

# Daniel Berthelot. Part III. Contribution to photochemistry

Jaime Wisniak\*

## ABSTRACT

Daniel Berthelot (1865-1927) used ultraviolet radiation from the mercury vapor lamp to carry out a series of oxidation and polymerization reactions, and proved that many reactions carried on by electrolysis could also be performed by photolysis. In doing so he discovered a myriad of unknown phenomena. By exposing to the action of UV a mixture of water and carbon dioxide, he achieved the synthesis of formic acid which then condensed and polymerized to produce vegetable sugars. A mixture of  $\text{CO}_2$  and  $\text{NH}_3$  gave rise to the simplest of the quaternary compounds, formamide, which represents the starting point for albuminous or proteinic substances, the basis of living matter.

**KEYWORDS:** photochemistry, synthesis of chemicals, photolysis, actinometer

## Resumen

Daniel Berthelot (1865-1927) usó la radiación ultravioleta de una lámpara de vapor de mercurio para efectuar una serie de reacciones de oxidación y polimerización, y así demostrar que mediante fotólisis era posible llevar a cabo muchos de los procesos que se realizan mediante electrólisis. Con este método descubrió una variedad de fenómenos desconocidos. Exponiendo una mezcla de agua y dióxido de carbono a la acción de la radiación UV consiguió la síntesis del ácido fórmico que, por condensación y polimerización, se convirtió en azúcares vegetales. Una mezcla de  $\text{CO}_2$  y amoníaco dio lugar a la formamida, el más simple de los compuestos cuaternarios, que representa el punto de partida para sustancias albuminoideas o proteicas, base de la materia viva.

## Introduction

In two previous publications we gave some details about the life and career, and the contributions of Daniel Berthelot to the subjects of thermodynamics and electrolytic solutions (Wisniak, 2010ab). Here we describe his contributions to the study of photochemistry, which should be judged against the state of the art at his time.

Berthelot used the invisible UV radiation from the mercury vapor lamp to carry on oxidation and polymerization reactions, and proved that many processes carried on by electrolysis could be also performed by photolysis. In doing so he discovered a myriad of unknown phenomena. For example, he found that under exposure to UV radiation, a mixture of water vapor and carbon dioxide dissociated, the vapor yielded

$\text{O}_2$  and  $\text{H}_2$ , and  $\text{CO}_2$  into  $\text{O}_2$  and carbon monoxide, and formic aldehyde, the simplest of a ternary compound of C, H, and O, was formed. The latter could condense and polymerize, signalling the first stage for the synthesis of vegetable sugars, starches, and celluloses. Adding  $\text{N}_2$  and operating under similar conditions at ordinary temperatures, Berthelot was able to synthesize formamide, the departure substance for the synthesis of albuminoidal substances that constitute the basis of living matter. In other words, he had split the  $\text{CO}_2$  and water vapor in the air in precisely the same way that the green cells of plants do it (Barrois, 1927). Berthelot summarized his findings in the area of photolysis in several publications (Berthelot, 1911ab, 1913).

The main photochemical subjects investigated are now presented according to the classification selected by Berthelot (Berthelot, 1917ab).

## The role of light in physico-chemical reactions

The effect of ordinary light or visible light on many chemical reactions is slow and hard to measure. For a long time physiologists and chemists had noticed that the chemical effects of light, almost nil with red radiation (slow vibrations), are much stronger with blue and UV radiation (fast vibrations). Ultraviolet radiation constitutes the most active fraction of light. The vibration frequency exhibited by radiating energy plays the role of the potential that temperature plays for thermal energy (Berthelot, 1917ab).

In 1865 Marcelin Berthelot (1827-1907) divided chemical reactions into two categories:

(a) Spontaneous transformations, exothermic, irreversible, accompanied by a reduction in the potential energy of the system. Light provides only the initial work to overcome certain links that prevent the reaction from occurring according to the natural slope of affinities. It can be said that light exerts a catalytic role; it accelerates a reaction that would take a long time to occur.

\* Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105.

Correo electrónico: wisniak@bgumail.bgu.ac.il

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(b) Provoked transformations, endothermic, accompanied by an increase in the potential energy of the system. This increase in energy is totally due to the incident luminous energy. This situation corresponds with that of equilibrium reversible reactions, such as the dissociation of inorganic compounds at high temperatures.

Chemical reactions accomplished by visible light correspond to the first category. Employment of sources rich in UV rays allow carrying on experiences of the second category, notably, the classical reactions of dissociation of cold and hot tube on the simplest inorganic compounds, carbon dioxide and water vapor.

Daniel Berthelot proposed dividing the useful UV spectra into three regions, which could be distinguished by their properties:

(1) First semi-octave,  $\lambda = 0.4 \mu$  to  $\lambda = 0.3 \mu$ . Solar UV radiation or initial UV. This is the solar radiation, traversing the atmosphere and arriving at the Earth surface. The rays have the same chemical and physiological action as blue or violet radiation; they strengthen but do not harm living organisms, which are acclimatized to it. The limit of the solar spectrum, near  $\lambda = 0.3 \mu$  diminishes little when going up in the atmosphere.

(2) Second semi-octave,  $\lambda = 0.3 \mu$  to  $\lambda = 0.2 \mu$ . Abiotic, sterilizing radiation, traversing water, producing chemical reactions, almost all irreversible, accompanied by a reduction of the chemical potential. This radiation has a catalytic role and is the agent of the degradation of energy, similar to ferments (enzymes).

(3) Third semi-octave,  $\lambda = 0.20 \mu$  to  $\lambda = 0.15 \mu$ . Abiotic like the previous category, does not traverse water but do traverse quartz. Its rays cause equilibrium chemical reactions; chemical dissociations of exothermic compounds such as carbon dioxide, and the formation of endothermic compounds such as ozone. This radiation restores the chemical energy.

Reactions of the first type (endothermic or catalytic) are accelerated by an increase in the frequency, which acts like an increase of temperature to diminish the passive resistances. Consider for example the classical combination between chlorine and  $H_2$ , slow in the red, rapid in the yellow, becoming explosive in the violet. Marcelin Berthelot kept a detonating mixture of  $H_2$  and  $O_2$  during 30 years under diffuse light, without detecting a beginning of combination. Daniel Berthelot proved that the combination was complete in a few hours of exposure to UV (Berthelot, 1911a, 1917ab).

According to Berthelot, there are some clear differences between ordinary chemical reactions and photochemical ones. The rate of chemical reactions increases exponentially with temperature. Near room temperature an increase of  $10^\circ C$  results in a doubling or trebling of the rate constant. In other words, the ratio  $k_{t+10} / k_t$ , the temperature coefficient, varies between 2 and 3. George Lemoine (1841-1922) found that for the reaction of  $FeCl_3$  with oxalic acid under the influence of light the temperature coefficient is 1.01 (Lemoine,

1888, 1895). Berthelot found a similar value for certain photochemical reactions such as the decomposition of fructose. This disparity can be explained well by fact that under the influence of light the electrons achieve a very large speed (1070 km/s under the influence of violet light, and 1510 km/s under the influence of UV, while at  $0^\circ C$  the speed of  $H_2$  molecules is only 1850 m/s and that of  $O_2$  460 m/s). This fact explains why temperature, which has such a strong effect on ordinary reactions, exerts no influence of photochemical reactions. On the other hand, the rate of photochemical reactions increases very rapidly with the frequency, following an exponential law similar to that of temperature on chemical reactions. It is then appropriate to consider a *coefficient of frequency* that plays the role of the temperature coefficient in ordinary reactions.

Reactions of the second type (exothermic), where light furnishes the energy necessary to overcome the chemical potential barrier, do not take place with rays of short wave length; most of them occur only for  $\lambda = 0.2 \mu$ .

Berthelot studied the temperature coefficient of several photochemical reactions (Berthelot, 1915) and concluded as follows: Photochemical reactions differ from the normal chemical reactions in that their rate is little influenced by temperature, as shown by the following two examples: (a) Ketoses such as dioxycetone and fructose were split by the action of light into the lower alcohol and CO. In diluted solutions the reaction was monomolecular, it begun in the UV solar light region and accelerated rapidly in the mid-UV range, (b) Oxalic acid and ferric chloride. Under day light the ferric salt was reduced to the ferrous state with release of  $CO_2$  and had a temperature coefficient of 1.01 in the range  $21^\circ$  to  $61^\circ C$ , essentially identical to the one found by Lemoine (Lemoine, 1895).

The smallness of these temperature coefficients showed that the reaction was purely photochemical and exempt of secondary reactions. Berthelot reasoned that if photochemical reactions are little affected by temperature, then there must exist a physical magnitude that plays in them the same role as temperature does in ordinary chemical reactions. Since the vibrational frequency represents the potential or intensity factor of radiating energy, the same as temperature represents the potential of intensity or intensity factor of thermal energy, then the rate of photochemical reactions should increase exponentially with the frequency of the light absorbed.

In previous publications Berthelot and Gaudechon had described the various modes of decomposition of oxalic acid under the influence of UV light (Berthelot and Gaudechon, 1911a, 1913e) and then Berthelot reported on the effect of the wavelength on the reaction as follows (Berthelot, 1914): (1) Initial UV ( $\lambda > 0.3 \mu$ ): Oxalic acid, solid or in aqueous solutions, was not decomposed after a 3-month exposition to solar light in the summer; (2) Medium and extreme UV. Solid oxalic acid, dried at  $100^\circ$ - $110^\circ C$ , was exposed for 12 hours at a distance of 20 mm from a mercury lamp. The temperature increased to  $90^\circ$ - $95^\circ C$ . The acid was decomposed into

CO<sub>2</sub>, CO, H<sub>2</sub>, and formic acid. The basic reaction was HOOC-COOH = HCOOH + CO<sub>2</sub>. Part of the formic acid was then decomposed into CO and H<sub>2</sub>.

### Photolysis

Berthelot and Gaudechon studied the photochemical decomposition of alcohols, aldehydes, acids, and ketones and reported the composition of the gaseous products (CO, CO<sub>2</sub>, H<sub>2</sub>, methane, ethane, butane) produced by methanol, ethanol, propanol, formaldehyde, acetaldehyde, propionaldehyde, and formic, acetic and propionic acids. While pure acetone (and diethyl ketone) decomposed into a gas mixture containing CO, methane, and ethane, its aqueous solution yielded CO, CO<sub>2</sub>, methane, and ethane. None of the ketones gave H<sub>2</sub> among its decomposition product, a fact that allowed differentiating them from aldehydes (Berthelot and Gaudechon, 1910f). In a following memoir (Berthelot and Gaudechon, 1910g) Berthelot and Gaudechon extended the previous work to include higher alcohols, such as butanol, heptanol, palmitic alcohol, isobutanol, *tert*-butanol, *tert*-pentanol, allylic alcohol, acrolein, citral, camphor, and butyric, heptylic, caprylic, caproic, palmitic, and stearic acids, indicating for each the different gases produced by the photolytic action.

A study of the photolysis of acids of complex structure yielded the following results (Berthelot and Gaudechon, 1911a): (1) *Dibasic acids*, normal series, solid compounds, decompose in a simple and characteristic manner. The dibasic acid splits into CO<sub>2</sub> and monobasic acid. Under prolonged luminous action the monoacids generated also experiment a partial photolysis, according to the scheme already described (Berthelot and Gaudechon, 1910fg), but in a weaker proportion. Acids in aqueous solution experiment the same changes. This is an additional verification of a law Berthelot and Gaudechon had already expressed: the mode of decomposition of a compound by UV radiation is independent of its state of aggregation. Thus, decomposition by photolysis seemed to be a more general process than decomposition by electrolysis; (2) *Unsaturated acids*. Photolysis of maleic and fumaric acids in the solid state yielded a mixture containing 90% CO<sub>2</sub> and 10% CO. The latter probably originated from a secondary decomposition of the acrylic acid formed; (3) *Keto acids*. These acids are unstable to heat but while between 80° to 100°C the  $\alpha$ - and  $\beta$ -keto acids produce aldehydes or ketones by loss of CO<sub>2</sub>, the  $\gamma$ -keto acids lose water and transform into lactones. UV light decomposed pyruvic acid (an  $\alpha$ -keto acid), where the two functions acid and ketone are neighbors, in the same manner that heat, although slower, and only CO<sub>2</sub> was released. The decomposition of levulinic acid (a  $\gamma$ -keto acid) released a the gas containing 30% CO<sub>2</sub> (characteristic of acids), 37% of gaseous hydrocarbons, and 30% of CO (characteristic of ketones). When the two functions acid and ketone were not neighbors, radiation decomposed them separately, the same as it would do with a *mixture* of an acid and a ketone; (4) *Acid alcohols*. Lactic acid released a gas containing 65% CO<sub>2</sub>, 9% CO, 18% H<sub>2</sub>, and 8% CH<sub>4</sub>.

All the above data showed that complex linear acids where the acid function is joined by an oxygenated function, tended to be decomposed by light with release of CO<sub>2</sub>, and that the decomposition of organic matter by UV radiation generated as final products H<sub>2</sub>, CO, and methane, followed by CO<sub>2</sub> and water in the case of oxidations (Berthelot and Gaudechon, 1910e).

The photolytic decomposition of a given substance yielded the same products, no matter what its state of aggregation (solid, liquid, or gas). The decomposition of solid organic substances into abundant gases was an unexpected result. Being a superficial phenomenon, it stopped rapidly and did not go beyond slight changes in coloration or surface alterations. The identity of the photolytic substances obtained with a solid gave led Berthelot and Gaudechon to think that the first effect of the radiation was to bring the different states aggregation to a common state, that of dissociation of radicals reacting in the state of ions. It was known that UV rays exerted an energetic reaction on solids or liquids, which were pulverized into gases and vapors and formed electrified nuclei and condensation centers. The memoir of Berthelot and Gaudechon contains a table listing the gases released by the most important chemical functions under the global influence of a quartz mercury lamp, without intermediate screen (Berthelot and Gaudechon, 1910efg, 1911a). Among other things, it showed that photolysis, contrary to electrolysis, did not tend to cut long straight chains, and its activity decreased as the chain increased. With ramified chains carrying the group CH<sub>3</sub>, photolysis separated these groups to produce methane. Substances having a cyclic structure were very stable, as they were with agents like heat or chemicals.

A following memoir (Berthelot and Gaudechon, 1911d) reported the action of UV light on the dehydration products of alcohols (ethers, anhydrides, and esters of linear and aromatic acids). Their results indicated that ethers decomposed into H<sub>2</sub>, CO, and hydrocarbons, without formation of CO<sub>2</sub>. Decomposition of acid anhydrides was characterized by the production of CO, CO<sub>2</sub>, and hydrocarbons and the absence of hydrogen. Esters yielded a complex mixture of CO, CO<sub>2</sub>, and light hydrocarbons, and no H<sub>2</sub>. Regarding the aromatic esters, benzyl formate decomposed into a mixture of CO and CO<sub>2</sub> but ethyl benzoate and ethyl salicylate were not decomposed, even when irradiated until they reached their boiling points. Esters of dibasic acids (such as methyl carbonate and ethyl oxalate) and acids alcohols (such as ethyl tartrate and ethyl lactate) also decomposed into a mixture of CO, CO<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>.

Berthelot and Gaudechon had already established (Berthelot and Gaudechon, 1910de) the extreme photochemical sensibility of the keto group CO and that the fast photochemical decomposition of formaldehyde and acetone was also present in fructose, the most common of the sugars containing a keto group. In a following work they extended their work to include other keto sugars containing 3 (dioxycetone), 4 (erythrulose), 6 (fructose and sorbose), and 7 (per-

seulose) carbon atoms (Berthelot and Gaudechon, 1912a). Their findings indicated that contrary to glucose, the photolysis of these keto sugars already took place in solar light, that the gas released was CO almost pure, and that the fundamental reaction was a split in which the sugar lost CO and gave an alcohol containing one carbon atom less. As with previous series of compounds studied, the reaction became slower and weaker as the chain was elongated.

Berthelot and Gaudechon studied then the influence of the wavelength of radiation on the decomposition of glucose and galactose (Berthelot and Gaudechon, 1912b). Visible rays and initial UV ones ( $0.4 \mu$  to  $0.3 \mu$ ) acted like a moderate temperature increase that attacked only the most heat labile substances; mid-UV radiation ( $0.3 \mu$  to  $0.2 \mu$ ) produced, the same like red heat, the decomposition of pyrogenic bodies and total combustion of organic matter, and ultra high UV ( $0.2 \mu$  to  $0.1 \mu$ ) dissociated the most stable compounds, such as water and CO<sub>2</sub> like high temperatures do. Thus, it was of interest to determine the minimum photochemical potential required for reaction, similar to determining the minimum potential for electrolysis. The substances elected for this study were sugars; Berthelot and Gaudechon had already established (Berthelot and Gaudechon, 1910e) that UV radiation allowed differentiating between keto sugars (such as fructose) and aldehyde sugars (such as glucose) by the rate of gas release and the composition of the same. Afterwards, they had determined that with keto sugars the reaction started already in the solar or initial UV radiation, and that although fructose or sorbose contain 5 alcohol groups and only one keto group, only the latter was attacked, and the gas contained only CO. Under the action of more extreme UV radiation, the alcohol groups were now attacked and H<sub>2</sub>, CO<sub>2</sub>, and methane were now among the gases released, signalling photolysis of alcohols, acidification, and advanced chemical degradation, respectively. They now found that the decomposition of keto and aldehyde sugars followed a similar path. It started in the mid-UV range ( $0.3 \mu$  to  $0.25 \mu$ ) where only the aldehyde function -CHO was gasified, H<sub>2</sub> and CO were released in the ratio 1:2, and the solution remained neutral. Increasing the frequency led to the decomposition of the alcohol groups where the H<sub>2</sub> content in the gas increased while the solution became acid, followed by increased release of CO<sub>2</sub> and methane.

Complex sugars (polyoses) may be considered the product of the condensation of two or more simple sugars (monoses) with elimination of water. The original sugar may be recovered by hydrolysis. Polyoses are known not to putrefy immediately and not be assimilated by animals and plants, but they do so after being split by hydrolysis with diastases. In a previous work Berthelot and Gaudechon (Berthelot and Gaudechon, 1910e) had shown that photolysis of aqueous solutions of maltose yielded the same gaseous products as one of glucose, and saccharose that of a mixture of fructose and glucose. These results indicated that UV radiation splits saccharose by hydrolysis into glucose and fructose, followed by de-

composition of the resulting monoses. They now extended their experiments to include slower UV rays (Berthelot and Gaudechon, 1912c). Their results indicated that photolysis of neutral solutions of polyoses went through a first stage characterized by a split of the molecule, without release of gas, followed by a stage of regular gas release. In other words, degradation of polyoses by radiation or by ferments, followed the same path.

In another memoir they compared the action of UV radiation upon organic compounds having a linear or a cyclic structure (Berthelot and Gaudechon, 1911b). Previous works had shown that different compounds having different chemical functions, but belonging to the fatty series (linear), decomposed under the action of UV radiation with release of gaseous products. Berthelot and Gaudechon found that this was not the case when the structure was cyclic. They studied the action of the radiation on aromatic hydrocarbons (benzene, phenylacetylene, etc.), phenols, aromatic alcohols (benzyl alcohol), aromatic monobasic acid (benzoic acid), dibasic acids (phthalic acids), and hexa basic acids (mellitic acid). The results were negative, not photolysis took place with gas release, or apparent transformation of the compound. Addition of uranium salts did not change these results. Thus, the well-known stability of aromatic structures to chemical agents, heat, and electricity, was also present with radiation by light.

This marked contrast between fatty and aromatic compounds gave additional support to the view stated previously (Berthelot and Gaudechon, 1911a) that the photolytic action of UV radiation was linked to a phenomenon of photochemical resonance between the medium (they used the word ether) and matter. It was well known that in order to act, radiations must be absorbed, and also that their absorption spectra is identical to those of luminescence. Eugen Goldstein (1850-1930) had remarked that the spectrum of remnant luminescence (after preliminary excitation by cathodic rays) of solid substances is continuous for the fatty materials, and discontinuous (formed by very thin bands) for aromatic compounds (Goldstein, 1902). The stability of cyclic structures, which contrasted with that of straight or ramified chains, was also present in non-aromatic cyclic structures. Berthelot and Gaudechon studied different non-aromatic structures containing a variety of chemical functions, such as pyrrol, furfural, pyridine, nicotine, codeine, caffeine, campholenic acid, etc., and found that they were not affected by UV radiation (no gas release and no alteration in color or other property)

Straight chains attached to cyclic rings were affected by radiation, although in an attenuated fashion. Thus cinnamic acid was decomposed with release of CO<sub>2</sub> but the amount of gas was about 70 times less the amount released by the first members of the fatty acids series (formic and acetic).

Berthelot and Gaudechon also studied aqueous solutions of mineral salts in order to observe more clearly the difference between electrolysis and photolysis. They subjected to UV radiation aqueous solutions of gold chloride, silver and

uranium nitrate, sulfates of nickel, copper, cobalt, chrome, etc. In every case the solution remained limpid, no precipitate was formed. Ferrous sulfate precipitated immediately red floccules, in which they identified the presence of iron and sulfuric acid, while the liquid remained colourless. No precipitation was observed when the solution was acidified with an organic or inorganic acid. This indicated that in the previous situation the precipitate was actually a basic sulfate (ferrous sulphate is not precipitated by UV radiation, except in the presence of the sulfates of nickel or cobalt).

The rule according to which in a given family of compounds, the stability to light decreases as the atomic weight increases, was also found to be true for the families of nitrogen and carbon (Berthelot and Gaudechon, 1913b), as shown by the following facts: (1) *Nitrogen family*. The decomposition of  $\text{NH}_3$  by radiations emitted by sparks between aluminium electrodes was observed by Emil Warburg (1846-1931) and Erich Regener (1881-1955) (Warburg and Regener, 1904). Using a large mercury lamp Berthelot and Gaudechon obtained almost complete decomposition in 3 hours. They were unable to get  $\text{N}_2$  and  $\text{H}_2$  to combine even in the presence of water. The latter was able to absorb minimal traces of  $\text{NH}_3$ , giving an alkaline reaction very easy to verify (Berthelot and Gaudechon, 1910f). There was a clear difference between the action of light and that of emanation (nuclear) on  $\text{N}_2$ ; (2) *Phosphine*. Louis-Jacques Thénard (1777-1857) and Joseph-Louis Gay-Lussac (1778-1850) had recognized that visible light has not effect on phosphine gas but decomposed it in the liquid state (Thénard and Gay-Lussac, 1812). Berthelot and Gaudechon kept the gas for five years under the influence of diffuse light without any alteration. When the gas was exposed at a distance of 20 mm to the action of a mercury lamp, in a thin quartz tube, a yellow mist formed within a few minutes and the walls of the tube became covered by a thin layer of phosphorus. Analysis of the gas obtained after radiation indicated that a small amount of solid  $\text{P}_4\text{H}_2$  was also formed; (3) *Arsine*. According to old experiments done by Augustus Vogel (1778-1867) (Vogel, 1835), in the dark arsine deposited in 8 days black floccules, and exposed to the sun the flask became covered with a layer of metallic arsenic. Vogel's product probably contained traces of impurities and humidity because a dry sample of arsine prepared in 1894 and kept in a glass flask under diffuse light, showed no deposit and was completely absorbable by cupric sulphate. After one month of exposure to solar light in a quartz tube, it had deposited a very light mist of arsenic on the walls. Exposition of two hours at a distance of 10 mm from a mercury lamp, enclosed in ordinary glass, resulted in no change. Hence the influence of radiation of  $\lambda > 0.25 \mu$  was very slow. When held inside a quartz tube, within 15 seconds it started to deposit a brown layer on the walls which become complete within one minute; after 10 minutes the deposit became mirror-like; (4) *Carbon family*. Methane is not affected by intensive and prolonged radiation, there is no carbon deposition or change in volume; (5) *Silane* exposed to

the action of a quartz mercury lamp produced instantly a mist and a yellow film of silicon deposited on the walls, together with  $\text{H}_2$  release; (6) *Organometallic compounds* such as zinc ethyl exposed for 5 minutes produced a mirror-like deposit of zinc, and simultaneously a gas phase composed almost of pure ethane with traces of ethylene. An unsaturated hydrocarbon was also formed which seemed to combine with liquid zinc ethyl; (7) *Phosgene gas*, formed by the combination of  $\text{CO}$  and  $\text{Cl}_2$  under the influence of visible light, and decomposed weakly when exposed to ultra UV light. In the presence of mercury, which fixed the chlorine, the decomposition continued and the volume was slowly reduced to one-half, and (8) *Sulfur hexafluoride*,  $\text{SF}_6$ , like other gaseous fluoride compounds, was found to be very stable, and not to dissociate under the rays of a mercury lamp. After 3 hours of radiation no deposit or change in volume is observed.

An additional publication (Berthelot and Gaudechon, 1913b) described the addition reactions between  $\text{CO}$  and other gases under the influence of UV radiation: (1) *CO and NO*. It was known that UV radiation oxidized  $\text{CO}$  in the presence of  $\text{O}_2$ , to give  $\text{CO}_2$ . This oxidation also occurred in the presence of  $\text{NO}$ , which decomposed acting as the source of  $\text{O}_2$  to carry on, under the influence of UV, the cold combustion. Berthelot and Gaudechon (Berthelot and Gaudechon, 1910d) had shown that  $\text{NO}$  is partially decomposed by UV radiation into nitrogen and  $\text{O}_2$ ; (2) *CO and water*. The action of UV radiation on a mixture of  $\text{CO}$  and water was very complex. Part of the water combined directly with  $\text{CO}$  to form formic acid, another part dissociated into  $\text{O}_2$  and  $\text{H}_2$ ;  $\text{CO}$  combined with the nascent oxygen to give  $\text{CO}_2$  and with the nascent hydrogen to yield formaldehyde as shown before (Berthelot and Gaudechon, 1910d); (3) *CO and halogens*.  $\text{CO}$  combined with chlorine under solar light to yield phosgene, but this reaction did not take place with  $\text{Br}_2$ ,  $\text{I}_2$ , or cyanogen; (4) *CO mixed with hydrogenated gases* such as  $\text{HCl}$ ,  $\text{H}_2\text{S}$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ , and  $\text{CH}_4$ , did not react. UV radiation acted only on the second component, decomposing it (except for methane) into its elements, with no reaction with  $\text{CO}$ . Irradiation with UV light of a mixture of  $\text{CO}$  and  $(\text{CN})_2$  produced a new compound, carbonyl cyanide  $\text{CO}(\text{CN})_2$  (Berthelot and Gaudechon, 1913c). This reaction is the same as the one by which phosgene is obtained from a mixture of  $\text{CO}$  and chlorine, formaldehyde from a mixture of  $\text{CO}$  and  $\text{H}_2$ , and formamide from a mixture of  $\text{CO}$  and  $\text{NH}_3$ . In all these situations  $\text{CO}$  combines in equal volumes with another gas to give an addition product. Berthelot and Gaudechon tried other means for producing carbonyl cyanide; one of them was using electric emanations. The reactions of the emanation, rich in UV rays, are hence similar to those of a mercury lamp, but they should not be confused with them. Contrary to UV radiation from a mercury lamp, emanation was able to combine  $\text{N}_2$  with  $\text{O}_2$ ,  $\text{H}_2$ , carbon disulfide, benzene, and numerous organic substances.

Berthelot and Gaudechon also looked into the possibility of synthesizing carbonyl cyanide by the action of heat. Mix-

tures of CO and (CN)<sub>2</sub> were heated up to 900°C with negative results; no change in volume was observed and analysis of the mixture gave the same composition as the initial one.

### **Simplicity of the gas ratios characterizing the beginning of photolysis (Berthelot, 1917b)**

When a body is decomposed by the action of light or photolysis, by acting with rays of decreasing wavelength, a simple primitive reaction is observed first, followed by secondary reactions, which become more and more complex. Thus an aqueous solution of glucose begins to decompose under the action of radiation of wavelengths of 0.30  $\mu$  to 0.25  $\mu$ , yielding CO and H<sub>2</sub> in the ratio 2:1. With radiations of less than 0.25  $\mu$  increasing amounts of CO<sub>2</sub> and methane begin to appear, while the proportion of H<sub>2</sub> increases little by little. This is the practical reason to decrease methodically the wavelength, in order to determine the minimum photochemical potential required to initiate the process. The three large categories of sugars, ketonic, aldehydic, and purely alcoholic (polyols), where the prototypes are fructose, glucose, and mannitol, respectively, have a different sensitivity to radiation. Ketonic sugars begin to decompose in the initial UV (> 0.3  $\mu$ ), that is to say, solar light. With dioxycetone, erythrose, fructose, and sorbose, the gas released is CO pure. Fructose contains 5 alcoholic functions and one ketone group, the latter is the only one attacked. Aldehydic sugars begin to decompose in mid-UV, with wavelength between 0.30 to 0.2  $\mu$ . The aldehyde function is the only one gasified producing CO and H<sub>2</sub> in the ratio 2:1. Polyols are more resistant, they are not attacked by radiation in the mid-UV range 0.30 to 0.25  $\mu$ ; they require wavelengths near 0.2  $\mu$ , and release CO and H<sub>2</sub> in the ratio 1:1. The ratio of the gases released is remarkable, showing that photolysis is characterized by volumetric ratio of the gases much simpler than electrolysis.

### **Reproduction of the principal types of fermentation by means of UV radiation. Dynamic interpretation of the role of diastases (Berthelot, 1917b)**

The role of diastase (ferments), from an energy viewpoint, consists only on triggering a spontaneous process, which is being held by passive resistances. The formula of the enzymes was unknown, in spite of the many efforts invested in finding the answer. For this reason it became of interest to reproduce the different diastasic reaction, without addition of foreign substances, using vibrational energies. Berthelot and Gauduchon succeed in carrying on the reactions of oxidation, hydrolysis, nitrification, etc., by irradiating different substances put inside a balloon of rock crystal. They first observed the division of saccharose into glucose and fructose, without release of gas, followed by a second stage characterized by the release of gas. The same behaviour was observed with disaccharides such as maltose, lactose, and gentiobiose, and trisaccharides such as raffinose and melecitose. In the case of the latter, Émile Bourquelot (1851-1921) (Bourquelot, 1885) had

shown that a first diastase split it into a molecule of biose and a molecule of monose and a second diastase completed the chemical process splitting the disugar into two molecules of monosugar.

UV radiations carried on the same reactions but simultaneously, indicating that they can probably be used to replace the hydrolyzing enzymes. In the same manner it was shown that UV radiation reproduced the phenomena present in digestion in absolute aseptic conditions, in the absence of enzymes, by simple irradiation of foods placed in a balloon of rock crystal.

### **Action of uranium salts and fluorescent substances**

Berthelot and Gauduchon investigated the possible modification of the chemical activity of light in the presence of fluorescent or radioactive compounds (Berthelot and Gauduchon, 1911a). For this purpose they used uranium nitrate, uranium acetate, thorium sulfate, radioactive barium chloride, barium platinocyanide, fluorescein, eosin, esculin, and quinine sulfate.

Their results indicated that with simple substances such as ethanol and acetaldehyde, pure or in aqueous solutions, the amount of photolysis decreased because the fluorescent bodies were degraded by the luminous energy. With acetic acid, pure or in solution, there was no action. They also tested their activity on aqueous solutions of complex acids (normal dibasic, maleic, fumaric, and keto acids). All the fluorescent substances used tested negative, but uranium salts, led to a quadruple or sextuple production of gases without changing the products of the reaction. The activation took place already at very low doses of the uranium salt and did not change when its concentration was increased up to 20 times. The catalytic action of uranium salts seemed to occur by a phenomenon of photochemical resonance, in which the vibrations of the medium amplified the vibrations of material atoms up to their rupture. Henri Becquerel (1852-1908; 1903 Nobel Prize for Physics) had already shown that the spectra of uranium salts presented a regularity not found in any other class of salts. Their vibrations represented the harmonic series of a fundamental luminous signal, and it was well known from mechanics and electricity that in this situation, vibratory movements were amplified by resonance up to their point of rupture of the equilibrium. To Berthelot, photochemical phenomena exhibited the same behaviour.

In 1859 Abel Niepce de Saint-Victor (1805-1870), and Lucien Corvisart (1824-1882) (Niepce de Saint-Victor and Corvisart, 1859) discovered that an acid solution of oxalic acid, added with a small amount of a uranium salt, decomposed instantly under the action of solar light and that the effect was not due to the acid of the salt because it also took place with the yellow, green, and black oxides of uranium. Further researches led some authors to believe that the action of these salts was due to their radioactivity, but Berthelot and Gauduchon had already proved that this was not true (Berthelot and Gauduchon, 1911a). For this reason Berthelot de-

cided to repeat some of their earlier experiments and add some new ones aqueous solutions of uranium nitrate, uranium acetate, radiation barium chloride, and fluorescein (Berthelot and Gaudechon, 1913e).

Their results indicated that a saturated aqueous solution of benzoic acid was not affected by the radiation. Addition of a uranium salt to ethanol or acetone retarded or stopped photolysis when the solution became turbid due to the formation of a precipitate. Addition of thorium oxide or sulfate had no effect on the reaction. Dibasic acids such as malonic, succinic, and glutaric, were known to decompose under the action of solar radiation; addition of uranium salts did not change the nature of the products formed. Under the action of mid- and extreme UV, an aqueous solution of oxalic acid decomposed into  $\text{CO}_2$  and H; the presence of uranium salts changed the mechanism and the products of the reaction; the solution now decomposed into  $\text{CO}_2$ , CO, and water. With solid oxalic acid UV produced an additional partial way of decomposition: formic acid and  $\text{CO}_2$ . Comparative experiments with an aqueous solution of glutaric acid, added with a very small amount of esculin, quinine sulfate, thorium oxide or sulfate, radioactive barium chloride, sodium acetate, or silver nitrate, indicated that in every case butyric acid was formed accompanied with release of  $\text{CO}_2$ . Except for uranium nitrate, the amount of gas formed was the same. With uranium nitrate the amount of gas formed was nine times larger. Irrelevant to the presence or not of uranium salts, none of the fluorescent or radioactive materials tested accelerated the photochemical reactions. The efficacy of uranium salts was restricted to a special class of reactions: decomposition of linear acids, particularly when dibasic and complex. These reactions took place spontaneously under the action of UV radiation, the photocatalyst allowed their realization under the influence of visible light by reducing the vibrational frequency of the photochemical reaction, in the same manner that an ordinary catalyst reduces the temperature of a chemical reaction.

### A new actinometer for UV radiation

During their researches of photochemistry Berthelot and Gaudechon felt the need of a new actinometer better adapted to the measurement of chemical activity of UV radiation than the old actinometers or photometers commonly used with visible light. This apparatus had to fulfil the following conditions: a reaction easy to follow and fast to measure, little sensitive to visible light and the initial UV, be very sensitive to medium and extreme UV, and becoming complicated by the minimum possible of secondary reactions as the wavelength is decreased (Berthelot and Gaudechon, 1913a).

They first considered an actinometer based on an aqueous solution of acetone. Under the influence of the initial UV radiation (solar light), acetone decomposed forming acetic acid, which could be titrated using colored reagents or by measurement of the electrical conductivity. Previous experiences had shown that acetic acid was not affected by the initial UV radiation, but it was in a growing manner, by UV radiation of

shorter wavelength. If such an actinometer was exposed to faster and faster monochromatic vibrations, the acidity would increase, go through a maximum value, and then start decreasing. Berthelot and Gaudechon reasoned that they could use the aqueous acetone solution to build an actinometer of a different nature. They had already discovered that among the pure substances, pure or dissolved acetone was the one that under radiation released the largest amounts of gas (equal volumes of CO and ethane). This release begun in the mid-UV and was accelerated as the wavelength decreased. If they used as a measurement of the photochemical activity of a luminous source the dose of acetic acid formed, or the dose of gas released by acetone, they would reach opposite results. In the first case we would say that when the temperature is increased, the chemical activity goes through a maximum, in the second case we would say that the activity increased regularly with temperature.

Often, when the wavelength was diminished, in addition to the simple primitive reaction, secondary reactions, more and more complicated, started appearing. For example, an aqueous solution of glucose, under the influence of radiation with wavelength between  $0.30 \mu$  and  $0.25 \mu$ , released only CO and  $\text{H}_2$  in the ratio 2:1; under  $0.25 \mu$ , appeared increasing amounts of the secondary gases  $\text{CO}_2$  and methane, and the proportion of  $\text{H}_2$  increased until it reached 6 volumes of  $\text{H}_2$  per volume of CO. In other words, the composition of the gas phase was changing substantially.

After many trials they found that all the specified requirements were fulfilled by the decomposition of sugars containing a keto group (ketoses) with release of carbon monoxide. Although dioxycetone was the most sensitive of these substances, it was hard to obtain, for this reason Berthelot and Gaudechon decided on fructose, easily accessible in large amounts.

In order to determine the temperature coefficient of the photolysis of fructose, they placed four thin tubes of quartz, full with a 10% wt aqueous solution of fructose at 30 mm distance from a small vertical quartz mercury lamp. Two of the tubes were exposed freely to the radiation and achieved temperatures of  $69^\circ$  and  $70^\circ\text{C}$ , respectively. The others, located on the other side of the lamp, were covered by cotton hoods, cooled by a thin layer of water; and reached a temperature of  $40^\circ\text{C}$ . After reaching the steady state of gas released, the amount of CO freed in each tube during half an hour was found to be  $0.61 \text{ cm}^3$  for the hot tubes, and  $0.55 \text{ cm}^3$  for the cooled ones. From these data Berthelot calculated that the temperature coefficient for the decomposition of fructose was 1.035 between  $40^\circ$  and  $70^\circ\text{C}$ .

These results indicated that the reaction seems to be of order 1 for low concentrations and order 0 for high concentrations. Intermediate concentrations presented orders in the range 0 to 1.

In this manner Berthelot and Gaudechon had in their hands a chemical photometer which allowed the precise comparison of the efficacy of different UV sources, the slow

or brusque alteration of quartz mercury vapor lamps, etc. This photometer was later on utilized successfully by Joseph de Kowalski in the experiments where he showed that the resonance transformer of Gustave Adolphe Hemsalech (1875-) and Commandant (Camille) Tissot (1868-1917) provided an economical source of UV radiation for the sterilization of water (Kowalski, 1915). Berthelot employed this actinometer particularly for following the aging of quartz mercury lamps. The photochemical experiences proved that that the efficiency of this lamp slowly decreased with use. Old lamps could then not be used for the photochemical reaction between carbon monoxide and water, which required extreme radiations.

Since UV radiations produce chemical effects that vary with the wavelength, it was of interest to develop a technique that allowed the successive elimination of the most refrangible rays. A large quartz vat having parallel faces containing a 1-cm layer of distilled water was able to eliminate extreme UV radiation. Replacing the water with chloride solutions of different concentrations allowed the successive suppression of the diverse sections of medium UV. Screens of very thin ordinary glass (0.14 mm thick), of mica, or special glass, allowed similar separations. A glass screen 2-mm thick did not allow the passage of the initial UV. Test glass tubes of thin ordinary glass permitted passage of UV up to  $\lambda < 0.3 \mu$ , which is almost the limit of the solar spectrum (Berthelot and Gaudechon, 1913a).

### Polymerization

Berthelot found that UV radiation is a powerful polymerization agent. The degree of condensation obtained immediately was very large, as could be seen by its action on acetylene, which did not yield benzene but a solid polymer (Berthelot, 1910a). The same characteristics are also present in the photosynthesis by plants. The polymerization ability of the radiation manifests itself of carbon compounds presenting double or triple bonds. Ethylene is polymerized into caprylene (1-octene), a waxy liquid boiling a little below 100°C (this was the first time that the gas had been polymerized in the laboratory). Acetylene precipitated after a few seconds in the form of a brown yellow solid. Allylene (propene) precipitated as a whitish solid. Methane was not polymerized; it was not affected by UV radiation except when in the presence of O<sub>2</sub>; then it lost hydrogen and formed homologues of highly condensed paraffins, which were not attacked by boiling sulfuric or nitric acids. At the same time water was produced with a little of CO<sub>2</sub>. Berthelot and Gaudechon speculated that these reactions may have occurred in other geological periods during the formation of petroleum and contributed to reduce the methane released by volcanoes or the decomposition of vegetable matter. UV radiation also condensed gaseous cyanogen into solid paracyanogen, (CN)<sub>x</sub>, a black solid which on heating decomposed partially back into cyanogen.

### Oxidation reactions (Berthelot, 1917b)

It is well known that the activity of atmospheric O<sub>2</sub> is greatly enhanced in the presence of light. This phenomenon manifests itself in the oxidation of oils, resins, waxes, varnishes, etc., and is utilized in the bleaching of cloth and tissues. UV rays have this oxidation ability in a very strong degree. It tends to formation of ozone, but exceeds the oxidation capability of ozone. It realizes also the combustion in cold of a large number of compounds; organic bodies containing hydrogen at carbon are immediately transformed into the final products of combustion, carbon dioxide and water. With gases these effects are very neat. H<sub>2</sub> burns completely into water; NH<sub>3</sub> burns with formation of N<sub>2</sub> and water; cyanogen burns with formation of CO<sub>2</sub> and N<sub>2</sub>.

This oxidation capability also manifests itself in the peroxidation of oxygenated compounds of sulfur and nitrogen. Under the action of UV radiation O<sub>2</sub> does not oxidize free N<sub>2</sub>, but N<sub>2</sub>O and NO are partially decomposed into nitrogen and oxygen, and the liberated oxygen reacts with the remaining as to convert it into higher oxides of nitrogen, which attack mercury forming nitrites and nitrates.

A significant reaction is the nitrification of NH<sub>3</sub> or nitrogen compounds. The work of Theophile Schloesing (1894-1919) and Achille Müntz (1846-1917) (Schloesing and Müntz, 1877) had shown that the natural nitrification of organic compounds occurred under the action of ferments. The process took place in two stages: a first ferment (nitrogenous ferment) brought the ammoniacal nitrogen to the nitrous state and a second ferment oxidized the nitrous nitrogen to the nitric state.

Berthelot and Gaudechon found that UV rays in the presence of air or O<sub>2</sub>, carried on the cold nitrification (35° to 50°C), but only up to the nitrous state, of aqueous solutions of NH<sub>3</sub>, strong or weak salts of NH<sub>3</sub> (sulfate, chloride, and bicarbonate), and other nitrogenated compounds (urea, methylamine, guanidine, etc.) (Berthelot and Gaudechon, 1911c).

Previous work (Berthelot and Gaudechon, 1910c) had shown that UV radiation do not carry on the combination of N<sub>2</sub> and O<sub>2</sub> in any appreciable amount, even in the presence of water. UV radiation can perform nitrification but only up to the nitrous state. This last result suggested the possibility of competition with industrial processes for the oxidation of N<sub>2</sub>, where the conversion is very low. To investigate this possibility Berthelot and Gaudechon employed compounds extremely pure, carrying in parallel the nitrification reaction on the control solution and the ones exposed to UV radiation for 3 to 9 hours, from a lamp situated at 3 to 6 cm. The results were as follows:

(1) Nitrification of an aqueous solution of NH<sub>3</sub>, by means of pure O<sub>2</sub> or air. In both cases the process stopped at the nitrite stage;

(2) Nitrification of aqueous solutions of NH<sub>3</sub> salts in the presence of air. Experiments with weak NH<sub>3</sub> salts, such as ammonium bicarbonate, and salts of strong acids, such as am-



monium sulfate and ammonium chloride, showed the formation of nitrites only;

(3) Aqueous solutions of urea showed first formation of  $\text{NH}_3$  followed by decomposition of  $\text{NH}_3$ ; the formation of nitrites was also observed when irradiating aqueous solutions of ethyl amine, ethyl amine, ethylene diamine, guanidine, acetoxime, hydroxylamine, acetamide, acetonitrile, etc.

Berthelot and Gaudechon reasoned that since all the above information indicated that the action of UV radiation stopped at the nitrite stage, it would be of interest to determine if nitrate compounds would reverse to the nitrite ones under radiation. Repetition of the experiments using now diluted or concentrated aqueous solutions of ammonium nitrate or potassium nitrate indicated not only that there was a retrogradation of the nitrate to nitrite, but that it was also accompanied by release of  $\text{O}_2$ . In the case of the ammonium salt, the  $\text{O}_2$  was accompanied by  $\text{N}_2$  indicating that the nitrite was coming not only from the oxidation of the  $\text{NH}_3$  group but also from the deoxidation of the nitrate group.

An additional important result was that UV radiation was able to decompose a concentrated solution of ammonium nitrite, with an abundant generation of  $\text{N}_2$ , the same phenomenon that occurs when the salt is heated up. Hence, in the same manner as ferments, UV radiation can lead to the gain or loss of combined nitrogen.

The most significant application that Berthelot and Gaudechon performed with the help of UV radiation was to reproduce assimilation by means of chlorophyll (Berthelot, 1910d).

Exposing to the action of UV a mixture of water and carbon dioxide, the first effect was a double decomposition,  $\text{CO}_2$  decomposed into  $\text{CO}$  and  $\text{O}_2$  and water into hydrogen and oxygen, relieving the potential of the system. Under the action of UV carbon monoxide combined with the nascent hydrogen present producing the simplest of the ternary compounds, formic acid, which then condensed and polymerized to produce vegetable sugars. It is seen how simply sugar is produced at the expense of the  $\text{CO}_2$  and water vapor present in air. UV light then allowed carrying on, in vitro, the same syntheses that plants do.

Previous work on the action of photochemical reaction under the influence of UV (Berthelot and Gaudechon, 1910a-d) had shown that the reaction temperature is lowered and below  $100^\circ\text{C}$ , oxidations and decompositions could be observed that normally took place at red heat, that the rate of reaction was accelerated, that the reactions were reversible, and that the degree of condensation achieved was higher, as shown by acetylene where instead of producing benzene, yielded a solid polymer. These four characteristics approached the action of light in living organisms, particularly vegetables, in which most of these characteristics were attributed to the action of diastases (Berthelot and Gaudechon, 1910e). The photochemistry mechanism seemed closer to that followed by nature in the formation of the main vegetable principles, than the classical laboratory experiments. They allowed the

following results: (1) Synthesis (based on the components of water vapor,  $\text{CO}_2$ , and  $\text{NH}_3$ ) of methyl derivatives such as formaldehyde, formamide, and formic acid; (2) immediate condensation of these products; (3) further decomposition of the condensed products by fermentation, photochemical processes, or similar paths.

From the above, among linear products, methylated compounds are formed directly, the ethylated, propylated, etc., will originate from the splitting of more complex material generated by light. Berthelot and Gaudechon added that although the formation of methylated derivatives by photochemical action was easy and abundant, the production of ethylated ones by analogue reactions was difficult and uncertain. It seemed to them that we have here an image of what happens in nature, methylated compounds (amines, ethers, etc.) are frequent, ethylated ones are less numerous.

The syntheses described above realized the photosynthesis of ternary compounds (C, H, O) starting from the simplest of them, formic acid. Berthelot and Gaudechon achieved the synthesis of quaternary compounds (C, O, H, N) by using the same gases and  $\text{NH}_3$ . Under the influence of UV radiation, a mixture of  $\text{CO}_2$  and  $\text{NH}_3$  gave rise to the simplest of the quaternary compounds, formamide, which represented the starting point for albuminoidal or proteinic substances, the basis of living matter, the same as formaldehyde represented the starting point of polysaccharides, starches, and celluloses. In this diverse syntheses,  $\text{CO}_2$  did not enter immediately in combination, but it was first transformed into  $\text{CO}$ , an unsaturated compound, very appropriate for giving addition compounds. It is thus that Humphry Davy (1778-1819) exposed a mixture of chlorine and  $\text{CO}$  to the action of solar light and obtained phosgene ( $\text{COCl}_2$ ), a gas having the property of hydrolyzing into  $\text{CO}_2$  and  $\text{HCl}$ . This reaction takes place in the lungs, which represent a hot and humid medium where the gas is in the presence of an excess of diastases, and contributes to the strong toxicity of phosgene. Based on the analogy of the cyanogen radical with chlorine allowed Berthelot and Gaudechon to use UV radiation to combine with the help of UV radiation  $\text{CO}$  with cyanogens and generate a very simple compound, carbonyl cyanide, which had not been synthesized by chemical means:  $\text{CO} + (\text{CN})_2 = \text{CO}(\text{CN})_2$ . This compound is produced in the gas phase a little below  $100^\circ\text{C}$ , but promptly, under the action, of UV radiation, it condenses into a solid. Hydrolysis converts it into  $\text{CO}_2$  and  $\text{HCN}$ , according to  $\text{CO}(\text{CN})_2 + \text{H}_2\text{O} = \text{CO}_2 + 2\text{HCN}$ . The compound is very toxic and represents the first example of new compound prepared by photosynthesis (Berthelot and Gaudechon, 1913d).

Berthelot and Gaudechon concluded that the photochemical synthesis of large classes of organic materials took place under very simple conditions. It was enough to mix the most common inorganic gases, water vapor,  $\text{CO}_2$ , and  $\text{NH}_3$ , and to irradiate them with UV light. There was no need of foreign substances, high temperatures, or electric currents.

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