white, hard, odorless and tasteless, melting at 126 °C and decomposing at higher temperatures. It was almost completely insoluble in water and cold alcohol, soluble in boiling alcohol, and slightly soluble in ether and carbon disulfide. Chemical analysis indicated that it contained, by weight, 44.42% of sulfur corresponding to the formula $C_3H_5(CNS)_3$ (Henry, 1869a).

Benzyl thiocyanate was easily prepared by heating in a reflux apparatus a mixture of benzyl chloride and potassium thiocyanate, in the presence of a large amount of ethanol. Benzyl thiocyanate crystallized as elongated white prisms, having a piquant odor and taste, insoluble in cold and hot water, slightly soluble in cold alcohol and very soluble in boiling alcohol, very soluble in ether, carbon disulfide, and hydrocarbons, melting at 56-58 °C and distilling at a temperature of 256-257 °C. It reacted lively with HBr, yielding a solid insoluble in ether and decomposing immediately in the presence of water. Chemical analysis indicated that its formula was C_7H_7CNS. Nitrobenzyl sulfocyanide was prepared by heating benzyl sulfocyanide with nitric acid or by reacting nitrobenzyl chloride with potassium thiocyanate and then with nitric acid. This compound appeared as small white needles, melting at about 70 °C and decomposing at higher temperatures

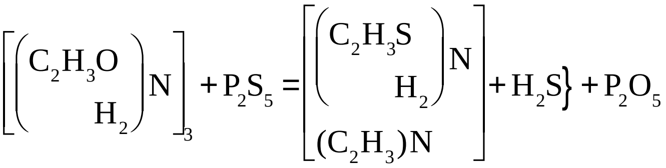
(Henry, 1869a). In a following publication Henry described the preparation of the isopropyl sulfide and thiocyanate (Henry, 1869b).

Nitriles

Henry published extensively on the subject of nitriles. In his first paper he postulated that monatomic nitriles should be considered to be primary amines where a positive triatomic radical had replaced the three hydrogen atoms of the ammonia. He demonstrated this assumption by comparing a series of reactions conducted with acetonitrile and benzonitrile, two nitriles belonging to two different series (Henry, 1867a).

Acetonitrile, C_2H_3N (here Henry is expressively considering C = 12, O = 16, and H =1), combined easily with the dry acids HBr and HI, with a strong exothermic reaction. The bromide and iodide of acetonitrile were white crystalline solids, soluble in alcohol and insoluble in ether, deliquescent, and decomposing rapidly in contact with humid air or water into acetic acid and the corresponding ammonia halide. Acetonitrile reacted similarly with aqueous NaOH or KOH, generating gaseous ammonium, and combined easily with HCl, although no formation of HCN was noticed. Benzonitrile, C_7H_5N, prepared by reacting benzamide with phosphorus pentachloride, reacted in a similar manner with HBr and HI. The behavior of thiocyanic acid, HCNS, and its esters, $(C_2H_5)CNS$, was analogous to that of cyanic acid, HCNO and its esters, $(C_2H_5)CNO$; all of them being attached to the ammonia type, and the group CS corresponding to the carbonyl radical CO. This was easily seen by the manner in which the ethers reacted with certain halides: ethyl thiocyanate combined strongly with gaseous HBr and HI in the same that allyl thiocyanate reacted with gaseous HBr. All these bromides and iodides were white crystalline solid bodies, insoluble in ether and soluble in alcohol. They were also decomposed by water regenerating the ester. In addition, acetonitrile and allyl thiocyanate combined with acetyl bromide yielding a crystalline product (Henry, 1867a).

In a following paper Henry presented a new general method for preparing nitriles based on the known facts that phosphorus pentasulfide easily exchanged its sulfur for oxygen, and the poor affinity of nitriles for hydrogen sulfide (Henry, 1869c). These led him to conceive the possibility of transforming amides into nitriles with the help of phosphorus pentasulfide. Under this reaction the amides would virtually convert into sulfurized amides (nitrile sulfides), before splitting into nitriles and hydrogen sulfide:



$$\left[\left(\begin{matrix} C_2H_3O \\ \quad H_2 \end{matrix}\right) N\right]_3 + P_2S_5 = \left[\begin{matrix} \left(\begin{matrix} C_2H_3S \\ \quad H_2 \end{matrix}\right) N \\ (C_2H_3)N \end{matrix}\right] + H_2S\Big\} + P_2O_5$$

The experimental results confirmed this assumption: under the action of phosphorus pentasulfide the amides transformed neatly and effectively into the nitrile, accompanied by formation of phosphorus pentoxide and abundant release of hydrogen sulfide. The reaction took place only under slight heating and indicated that phosphorus pentasulfide acted as an indirect dehydration agent, in the same manner as phosphorus pentachloride (Henry, 1869c).

In this particular paper Henry applied his procedure to acetamide and benzamide, reacting one mole of pentasulfide with five of the amide. The resulting crude acetonitrile was purified with a concentrated solution of NaOH (which did not dissolve the nitrile), followed by drying with calcium chloride and distillation. The purified acetonitrile boiled at 82 °C. Benzonitrile was prepared in a similar manner and found to boil at 187 °C (uncorrected) (Henry, 1869c).

In a subsequent paper Henry used the reaction between phosphorus pentasulfide and amides to prepare the butyric (C_4H_7N), valeric (C_5H_9N), caproic ($C_6H_{11}N$), cuminic ($C_{10}H_{11}N$), cinnamic (C_9H_7N), and metachlorobenzoic (C_7H_4ClN) nitriles. The amides were prepared by reacting the corresponding acid chloride with powdered ammonium carbonate and treating the resulting solid mass with boiling alcohol to separate the amide formed. The acid chlorides were prepared reacting three moles of the corresponding acid with two of phosphorus pentachloride (Henry, 1869d).

Henry prepared acetonitrile and used it to synthesize what he called *synthetic acetic acid* (Henry 1887).[26] According to Henry there were two general procedures for preparing linear nitriles of formula C_nH_x-CN: (a) distillation of a mixture of KCN with a alcohol mono sulfate, $(C_nH_{2n+1})RSO_4$, or (b) reacting KCN with an alkyl halide C_nH_mX. The first method was inappropriate for preparing large quantities of acetonitrile because the chemical reaction was very complex, produced methanol as byproduct, and a good part of the cyanide was converted into hydrogen cyanide. These disadvantages were not present with the second mixture, particularly when using methyl iodide (boiling at 44 °C). This halide was easily prepared from methanol, commercially available in excellent quality. Henry found that methyl iodide by itself did not react with KCN at low or high temperatures (up to its boiling temperature), but that the reaction took place in the presence of alcohols, particularly aqueous methanol or ethanol. After some time, the reaction begun by itself at ordinary temperatures and the mass became hot until it entered into lively boiling, forcing to carry the reaction under reflux conditions to avoid loss of the alcohol. During this period, the potassium cyanide changed from a soft mass into an opaque crystalline white deposit of potassium iodide. The liquid remained colorless but its volume decreased sensibly because of the volume contraction that took place during the substitution of the iodine by the radical -CN. The excess of methanol was eliminated by distillation and addition of phosphorus pentoxide. Henry reported that the average yield of this process was 81%, generating a product identical to the one prepared by dehydration of acetamide (Henry 1887).

Henry converted acetonitrile into acetic acid by reacting it with sulfuric acid or with aqueous HCl. For this purpose, he heated under reflux 82 g of acetonitrile with 300 g of a mixture of three volumes of concentrated sulfuric acid with two volumes of water, for several hours to ensure total conversion. Upon cooling the ammonium sulfate precipitated as a crystalline mass. The same procedure was conducted with 41 g of acetonitrile mixed with 100 of fuming HCl (containing 40% acid). Upon cooling the ammonium chloride precipitated as a crystalline mass. The filtrate was then distilled to produce aqueous acetic acid, which was then converted into glacial acetic acid. For this purpose, the aqueous acid, saturated with HCl, was neutralized with sodium carbonate and the resulting liquor evaporated to dryness. The resulting sodium acetate was then decomposed with dry gaseous HCl and distilled with phosphoric anhydride (Henry 1887).

In another paper Henry reported the synthesis of the dinitrile of malonic acid, CN-CH_2-CN (malononitrile) (Henry, 1886a). For this purpose, he heated in a water bath an equimolar mixture of cyanoacetamide and phosphorus pentoxide; upon melting the mixture became brown, swelled significantly, and began distilling a slightly yellow liquid, which promptly solidified. Chemical analysis indicated that it was malononitrile, quite pure. Henry described as a white, odorless and tasteless crystalline solid, melting at 29-30°C, although in contact with the tongue it produced a cooling effect. It was easily soluble in water, alcohol, and ether, and burned with the purple colored flame characteristic of the nitriles. Concentrated HCl dissolved it promptly, accompanied by generation of heat and swelling, deposition of a large amount of ammonium chloride, and formation of malonic acid. Heating malononitrile with concentrated HCl in closed tube transformed it into monochloroacetic acid, accompanied by release of CO_2. According to Henry, the intermediate group $-CH_2-$ presented an acid character; its aqueous solution reacted with silver nitrate producing an abundant white precipitate, which became yellow in the presence of light and exploded weakly. Chemical analysis indicated that it was probably a silver compound of formula $CN-CAg_2-CN$ (Henry, 1886a).

Henry also achieved the direct synthesis of glycolonitrile by heating in a water bath an equimolar mixture of formic aldehyde and hydrogen cyanide. Both reagents were employed as their liquid solutions, the aldehyde at 40% and the acid at 16%. The reaction was slightly exothermic and the solutions remaining colorless all the time. The product was concentrated by evaporation and the glycolonitrile extracted with ether from the concentrate. The ethereal extract was then evaporated and dried under vacuum in a desiccation vessel. Glycolonitrile appeared as a mobile liquid, colorless and odorless, having a strange sweet taste, relative density 1.100 (12 °C), and crystallizing at -67 °C. It was very soluble in water, alcohol, and ether, and insoluble in carbon disulfide, chloroform, and benzene. It boiled at 183 °C (759 mmHg), decomposing partially and releasing a strong odor of HCN. Mixed with a double its weight of HCl it decomposed violently and began to boil, releasing ammonium chloride and glycolic acid (Henry, 1890).

Henry wrote that many chemists had prepared normal pyrotartaric acid [glutaric acid, $C_3H_6(COOH)_2$] and its derivatives, but no one had synthesized its nitrile derivative or its predecessor, trimethylene cyanide, $CN-(CH_2)_2-CN$ (glutaronitrile) (Henry, 1885). Henry went on the synthesize this compound by reacting KCN pure and in pieces, dissolved in a solution of HCN in alcohol of 95% with four times its volume of trimethylene dibromide. He carried on the reaction for 8 hours, in a vessel provided with reflux. At the end of this period the KBr formed rested at the bottom of the flask as a pulverulent solid, while the alcoholic liquid assumed a slight yellowish color. The filtrate was then distilled to eliminate the alcohol, until the temperature reached 160°-165 °C. The additional KBr precipitated was eliminated by filtration. The resulting liquid was almost pure pyrotartaric nitrile, which passed over at temperatures between 270° and 280 °C.

Henry described pyrotartaric acid nitrile (glutaronitrile) as colorless viscous liquid, totally limpid, tasteless and odorless, having relative density 0.9961 at 11 °C, soluble in water, less soluble in alcohol and chloroform, and insoluble in ether and carbon disulfide. It boiled at 274 °C without decomposing and remained liquid when cooled to -23 °C. It dissolved easily in fuming HCl but after sometime a lively reaction took place, which resulted in the formation of an abundant deposit of ammonium chloride and formation of pyrotartaric acid (Henry, 1885).

Henry wrote that Joseph Tcherniac and Thomas Herbert Norton had recently reported the synthesis of succinonitrile, with a very low yield (23%), probably because they had used ordinary KCN of purity 90% (Tcherniac and Norton, 1883-1884). Henry carried on the synthesis of succinonitrile using the same procedure he had used for preparing glutaronitrile, taking care to use very pure KCN, containing a little of HCN, and succeeding achieving a yield of 82%. This compound was solid, composed of fine dendrites, soluble in water, alcohol, and chloroform, and sparingly soluble in ether and carbon disulfide. It melted at 51°-52 °C and boiled at 265°-267 °C, at atmospheric pressure (Henry, 1885).

Iodine chloride derivatives

Henry studied the reaction of iodine chloride with a variety of compounds (Henry 1870c, 1884abc). It was a known fact that allyl compounds combined by addition with chlorine and bromine and other equivalent systems, notably iodine chloride and hypochlorous acid, HClO. These reactions were easily performed and were generally accompanied by a strong exothermic effect (Henry, 1870c). Allyl alcohol combined easily with chlorine dissolved in water because it was also soluble in water. Drop wise addition of the alcohol to the aqueous solution of ICl resulted in the immediate discoloration of the latter until the solution began to separate into two liquid phases; the addition was continued until the liquid reassumed its original yellowish color. The heavy thick liquid was a chloro-iodhydrin, C_3H_5ICl, identical to the one prepared by Pierre Edmond Reboul (1829-1902) by reacting HI with epichlorhydrin (Reboul, 1860). The reaction of allyl bromide with ICl yielded bromo-iodhydrin, C_3H_5BrICl, identical with that prepared by the action of phosphorus pentabromide on chloro-iodhydrin or of phosphorus pentachloride on bromo-iodhydrin. Allyl chloride also combined easily with iodine chloride yielding dichloro-iodhydrin. The reactions with hypochlorous acid followed a similar path. Allyl bromide generated chlorobromhydrin, $(C_3H_5)BrCl(OH)$, allyl chloride yielded dichlorhydrin, $(C_3H_5)Cl_2(OH)$, and allyl alcohol produced monochlorhydrin, $(C_3H_5)(OH)_2Cl$ (Henry, 1870c).

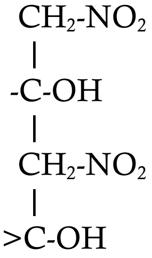
In the following two publications Henry presented the results of his work on the action of iodine chloride on ethylene monobromide and monochloride (Henry, 1884ab). He found that the aqueous solution of iodine chloride absorbed ethylene monochloride slower than ethylene; as a result, the brown product of the reaction dropped to the bottom of the vessel, from where it was easily removed. Ethyl iodide dichloride, $C_2H_3Cl_2I$, was a colorless liquid, which promptly acquired a purple color in contact with light. It had a relative density of 2.2187 at 0 °C and boiled at 171-172 °C at 774 mmHg. Henry treated this compound with strong bases in order to determine the location of the added atoms of chlorine and iodine in the ethylene molecule. The dichloride reacted immediately with KOH dissolved in absolute alcohol; the resulting precipitate was found to be an equimolar mixture of KI and KCl. This meant that 4/5 of the dichloride had lost one mole of HI and the remaining 1/5 one mole of HCl as their alkaline salts. The reaction with NaOH in absolute alcohol proceeded in the same manner, except that now the precipitate consisted only of NaCl. Since NaI was soluble in alcohol this meant that both results were completely concordant. Water precipitated from the alcoholic liquor insoluble oil colored brown by iodine. Upon distillation this oil separated into two phases, the largest constituted by asymmetric dichloroethylene, $CH_2=CCl_2$, and the smallest, by chloro-iodo ethylene also asymmetric. According to Henry these results indicated that the product of the original reaction was $CHCl_2-CH_2I$ (asymmetric with respect to chlorine); in other words, the two radicals, Cl, and I attached *simultaneously* to both CH_2 groups (Henry, 1884a).

The addition of iodine bromide to monobromo ethylene was not instantaneous; it was complete only after several days, under agitation. The raw chlorobromo ethylene iodide, C_2H_3ClBrI, was purified by distillation and desiccation with calcium chloride. The purified product was a colorless liquid, becoming rapidly colored under the influence of light. It had an agreeable odor, slightly piquant, and a sweet burning taste. It had a relative density of 2.53 at 0 °C, and boiled at 193°-195°C with partial decomposition. Henry used the same procedure to determine the relative position of the iodine and chlorine atoms added to ethylene bromide. In this case he concluded that the final product was not a pure compound but a mixture of two isomers, $CH_2I\text{-}CHBrCl$ and $CH_2Cl\text{-}CHBrI$, not present in equal amounts. The chlorine added preferentially to the most hydrogenated group, $\text{-}CH_2$ (Henry, 1884b). In a following publication Henry gave a detailed description of the physical properties of the new derivatives he had synthesized (Henry, 1884c).

Nitro comopounds

In 1895 Henry wrote that his attention had been called by the similarity between nitromethane, ($CH_3\text{-}NO_2$) and hydrogen cyanide; one of the hydrogens of nitromethane had a basic character while hydrogen cyanide combined easily with aldehydes and ketones to form nitro-alcohols (Henry, 1895a). This analogy suggested the possibility that nitromethane could also combine with aldehydes and ketones to form nitro alcohols conforming the general system of the alcohols:

$OH\text{-}CH_2\text{-}CH_2\text{-}NO_2$ (primary)
$\text{-}CHOH\text{-}CH_2\text{-}NO_2$ (secondary)



$$\begin{array}{l} CH_2\text{-}NO_2 \\ \;| \\ \text{-}C\text{-}OH \\ \;| \\ CH_2\text{-}NO_2 \\ \;| \\ >C\text{-}OH \end{array}$$

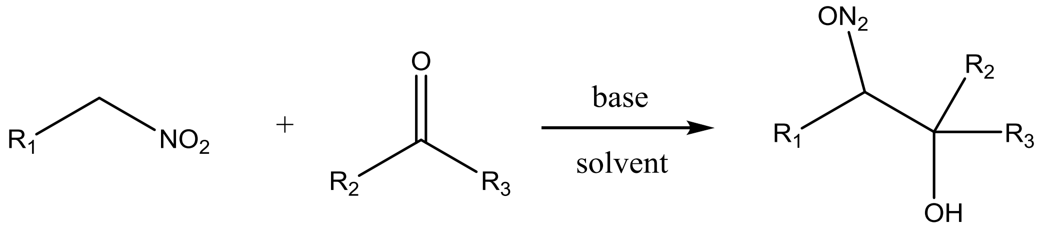
(tertiary)

The experimental results confirmed this possibility. Henry heated a mixture of ethanal, nitromethane, and water while adding potassium carbonate piece by piece (to allow a better control of the rate of reaction). At about 40 °C the mixture became homogeneous and began to react at 70 °C. The liquor was then left to cool and afterwards extracted wih ether. The ether extract was evaporated and then distilled under vacuum. The resulting nitro isopropanol, $CH_3\text{-}CH(OH)\text{-}CH_2(NO_2)$, was the product of the integral addition of nitromethane to ethanal. It was a colorless and limpid liquid, slightly thick and odorless, with a bitter and alliaceous taste, relative density 1.1910 at 18 °C, very soluble in water, ether, aclohol, and acetone, melting at about -20 °C, and boiling at 112 °C at 12 mmHg. It presented both the properties of an alcohol and a nitro derivative; it reacted with acetyl chloride to form HCl and its acetate, $CH_3\text{-}CH(C_2H_3O_2)\text{-}CH_2(NO_2)$; with phosphorus pentachloride it yielded nitro-isopropyl chloride, $CH_3\text{-}CHCl\text{-}CH_2(NO_2)$ a liquid boiling at 172 °C at atmospheric pressure (Henry, 1895a).

According to Henry, nitromethane reacted with aqueous formaldehyde in a more violent manner, yielding a solid crystalline compound, soluble in water, alcohol, and acetone, and less soluble in ether. Henry also described the reaction of nitromethane with propanal and isobutylaldehyde and reported that this compound did not react with acetone (Henry, 1895a). In the second part of this publication Henry described the reaction of formaldehyde with nitromethane, nitroethane, and secondary nitropropane, and the properties of the different derivatives. The results indicated that the reaction capacity of formaldehyde corresponded to the number of hydrogen atoms present in the nitrated carbon atom C-NO_2 (Henry, 1895a).

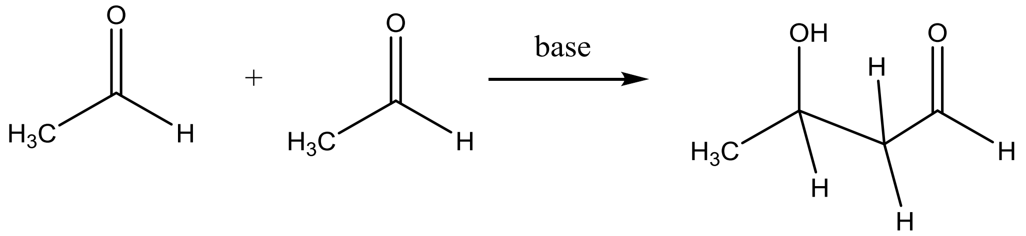
In two following publications Henry described the preparation and properties of a large number of new nitro derivatives, synthesized according to his new procedure (Henry, 1896, 1897), among them, nitro-isoproyl trichloride alcohol, nitropropanol, nitrobutanol, nitro-isobutanol, isoamyl nitroglycerin, isobutyl nitroglycerin, nitro isoproyl chloride, trimethylene nitropropanol, nitropropanols, nitrohexanols, chloro and bromo nitropropanols, etc. As can be observed, the reaction discovered by Henry (Figure 2):

Figure 2: Henry's reaction



allows combining a nitroalkane with an aldehyde or ketone in the presence of a base, to form β-nitro alcohols, hence it is known as *Henry's nitro-aldol reaction* (Figure 3). This procedure is very similar to the Würtz aldol reaction, which combines two carbonyl compounds to form β-hydroxy carbonyl compounds:

Figure 3: Henry's nitro-aldol reaction



Glycerin derivatives

Henry studied glycerin and its derivatives in great detail (Henry, 1870ab, 1873b, 1874a, 1878). In his first paper (Henry, 1870a) he wrote that the study of the phenomenon of isomerism in glyceric compounds had led him to examine in particular tribromhydrin, $(C_3H_5)Br_3$, because it could be prepared from two completely different compounds: glycerin $(C_3H_5)(OH)_3$, and allyl alcohol $(C_3H_5)OH$. The fact that the latter could be obtained from the former by elimination of two groups OH suggested that their numerous derivatives contained a common radical, C_2H_5. In other words, compounds of composition $C_3H_5X_3$ of both the glyceric and allylic series should be physically and chemical identical, in spite of their different origin (Henry justified his assumption listing the boiling points of 10 halogen derivatives prepared from both sources). The only notable exception was tribromhydrin, which Marcelin Berthelot (1827-1907) and Sebastiano de Luca (1820-1880) had prepared from the reaction of phosphorus pentabromide on dibromhydrin or epibromhydrin (Berthelot and De Luca, 1856b) and Charles-Adolph Würtz (1817-1884) from the reaction of bromine on allyl alcohol (Würtz, 1857). According to Berthelot and De Luca, tribromhydrin was a heavy volatile liquid boiling at about 180 °C and fuming light in air, while Würtz described it as a solid, crystallizing in brilliant prisms, melting at 16 °C and boiling between 217° and 218 °C. All of them wrote that under proper conditions it was possible to regenerate glycerin from their product.

According to Henry, the isomerism of these two products had remained without explanation even after Alphons Oppenheim (1833-1877) had demonstrated the identity between trichlorhydrin and allyl trichloride (Oppenheim, 1866). Henry believed that Berthelot had erred in his analysis of tribromhydrin (12.8% carbon, 1.8% hydrogen, and 85.4% bromine) and for this reason he decided to repeat the synthesis of the compound, using Berthelot's procedure. He first prepared dibromhydrin by reacting phosphorus tribromide with slightly warm syrupy glycerin (in amounts proportional to their molecular masses). The resulting raw dibromhydrin was purified by repeated distillation and washing with KOH. The pure dibromhydrin was then reacted with phosphorus pentabromide and the resulting tribromhydrin purified by washing with a solution of sodium carbonate, drying with calcium chloride, and fractional distillation. The resulting product boiled at 219-221 °C and was found to contain, by weight, 12.81% carbon, 1.78% hydrogen and 85.13-85.16% bromine. Henry described tribromhydrin as a neutral colorless liquid, having a faint ethereal odor, relative density 2.407 at 10 °C, crystallizing as fine elongated prismatic crystals, melting at 16-17 °C, boiling at 219-220 °C, and insoluble in boiling water. These and other properties showed that it was identical with allyl tribromide (Henry, 1870a).

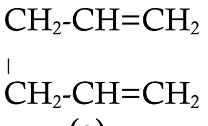
The following publication described the chloro- and bromonitro derivatives of glycerin (Henry, 1870b). Glycerin was a tri-alcohol hence it should form with nitric acid and other monobasic acids three different esters, by the successive replacement of 1, 2, or 3 atoms of hydrogen by NO_2. According to Henry, only the trinitrate was known; it was not possible to prepare the mono and dinitric derivatives by the direct action of nitric acid on glycerin. For this reason, he selected an alternative path: reacting the partial chloro and bromo derivatives (particularly mono and dichlorhydrin) with nitric acid. The experimental procedure was similar to the one used for preparing trinitroglycerin: The mono or dichlorhydrin were added drop-wise and under agitation, into a cold mixture of equal volumes of fuming nitric acid and concentrated sulfuric acid. After sometime the resulting chloronitro glycerin separated and floated over the liquid as an oily layer. The reaction was strong but quite and slightly exothermic. Upon pouring the resulting liqueur on cold water the oily layer precipitated to the bottom. It was separated, washed with sodium carbonate, and dried with calcium chloride. The monochlorodinitro derivative, $(C_3H_5)(NO_3)_2Cl$, was prepared by reacting epichlorhydrin, $(C_3H_5)ClO$, with fuming nitric acid (Henry, 1870b).

Henry described his new compounds as follows: (a) dichloro mononitroglycerin was a colorless oily liquid having weak and piquant nitrous odor and sweet taste, insoluble in water, soluble in alcohol and ether, having relative density 1.465 at 10 °C and distilling at 180-190 °C. It burned over a platinum strip with a white flame. It reacted with alcoholic KOH at room temperature yielding potassium nitrate and chloride and epichlorhydrin, and eventually, glycerin; (b) the properties of monochlorodintroglycerin were similar to those of dichloro mononitroglycerin, except that it was thicker and more viscous and had a relative density 1.5112 at 9 °C (Henry, 1870b).

In 1856 Berthelot and De Luca announced the discovery of a new hydrocarbon, which they named *diallyl*, C_3H_5-C_3H_5 (Berthelot and De Luca, 1856a). They also reported the preparation of its tetrabromide; $C_6H_{10}Br_4$. Afterwards Würtz reported the preparation of the halides, hydroxy derivatives, and esters of the same (Würtz, 1864), and William Robert Jekyll the synthesis of the monohydrate (hexylene oxide) (Jekyll, 1871). Henry published several papers (i.e. Henry, 1873b, 1874a) describing the preparation of a large number of new derivatives of diallyl, among them tetrabromide of diallyl dibromide, diallyl dichlorhydrin, a new hydrocarbon, *dipropargyl* (dipropinyl) $C_3H_3{\equiv}C_3H_3$, which was isomeric with benzene although very different, dipropargyl tetrabromide and octabromide, etc.

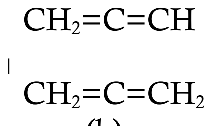
Dipropargyl was produced by reacting caustic alkalis twice with diallyl tetrabromide (Henry, 1873b). The first step transformed the tetrabromide into dibromide, and the second, the dibromide into dipropargyl. For this purpose, a mixture of diallyl tetrabromide with a large excess of powdered NaOH or KOH was heated and distilled in an oil bath. The distillate promptly separated into two liquid phases, a lower one, colorless and very dense, and an upper aqueous one. The upper phase was dried with calcium chloride and distilled again. The diallyl dibromide was a colorless liquid having a bitter and piquant taste, relative density 1.6560 at 18 °C, and boiling at about 210 °C (765 mmHg). It was insoluble in water and soluble in alcohol and ether. It reacted with bromide yielding the tetrabromide of diallyl dibromide and its reaction with caustic alkali provided the dipropargyl. This new hydrocarbon was a colorless liquid, strongly refractive, having relative density 0.8186 at 18 °C, and boiling at 58-60 °C at room pressure. It was insoluble in water, soluble in alcohol and ether, and burned with a brilliant sooty flame (Henry, 1873b).

According to Henry the global formulas of diallyl (a) and dipropargyl (b) corresponded to respectively



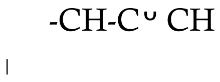
$$\begin{array}{l}CH_2\text{-}CH{=}CH_2\\ |\\ CH_2\text{-}CH{=}CH_2\end{array}$$

(a)



$$\begin{array}{l}CH_2{=}C{=}CH\\ |\\ CH_2{=}C{=}CH_2\end{array}$$

(b)



$$\begin{array}{l}\text{-}CH\text{-}C{\equiv}CH\\ |\\ \text{-}CH\text{-}C{\equiv}CH\end{array}$$

(b) Today

The next publication was a long paper (70 pages) divided in five parts, describing the preparation and properties of a large number of derivatives of dipropargyl, diallyl, and allyl, and their physical and chemical properties (in particular, the reaction with hypochlorous and hypobromous acids) (Henry, 1874a). Henry wrote again, and in more detail, that dipropargyl was an isomer of benzene. Both compounds were built on a C_6 core, which in dipropargyl was an open chain and in benzene a closed one. This time he compared hexabromobenzene with octabromo dipropargyl. The former was a crystalline powder composed of microscopic needles, sparingly soluble in ether, and melting above 200 °C; the latter appeared as colorless prismatic crystals, very hard and refractive, soluble in ether and carbon disulfide, totally insoluble in water and little in boiling alcohol, melting at 140-141 °C (Henry, 1874a).

In 1878 Henry reported the synthesis of *diallylene*, C_6H_8, a new hexavalent unsaturated hydrocarbon, derived from the reaction between phosphorus pentachloride and mono allyl acetone (Henry, 1878). Diallylene was a colorless and limpid liquid, lighter than water, with the typical smell of acetylenic hydrocarbons. It was insoluble in water and soluble in alcohol, ether, carbon disulfide, and petroleum ether. It had a relative density of 0.8579 at 18 °C and boiled at 70 °C (atmospheric pressure). It combined energetically with bromine, halogen acids, and sulfuric acid. Diallylene produced colored precipitates with inorganic salts: canary yellow with an ammonia solution of cuprous chloride, white and voluminous with an alcoholic solution of silver nitrate, black with mercurous nitrate, white with mercuric chloride, etc. (Henry, 1878).

Lactic acid

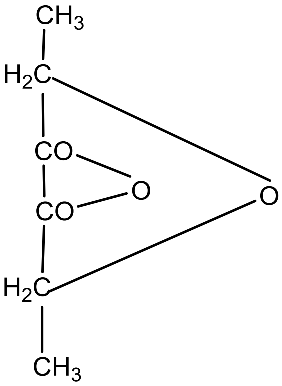
Henry wrote that the product of the thermal dehydration of lactic acid was known under the unusual name *lactide* (Henry, 1874b). This crystallizable solid that had been discovered in 1835 by Jules Gay-Lussac (1810-1077) and Théophile-Jules Pelouze (1807-1867), was represented by the formula $C_3H_4O_2$ differing from that of lactic acid, $C_3H_6O_3$ by at least one mole of water (Gay-Lussac and Pelouze, 1835). According to Henry, this relation was the same that existed between a diacid and its anhydride (for example, succinic acid and succinic anhydride). Thus lactide had been assumed to be lactic anhydride because it re-hydrated easily back into lactic acid. Now, dibasic acids did not yield their anhydride under the action of heat, and in addition, lactic acid was *monobasic.* This supposition was easily discarded when considering the action of ammonia upon lactide (Henry, 1874b).[50] In 1865 Johannes Wislicenus (1835-1902) proposed that lactide should be considered lactic ether, where the water elements had been taken simultaneously of the hydroxyl (acid) and the hydroxyl (alcohol) (Wislicenus, 1865).

To Henry this assumption required depicting how the formula of lactic acid was able to represent this ether. One possibility that had been assumed was that the ether was formed by an *internal* etherification between the -OH and the -COOH groups of lactic acids; this elegant explanation described very well the result of the thermal splitting of lactide into acetic acid and CO. Nevertheless, Henry believed that the formula $C_3H_4O_2$ was unable to express the molecular structure of lactide because it made it an isomer of acrylic acid, which was solid at room temperature and boiled at about 140 °C, while lactide did it at 220 °C. It was hard to explain this difference in volatility for two bodies having the same molecular mass (Henry, 1874b).

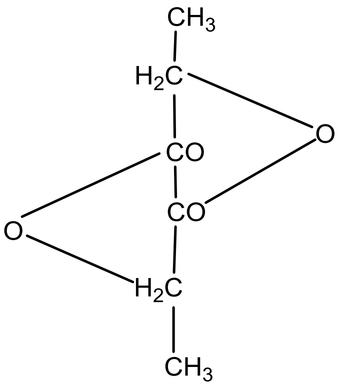
Henry determined that the density of the vapor of lactide was 4.81 at 766 mmHg and 185 °C and compared it with the theoretical values of the density for different multiples of $C_3H_4O_2$:

$C_3H_4O_2$	2.48
$(C_3H_4O_2)_2$	4.96
$(C_3H_4O_2)_3$	7.44

These results showed clearly that the actual formula of lactic acid should be $(C_3H_4O_2)_2$ or $C_6H_8O_4$; thus lactide was actually a *dilactic substance*, represented by two molecules of lactic acid minus two molecules of water, according to the two possibilities:



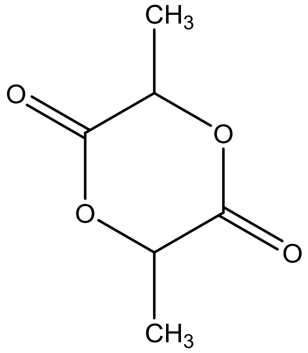
(a)



(b)

The first structure (a) represented a double functionality: an acid anhydride and simple ether. The second (b) was very special because it was a composite ester: *lactic lactate*. Once again, in a brilliant deductive stroke Henry reasoned that he could discriminate between these two structures by reacting lactide with a stream of dry ammonia gas. If (a) was the correct structure, then the product of the reaction would be a dilactic diamide or the corresponding ammonia salts. If (b) was the correct formula then the product would be the *lactamide*, CH_3-CH(OH)-CO-NH_2. Henry found that the product of the reaction was lactamide, the same compound that was produced by the action of ammonia upon ethyl lactate, and fusing identically at 74 °C, proving that structure (b) was the correct one.

The actual structure of lactide is the cyclic di-ester of lactic acid:



Henry reasoned correctly that lactide was composed two condensed molecules of lactic acid but gave the wrong shape to the hexacyclic compound. It was known that the oxidation of fatty and aromatic substances by nitric acid was always accompanied by the formation of HCN. Henry provided an additional example by means of the spontaneous oxidation of nitrolactic acid, HOOC-CH(NO_2)-CH_3 (Henry, 1879). Abandoned to itself at room temperature, nitrolactic acid decomposed abundantly into oxalic acid, water, and HCN:

$\text{HOOC-CH}(NO_2)\text{-}CH_3 = \text{HOOC-COOH} + H_2O + \text{HCN}$

In another publication Henry reported the synthesis of the new compound, methylene lactate. For this purpose, he reacted in a water bath trixoymethylene, $(H_2C\text{-}O)_3$ (actually 1,3,5 trioxane) with lactic acid (Henry, 1895b). Distillation of the product yielded monomethylene lactate, a colorless liquid, smelling strongly like formaldehyde, having a strong piquant taste, relative density 1.1974 sat 2.5 °C, boiling at 153-154 °C (754 mmHg), and insoluble in water. Hot water decomposed it into lactic acid and formaldehyde and it dissolved in bromine without apparent reaction (Henry, 1879).

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