Chapter 2
In Pursuit of a Pathway (1843–1918)

> If we try to nail down the present state of our scientific views on the assimilation of carbon in the chlorophyllous parts of plants, we are forced to confess that [. . .] in this fundamental question of plant physiology we are still at the stage of discussing the possible and the probable.[1]

The quote above succinctly characterises the state of photosynthesis research in the second half of the nineteenth century. The author of this quote openly acknowledged that so little was known about photosynthesis that the formulation of "hypotheses", which in this case were taken to be equivalent to "speculations", seemed to be the only, and, therefore, justified, resort. The body of knowledge at the time, concerning organic reactions in general and the processes in the living organism in particular, was scant and the methods available went hardly beyond input–output measurements without any means to access the stages in-between. This situation was not to change for decades to come. Even as late as 1925 the British plant physiologist Walter Stiles still maintained, in his monograph on carbon assimilation in plants, that "the nature of the intermediate substance or substances formed in photosynthesis is a subject on which [. . .] our real knowledge is practically negligible".[2]

Yet, photosynthesis still attracted the attention of a number of scientists, some of which concerned themselves with possible mechanisms and pathways of photosynthesis, as will be introduced in this chapter. The period analysed stretches from 1843, the year in which the German organic chemist Justus Liebig brought forward a rudimentary idea of the photosynthetic mechanism—the first attempt to account for photosynthesis in terms of a chemical pathway—until 1918, the date of publication of the voluminous monograph compiled by the German organic chemist Richard Willstätter together with his Swiss collaborator Arthur Stoll. Finding the biochemical pathway for the reduction of carbon dioxide to the stage of carbohydrates in plants was no trivial task given the situation described above. The main topic of this chapter is to elaborate the characteristic features of the models that chemists came up with and to spell out the chemists' strategies to deal with the enormous methodical

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[1] Reinke (1882, p. 289).

[2] Stiles (1925, p. 193).

K. Nickelsen, *Explaining Photosynthesis,* History, Philosophy and Theory
of the Life Sciences 8, DOI 10.1007/978-94-017-9582-1_2

difficulties. The highly critical attitude held by several plant physiologists in view of this methodology provides evidence for the fact that the chemists' strategies were deeply embedded in a specific research context and community that complied to conventions which were far from universally accepted.

2.1 The Nineteenth-Century Conception of Photosynthesis

"The leaves and other green parts of a plant absorb carbonic acid, and emit an equal volume of oxygen", the German organic chemist Justus Liebig, a towering figure at the time, maintained in 1842.[3] He thereby captured one of the central features of photosynthesis that had been generally known since the work of Joseph Priestley and others in the eighteenth century: the gas exchange that took place in the green parts of plants. Liebig went on to explain in some detail how the assimilated carbon then might be used in the plant to synthesise a wide range of compounds, primarily, he thought, carbohydrates. The latter was confirmed in the early 1860s by the German plant physiologist Julius Sachs, who identified starch—a polysaccharide—as the first distinctly recognisable product of photosynthesis.[4] It was also clear that sunlight was related to this process: in 1845, the German physician Julius R. Mayer described the plant as a reservoir of "solar force", which the plant absorbs and then transforms into a different type of force that Mayer called "chemical potential" ("*chemische Differenz*"). The latter would then be used, Mayer suggested, in the plant's growth and metabolism.[5] The resulting, widespread notion of photosynthesis—or "carbon assimilation", as it was usually referred to at the time—was extremely stable, up to the late 1920s.[6] A characteristic formulation is provided in the following lines, which were published in an encyclopedia for the German educated middle class of 1907:

> Assimilation in the botanical sense of the word is the formation of carbohydrates from carbonic acid and water while oxygen is released. This process is limited to the chlorophyllous assimilation system (assimilation tissue) and requires the involvement of sunlight.[7]

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[3] Liebig (1842, p. 24). In 1845, Liebig was ennobled and, henceforth, became known as Justus *von* Liebig. Further literature on Liebig will be cited below, when his specific photosynthesis model is being discussed.

[4] See Sachs (1862, 1864) for the original papers; the most informative biographical work on Sachs still is Pringsheim (1932).

[5] See Mayer (1845, particularly pp. 37–42). On Mayer's contribution to the discussion of physical forces ("*Kräfte*"), see Caneva (1993); Smith (2003).

[6] See, for example, the definition in the textbook by Heinrich Schroeder in 1928: "Carbonic acid assimilation (photoenergetic assimilation) [...] is the specific ability of the chlorophyllous plant to reductively synthesise organic compounds—in the first step carbohydrates—from carbonic acid (carbon dioxide and water) by using radiant energy, while, at the same time, releasing oxygen". Schroeder (1928, p. 653); paragraph 1a. All translations into English, if not otherwise declared, are by the author (K.N.). See also Gest (2002) for a brief history of the term "photosynthesis" and its definitions.

[7] Anonymous (1907a).

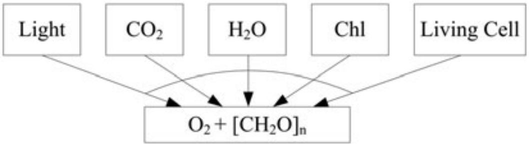

Fig. 2.1 The elementary one-step model of photosynthesis: the basic consensus on the causal factors of the overall process from the mid-nineteenth century until the beginning of the twentieth century.

Carbon dioxide (mostly taken to enter the reaction in the form of carbonic acid) and water, absorbed from the atmosphere and the soil, were taken as the starting materials of the process, which, in the green cells of plants, were then converted, under the influence of light, into carbohydrates and oxygen. From the work of Henri Dutrochet, Julius Sachs and others, chlorophyll pigments were known to play a crucial role in this process, although the precise character of this role was highly disputed.[8] Equally disputed was the reason for the fact that photosynthesis stopped as soon as the cell was damaged; the "living cell", or some specific aspect of it (usually suspected to be either some part of the protoplasm or a structural component), also seemed to be a necessary factor.

This (rather limited) body of knowledge on the mechanism of photosynthesis can be conceived of as a simplistic, one-step model, which is visualised in graph form in Fig. 2.1.[9] Molecular oxygen and carbohydrates, the general chemical formula of which is $[CH_2O]_n$, were taken to be the effects of a process in which carbon dioxide and water, light, chlorophyll ("Chl" in the figure) and the "living cell" acted as causally relevant factors—yet, how these factors interacted with each other was highly debated. Given the complexity of the process, everybody knew that, of course, a great many different steps were required to reach the final stage of photosynthesis, passing through a wide range of intermediate compounds. Photosynthesis researchers agreed neither on the order of the processes involved nor on the question as to which of these processes were light driven and which were not. Yet, everyone was aware that, in whatever way the more complex model would be drawn up, the basic causal links that are represented in the basic one-step model had to be accounted for some way or another. This made it the starting point for all investigations of the photosynthetic process in the period under study and, therefore, also for the subject of this chapter.

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[8] Dutrochet (1837); Sachs (1864).

[9] This notation is largely in line with the wide-spread conventions of representing causal graphs; see, e.g., Pearl (2000); Baumgartner and Graßhoff (2004). However, in contrast to the more rigid use of this notation, in this book no metaphysical commitment is implied concerning the factors included in these graphs. Specifically, while causal graphs usually name "events" as relata of the causal links, the adequacy of this interpretation for representing biochemical mechanisms, which rather outline the interaction of concrete entities, is doubtful.

2.2 Finding the Chemical Mechanism

The community that accepted this limited knowledge of photosynthesis as a common denominator is not easy to define. Already in the nineteenth century, photosynthesis research spread over a range of different disciplines, as was observed in one of the first monographs on the subject matter, published in 1925. The author, Walter Stiles, maintained that "the processes taking place in the green leaf, which involve the absorption of carbon dioxide from the air and the manufacture of carbohydrates from it and the water supplied by the soil [. . .] are among the very few problems of botany which have attracted the attention of workers in other fields".[10] The methods of research taken to be necessary to make any progress at all in elucidating photosynthesis included microscopical anatomy, experimental physiology as well as analytical and theoretical chemistry.[11] This range of techniques corresponded to the range of very different aspects of the process to be considered. The structural prerequisites of photosynthesis, for instance, were studied by plant anatomists and morphologists, who tried to explore the close relationship between the morphology of the leaf and its functional requirements;[12] others investigated the development, organisation and distribution of chloroplasts in the green organs of plants.[13] Plant physiologists concentrated on the influences of several macro-parameters on the process, such as light intensity, temperature and carbon dioxide concentration; while the effects that the incident illumination had on the pigments were mainly explored by physicists, who were interested in the mechanism of light absorption and the chemical efficiency of rays.[14] The question of the (bio)chemical mechanism of photosynthesis, finally, was predominantly, if not exclusively, the domain of chemists; and this is the aspect of photosynthesis research that I shall focus upon in the following sections.

It was primarily a number of German nineteenth-century chemists who felt attracted to the problem of the photosynthetic mechanism and who tried to elucidate as far as possible the course of events by which in the leaves of plants carbon dioxide (in its dissolved condition, that is, as carbonic acid) was worked with water into sugar.[15] From the point of view of chemistry, there were two key questions to be answered in this search for the pathway of photosynthesis: (1) How was carbon dioxide, a highly stable compound, reduced? This question was closely related to the release of oxygen, as reduction still was mostly conceived of as oxygen disposal. However, the second question immediately followed: (2) How were the one-carbon units that

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[10] Stiles (1925, p. 1).

[11] Cf. Reinke (1882, pp. 290–291).

[12] See, e.g., Haberlandt (1881, 1884).

[13] See, von Mohl (1837) for a seminal contribution along these lines.

[14] These early photochemical studies were greatly inspired by the new technique of photography; see, e.g., Boberlin (1993).

[15] On the development of physiological chemistry, or: chemical physiology, in Germany and elsewhere, see Höxtermann (2007b); Holmes (1985); Kohler (1982); Fruton (1972a). On the general situation of chemistry in Germany around 1900, see Johnson (1990).

(presumably) resulted from the carbon dioxide reduction joined together to form large molecules such as sugars?

Above all, it was the first question that puzzled the chemists, as carbon dioxide was one of the most chemically inert molecules known to exist: How could this molecule be made to undergo complex reactions without exposing it to extremely high temperatures or atmospheric pressure? In the following sections of this chapter, the main approaches developed by the nineteenth-century chemists involved in photosynthesis research will be described in terms of background, content, evidence and their relationship to each other. Although some of these approaches are well-known—notably Adolf von Baeyer's formaldehyde model—no in-depth comparative analysis has yet been undertaken, so that some detail is required in order to understand the dynamics of this line of research.[16]

2.2.1 Justus Liebig and the Organic Acid Model

It was the aforementioned Justus Liebig who first put forward a possible pathway for the process of photosynthesis.[17] Liebig started to think about this theme around 1840, that is, when he began to consider the impact of chemical knowledge to problems within the domain of life processes: an interest that was at least partly stimulated by the increasing demand at the time in Germany to improve the foundations of agriculture.[18] One of the first results of this line of thinking was the highly influential book *Chemistry in its Applications to Agriculture and Physiology* (1840), which was translated almost immediately in several languages and went through numerous editions.[19] Therein, Liebig emphatically propagated that it was high time to integrate chemical methods and concepts into the study of plants and their internal functioning, among others: his method of studying metabolic changes in terms of input–output balances.[20]

Liebig found the investigation of plants as it was practiced (or so he thought) by his colleagues in the botany departments deeply unsatisfying: "In botany the talent and labour of inquirers has been wholly spent in the examination of form and structure: chemistry and physics have not been allowed to sit in council upon the

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[16] See, e.g., Florkin (1977, pp. 147–151), for a discussion of Baeyer's formaldehyde hypothesis. The latter is also treated in Rabinowitch (1945, pp. 255–260), in which Baeyer's approach is compared with Liebig's point of view.

[17] For Liebig's biography, see Brock (1997).

[18] Cf. Allen (1975, pp. 154–157). On Liebig and his influence on agricultural science, see also Rossiter (1975).

[19] The original German version was published as Liebig (1840).

[20] On the integration of chemical and physical methods and concepts into botanical research during the nineteenth century see, e.g., the contributions to Hoppe (1997b) and Janko and Strbánová (1991).

explanation of the most simple processes"[21] Liebig complained. Yet, the botanists were unable to solve the central issues of inquiry, Liebig went on, because they lacked the skills to perform the necessary experiments, "it being an art which can be learned accurately only in the chemical laboratory".[22] Liebig's arrogance in this matter, in combination with his far-reaching ignorance of the actual state of plant physiology at the time (he seems to have taken his knowledge of the field from one single textbook), did not go unnoticed, as is documented in the reactions by, for example, the renowned plant physiologist Matthias J. Schleiden, who was never shy of polemics, and the equally distinguished Hugo von Mohl.[23] If Liebig chastised the plant physiologists for their lack of knowledge in chemistry, Hugo von Mohl wrote, Liebig's lack of knowledge of plants and their organisation surely would have to be considered equally disadvantageous. Mohl was ready to admit that the study of plants, insofar as it was of an experimental nature, was "more in the sphere of the chemist than of the botanist". However, Liebig's own suggestion to solve the pertinent problems presented "splendid evidence for the proposition that chemistry has not yet found out much more than nothing at all about the chemical processes in the interior of plants".[24]

In fact, Liebig's plea for experimental research in physiology and his pride on the chemists' achievements in this respect should not be overrated. Liebig was able to quantitatively determine what the plants took in and what they gave off; yet, like everybody else in the field, he lacked the techniques to investigate the processes that went on within the organism. Liebig nevertheless developed a proposal, which was first brought forward in a publication of 1843, while he repeated the principal idea in a number of other places, among those, several editions of his own chemistry textbook.[25] (A slightly simplified reconstruction of Liebig's model, in the form of a graph, is given in Fig. 2.2) This is how Liebig introduced his suggestion:

> If one considers that unripe fruit, for example, grapes, cannot be enjoyed due to their high acid content; that in sunlight these fruits behave in the same way as leaves, namely, that they are capable of absorbing carbonic acid and releasing oxygen; that at the same time as the acids decrease, the sugars increase: in view of these points, one cannot reject the idea that the carbon of the organic acids in unripe fruit becomes part of the sugars in ripe fruit; that, therefore, the acid is transformed into sugar, effected by the release of oxygen and the components' absorption of water.[26]

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[21] Cited: 2nd edition, Liebig (1842, pp. 37–38).

[22] Liebig (1842, pp. 39–40).

[23] See Werner and Holmes (2002) for a detailed analysis of this controversy; Werner (2001) describes how Alexander von Humboldt tried to resolve the disagreement.

[24] Cited Werner and Holmes (2002, pp. 436–438). Mohl's defence was published as von Mohl (1843).

[25] For the first version, see Liebig (1843); see also Florkin (1977, p. 147); Stiles (1925, p. 194); Schroeder (1917, pp. 2–3), and Rabinowitch (1945, p. 255).

[26] Liebig (1843, pp. 61–62).

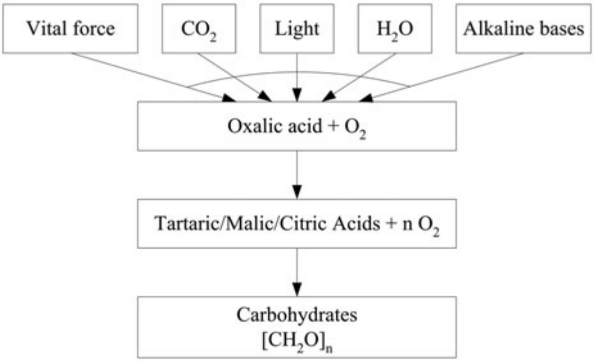

Fig. 2.2 The different processes involved in photosynthesis according to the organic acid hypothesis, which was originally proposed by Liebig (1843). The precise sequence of organic acids was unclear.

Starting from the observation that fruits gradually sweeten as they ripen, Liebig surmised that the tartaric, citric, malic, etc. acids in fruits might be the intermediates on the pathway from carbonic acid to sugar. And since all these acids were usually found in leaves in the form of their ions combined with the ions of alkalis, such as potassium or calcium, to a salt, Liebig concluded that these alkalis played a crucial role in the process too. (He took this to be the reason for the fact that plants would not grow without a minimal amount of these alkaline substances being available, either in the natural soil itself or added in the form of artificial fertilisers).

Liebig's account of the actual sequence of acids in the pathway of photosynthesis was rather vague, although he suggested that initially oxalic acid might be produced from carbonic acid by the release of oxygen—given the presence of an alkaline base, light and some hypothetical vital force. The latter was his interpretation of the unspecified "living cell" factor that was mentioned earlier, since the vital force was thought to fade away when the living organism was damaged or destroyed.[27] Liebig thought that, in later stages, oxalic acid might be reduced to tartaric, malic or citric acid, from which carbohydrates were then formed, thereby releasing additional oxygen. Thus, Liebig postulated a stepwise path from carbonic acid to carbohydrates via compounds that became increasingly poor in oxygen and rich in hydrogen. Some empirical support was taken from the fact that, in the presence of alkali and at high temperatures, the decomposition of oxalic, tartaric and citric acids to carbon dioxide had been observed in the test tube by the French chemist J. L. Gay-Lussac; and in view of this finding, Liebig considered it entirely feasible that the reverse reaction could take place in plant cells.[28] (Note that this assumption of reversibility was, at the time,

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[27] See Schroeder (1917, p. 2). Although, in many instances, Liebig rejected the practice of using a vital force as an explanatory factor, he still acknowledged that there were some phenomena that could not be explained without this force. On Liebig's position between reductionism and vitalism, see Lipman (1967) or Hall (1980). See also Caneva (1993) on this point.

[28] Liebig (1843, p. 63).

only supported by the observation that there were some inorganic reactions, notably in the context of metal combustion, that were found to work in both directions, while very little was known about the behaviour of organic compounds).

Liebig was also rather cautious when it came to describing how this sequence of reaction in plants might be brought about. He skipped the questions of possible sources of hydrogen or of the potential roles for chlorophyll and light in the process, and he did not even touch upon the problem of how carbohydrates might be formed from the organic acids. Liebig had never been afraid of formulating sweeping hypotheses on the course of metabolism without going into any much detail.[29] Yet despite the lack of detail, the principal idea of Liebig's model—that organic acids were the intermediates in the gradual reduction of carbon dioxide to carbohydrates—was still being debated in the 1920s, even though both the vital force and alkalis had by then been abandoned as relevant factors of the process. The main points in favour of Liebig's model were: *first*, that it was, in fact, possible to construct a stoichiometrically plausible pathway from carbon dioxide to carbohydrates through the stages of various organic acids; and, *second*, that this approach provided an explanation for the fact that organic acids were found in surprising abundance in all parts of the plant, while nobody had been able, up to then, to identify their physiological function.[30]

2.2.2 Adolf von Baeyer and the Formaldehyde Model

One could hardly say that Liebig's proposal aroused either passionate interest or decisive rejection among his contemporaries. In fact, it was only in 1870 that a serious alternative was being advanced by the German organic chemist Adolf von Baeyer. In essence, Baeyer's model comprised the assumption that the first reduction product of photosynthetic assimilation was formaldehyde: a small (and highly noxious) organic molecule, which resulted, Baeyer surmised, from the photolysis of carbon dioxide in the presence of water, light and chlorophyll, while at the same time oxygen was released. As we shall see in later chapters of this book, even far into the 1930s, parts of this hypothesis were still counted among the most promising candidates for a photosynthesis model.[31]

It is worth taking a quick look at Baeyer's general preoccupations at this time.[32] He is, of course, particularly renowned for his research on the plant dye indigo: Baeyer

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[29] See Werner (2001). Werner and Holmes (2002) provides an analysis of the dispute between Liebig and Matthias Schleiden and Hugo von Mohl on this point.

[30] Many of these acids are central intermediates of cellular respiration, namely, of the citric acid cycle, as is well-known today. As Liebig rejected the thought that there was respiration in plants, this explanation was not even conceptually available to him.

[31] See on Baeyer's model and its broad reception also Nickelsen and Graßhoff (2011).

[32] See Baeyer (1905) for his autobiography. Further information on his life and work is provided by Klemm (1953) and in Baeyer (1966).

successfully synthesised this important dye in the test tube in 1880, and by 1883 he had completely elucidated the molecule's structure. (Baeyer was awarded the 1905 Nobel Prize in Chemistry, in part because of these achievements.) However, around 1870, Baeyer was also interested in condensation reactions, and he achieved a major breakthrough in 1872 when he succeeded in carrying out the poly-condensation of phenol and formaldehyde. Formaldehyde had been discovered in 1855 by the Russian chemist Alexander M. Butlerov and had since become a product of central interest in the field of organic chemistry. Baeyer based his photosynthesis model on empirical evidence that Butlerov had presented in 1861: on heating trioxymethylene (a condensation product of formaldehyde which today is known as 1,3,5-trioxane) in an alkaline medium, a viscous fluid was produced, which seemed to have some of the properties of sugar.[33] Baeyer took this as the starting point for his proposal of how carbohydrates were synthesised in living plants. In a short paper devoted not even entirely to the problem of carbon assimilation Baeyer made the following argument:

> The general assumption in regard to the formation of sugar and related bodies in the plant is that, under the action of light, carbon dioxide is gradually reduced in the green parts [of a plant] and by subsequent synthesis is converted into sugar. [. . .] Butlerov's discovery provides the key [to the alternative assumption that sugar is formed directly from carbon dioxide], and it is indeed surprising that it has up to now been so little utilised by plant physiologists.
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> The similarity that exists between the blood pigment and the chlorophyll has often been referred to; it is also probable that chlorophyll as well as haemoglobin binds carbon monoxide. Now, when sunlight strikes the chlorophyll, which is surrounded by CO_2, the carbon dioxide appears to undergo the same dissociation as at higher temperatures: oxygen escapes and carbon monoxide remains bound to the chlorophyll. The simplest reduction of carbon monoxide is to the aldehyde of formic acid—it only needs to take up hydrogen, $CO + H_2 = COH_2$. Under the influence of the contents of the cells, as well as through the alkalines, this aldehyde is then converted into sugar. [. . .] Glycerol could, in addition, be formed by the condensation of three molecules and the subsequent reduction of the thus formed glyceric aldehyde.[34]

According to this proposal, the carbon reduction in photosynthesis consisted of several processes, which are reconstructed in Fig. 2.3. First, carbon dioxide binds to the chlorophyll, which is shown as [Chl–CO_2] in the figure; in this state and under the influence of light the carbon dioxide is reduced to carbon monoxide, upon which oxygen escapes. Baeyer justified the assumption of this step by referring to the structural similarity between chlorophyll and haemoglobin: since the latter was known to bind carbon dioxide, it was reasonable to assume, he thought, that chlorophyll could do so as well. The carbon monoxide is then reduced further to formaldehyde by the bonding of either molecular hydrogen or two atoms of hydrogen from other sources (which were not specified). Thus, in contrast to the conceptualisation of the

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[33] See Butlerov (1861). The episode is also discussed in Stiles (1925, p. 194); Florkin (1977, p. 147); and Rabinowitch (1945, p. 255).

[34] Quoted in Stiles (1925, p. 194); also in Florkin (1977, pp. 147–148). Translation provided by Jörgensen and Stiles (1917), with minor changes introduced by the author, K.N. For the German original, see Baeyer (1870, pp. 67–68).

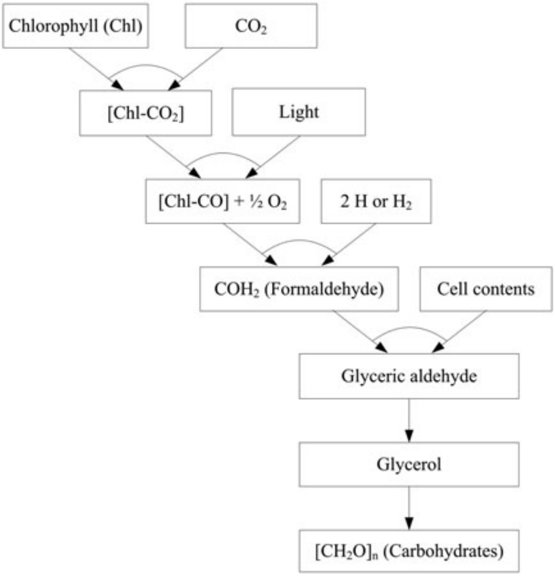

Fig. 2.3 The processes involved in photosynthesis according to Baeyer's formaldehyde model (1870).

process in the organic acid hypothesis, the actual reduction of carbon dioxide to the oxidation state of sugars (which was instantiated in formaldehyde) was assumed by Baeyer to occur without the formation of any intermediates. In subsequent reactions, the formaldehyde was then thought to produce carbohydrates—a process that was presumably promoted somehow by the contents of the cell. Baeyer hypothesised, for example, that the first sugar product might still be associated with the components of the cell, and that it would only later be released as sucrose, starch or cellulose.[35] However, before Baeyer presented his own point of view, he dismissed the organic acid hypothesis:

> The intermediate steps [of the gradual reduction process] have been sought in the organic acids—formic acid, oxalic acid, tartaric acid, etc.—which can be regarded as the reduction products of carbon dioxide. According to this opinion, at those times when the green parts of the plant are most strongly subjected to the action of the sun's rays, a strong accumulation of acids should take place, and these should then gradually give way to sugar. As far as I know, this has never been observed, and when it is remembered that in the plant sugars and their anhydrides are found under all circumstances, whereas the presence of acids varies according to the type of plant, the particular part and its age, then the opinion already often put forward, that the sugar is formed directly from the carbon dioxide, increases in probability.[36]

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[35] Baeyer (1870, p. 68).

[36] Quoted in Stiles (1925, p. 194); also in Florkin (1977, pp. 147–148). Translation provided by Jörgensen and Stiles (1917). For the original German text, see Baeyer (1870, pp. 67–68).

Hence, Baeyer's main objection to the organic acid hypothesis was that one of its (conjectured) empirical consequences, namely the accumulation of intermediate products at times of strong photosynthetic action, had, as yet, not been observed. Furthermore, Baeyer pointed out that the acid content of a plant was strongly dependent on parameters that were probably not connected to photosynthesis—such as the species, the part of the plant, the time of year, and so on—which did not tie in with the assumption that these acids were the intermediates of the general photosynthesis pathway. At the same time, Baeyer stressed that he was able to propose a much easier and more direct pathway than Liebig had done: "Indeed, it would be difficult to attain the goal so easily through a gradual synthesis following the other theory!"[37] As a matter of fact, his proposal does seem pretty straightforward if one writes it down as a formula:

$$\begin{aligned}&CO + 2\,H \longrightarrow COH_2 \;(= \text{formaldehyde})\\ &n\,[COH_2] \longrightarrow [CH_2O]_n \;(= \text{carbohydrates})\end{aligned}$$

Put into prose: if carbon monoxide is formed, you only need to add two atoms of hydrogen to arrive at formaldehyde. The latter is already very close to the basic unit of carbohydrates (which is $[CH_2O]$), so that in order to form carbohydrates the formaldehyde only needs to be slightly rearranged and its units multiplied (in condensation reactions); and finally the resulting glyceric aldehyde would be transformed into a sugar—although Baeyer never explicitly discussed this additional complication. In fact, after this short contribution, barely fleshed out on a couple of pages, Baeyer never again returned to the subject matter.

2.2.3 Testing and Modification

While the reception of Liebig's model had been rather lukewarm, Baeyer's contribution undoubtedly sparked off a lively discussion. Over the decades between the two proposals the audience for the theme had dramatically multiplied: physiological (and agricultural) chemistry, or biochemistry as it was later called, had become a field of growing interest.[38] In 1861, the first independent institute of physiological chemistry had been founded in Tübingen, Germany, headed by Felix Hoppe-Seyler, who, in 1877, had started the first journal of the field, the *Zeitschrift für physiologische Chemie*. In the first issue Hoppe-Seyler confidently stated that "biochemistry [...] has grown to a science that has not only placed itself on a par with biophysics, but in activity and success competes with it for rank".[39] The importance of metabolic

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[37] Baeyer (1870, p. 68).

[38] On the uneasy relation between "pure" and "applied" chemistry (such as, e.g., agricultural and animal chemistry) in the decades around 1900, see Johnson (1990, pp. 25–27).

[39] Quoted in Fruton (1972a, p. 8). On the history of metabolism studies in the early twentieth century, see Holmes (1986). An exemplary reconstruction of the roots of (plant) biochemistry in botanical research is given in Höxtermann and Sucker (1989).

studies was increasingly recognised, and slowly research themes also beyond the processes of digestion, respiration and fermentation, which had been the first to attract the chemists' interest, were being investigated. Owing to these developments, also the processes of photosynthesis received more attention. It was more and more considered a question not only of scientific interest but also of economic importance: first, in view of its value for the fields of agriculture and horticulture but, second, also in view of the fact that a pathway might emerge that enabled scientists to artificially synthesise sugar. Thus, interest in elucidating the photosynthetic mechanism was high, and Baeyer's suggestion was followed by a period of intense investigation that put the models to the test.

However, while Liebig's organic acid model continued to be debated—scientists tried to find out more about the conversion of one acid into another, about the function of acids in plants and about a possible pathway of carbohydrate formation—many of his contemporaries came to regard Baeyer's model as the most promising proposal to explain carbohydrate synthesis, inside and outside the living plant. This was due to the fact that, under certain conditions, formaldehyde was repeatedly found to be formed in artificial systems that contained carbon dioxide, water, and sometimes chlorophyll—among these instances were, for example, the reduction of carbon dioxide caused by magnesium or by silent electric discharge.[40] The conditions in question were usually very different from those predominant in the plant; most of the time, they were, in fact, extremely unfavourable for any life-sustaining process to occur. Yet, the results still seemed to endorse the assumption that there was, in principle, a pathway from carbon dioxide to formaldehyde. This was complemented by findings which demonstrated the occurrence of the second step: the formation of sugars from formaldehyde.[41] The final triumph came when, in 1890, one of Baeyer's former students, the German organic chemist Emil Fischer, succeeded in demonstrating that formaldehyde was, indeed, a possible starting point for the synthesis of the two hexoses, which were thought to be among the major products of photosynthesis (*d*-glucose and *d*-fructose). At the same time Fischer demonstrated that glyceric aldehyde, the possible importance of which Baeyer had already hypothesised, and glycolic aldehyde, which can also be derived from formaldehyde, were potential intermediates.[42] In view of these findings, even the eminent German plant physiologist Wilhelm Pfeffer, who was the author of the standard plant physiology textbook of the time, admitted that the formaldehyde model of photosynthesis was "very appealing".[43]

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[40] See, e.g., Fenton (1907) (magnesium); Löb (1906) (electric discharge). Among the most influential contenders of these findings are, e.g., Spoehr (1913); Warner (1914); Ewart (1915); Spoehr (1916); Spoehr and McGee (1923).

[41] See, e.g., Loew (1886, 1887, 1888, 1889); Fischer (1888, 1890a); Fischer and Passmore (1889); Euler and Euler (1906a, b) and particular Nef (1910, 1913).

[42] See Fischer (1890b, c). For further discussion of these achievements see also Schroeder (1917, p. 20, pp. 59–60 and p. 67). Fischer was deeply influenced by his teacher's work and explicitly related his study of sugar synthesis to Baeyer's formaldehyde hypothesis. Fischer himself later summarised his achievements in this field, see Fischer (1909, p. 22).

[43] See Pfeffer (1897, p. 339); Pfeffer used the attribute *"sehr ansprechend"*.

Nevertheless, at the same time various aspects of Baeyer's model were being challenged and several modifications were put forward. The possibility of a direct reduction of carbonic acid was discussed; methane was surmised to be an intermediate product between carbon monoxide and formaldehyde; and very soon it was suggested that hydrogen peroxide was also formed in the process, although it was supposed to be immediately removed by the action of the enzyme catalase.[44] Some scientists thought that the reduction of carbonic acid was brought about by hydrogen, either from the decomposition of organic compounds or from a splitting of water by light action.[45] Thus, while many chemists thought Baeyer's idea that carbohydrates were formed through the condensation of formaldehyde was a promising approach, they were not so convinced by Baeyer's assumption that the reduction of the carbon moiety occurred in one single step. They preferred to look for other solutions—possibly incorporating a Liebig-like mechanism via organic acids. Thus, a significant number of scientists started looking for variants that recombined what were considered to be the respective strengths of the alternatives: a highly interesting move in a situation that, according to traditional philosophy of science, would have called for the application of some rational criterion of theory choice.

Figure 2.4 tries to capture schematically the situation up to this point in terms of the goals pursued and the actions undertaken.[46] The chemists' part in the attempt to elucidate the processes of photosynthesis was to find the biochemical pathway (or mechanism), from the raw materials to the end products. The two main problems have already been mentioned: The reduction of carbon dioxide and the synthesis of carbohydrates from the reduced one-carbon units. The two first alternatives, developed by Liebig and Baeyer, were attempts to provide a solution to these problems, which were vigorously debated in the last third of the nineteenth century. Liebig thought that the carbon was reduced gradually in a process that consisted of a number of small steps and which assumed that carbohydrates were formed via organic acids (alternative A in the figure); while 30 years later Baeyer proposed that the reduction occurred in one single step and that carbohydrates were formed via formaldehyde (alternative B). These two alternatives then were being tested and, if considered appropriate, modified. However, at the same time a new goal emerged that required the scientists to combine the strengths of the alternative options, hence, to find a model that included: (1) a path in which carbon dioxide was reduced via organic acids to formaldehyde; and (2) the synthesis of carbohydrates from formaldehyde. In the following decades, a number of suggestions were put forward that tried to meet these criteria, four of which received particular attention at the time and are discussed in

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[44] See, e.g., Reinke (1881a, b) (for the direct reduction mechanism); Maquenne (1882) (methane); Bach (1893) (hydrogen peroxide); Usher and Priestley (1906b) and Usher & Priestley (1906a) (catalase).

[45] See, e.g., Pollacci (1902a, b) and Stoklasa and Zdobnicky (1911) (hydrogen from organic compounds); Löb (1906) and Kimpflin (1908) (hydrogen from the splitting of water).

[46] Arrows leading from one level to the other denote the order of hierarchy; potential relevant influences from bottom to top have been neglected for the moment.

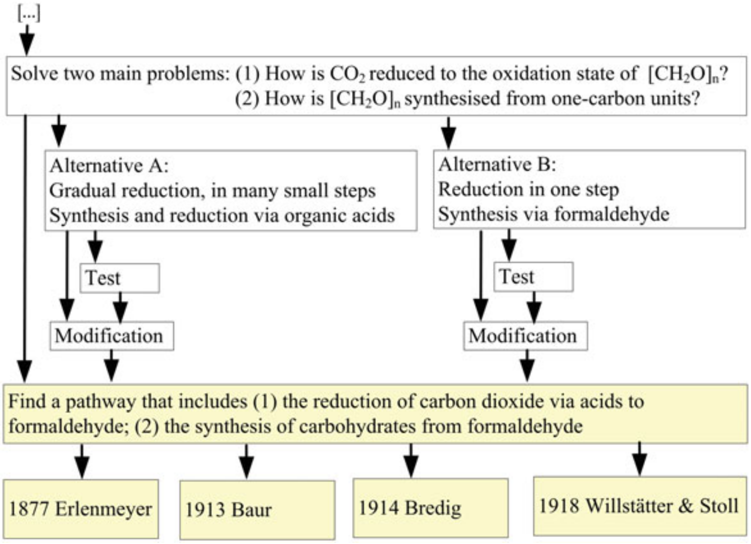

Fig. 2.4 The chemists' goal after 1870: find a model that preserves the strengths, but not the weaknesses, of the two pioneering suggestions by Liebig and Baeyer.

more detail in the following sections: these are the formic acid model, proposed in 1877 by Emil Erlenmeyer; the organic acid-formaldehyde model, advanced in 1913 by Emil Baur; the water cleavage model proposed by Georg Bredig in 1914 and the chlorophyll complex model of 1918, developed by Richard Willstätter and Arthur Stoll.[47] This list of well-known names, which includes the most eminent chemists of the time, makes it clear that the elucidation of photosynthesis had developed into a problem that was being taken seriously, and that many of the period's best chemists were intent on solving it.

2.2.4 The Formaldehyde Problem

However, before the four hybrid suggestions are presented, it may be helpful to clarify the status of these models and their evidence. Photosynthesis researchers of later periods—up to today—have been rather quick to dismiss the nineteenth-century approaches as being based on nothing but speculation. The formaldehyde model, in particular, suffered not only from a lack of positive evidence but also from a wealth of

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[47] The titles of these models were not used in the discussion on photosynthesis research in the nineteenth century but dubbed only in Stiles (1925).

negative findings: despite almost innumerable attempts, with the most refined techniques, nobody was able to detect substantial amounts of formaldehyde in the green parts of plants. Not only were the ashes of plants meticulously scrutinised; scientists also attempted to “feed” plants with formaldehyde via the atmosphere or an aqueous medium. But neither approach conclusively demonstrated that formaldehyde occurred in plants or detect that supply of formaldehyde had a stimulating effect on photosynthesis—every positive finding was countered by an equally convincing rejection.[48] Yet, the principal idea that photosynthetic carbohydrate formation went through the stage of formaldehyde remained part of the standard account of photosynthesis for the next decades—it was taken for granted as late as 1938.[49]

It may be tempting to assign the reluctance to drop the formaldehyde model either to psychological immobility or to reverence of Baeyer’s authority on part of the scientists of succeeding generations. However, this seems very implausible in view of the fact that the crowd of supporters included scientists such as Emil Fischer, Emil Erlenmeyer and Richard Willstätter, none of whom one would reasonably attest a lack of critical thinking or scientific originality. The problem rather lies in the very nature of the model, which can be conceived of as a complex causal hypothesis. A typical test of hypotheses on causal relevance is an experiment designed along John S. Mill’s experimental methods, in particular the “method of difference”, in a more elaborate version also known as “difference tests”.[50] This method requires to look at differences in two situations: one in which a factor is realised, the causal relevance of which is under investigation; and another in which this factor is absent, while all other relevant circumstances are kept the same. If now the effect only emerges in the situation in which the test factor was present, one can conclude that it was causally relevant for the effect to be brought about.[51] A slightly modified variant of this method was Mill’s method of “concomitant variation”: effects that were brought about by some key factor of the environment were expected to intensify if the latter factor was present to a higher degree. The various “feeding experiments” attempted by many nineteenth-century chemists were set-up precisely along these lines: given the fact that formaldehyde was thought to be a key intermediate in photosynthetic assimilation, one could investigate whether the rate of photosynthesis changed, when

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[48] Experimenters who record the identification of formaldehyde in green leaves after illumination include Pollacci (1902a, b); Grafe (1906); Kimpflin (1907); Pollacci (1907); Gibson (1908), Angelico and Catalano (1913); Chodat and Schweizer (1915). Schroeder (1917) provides a forceful rejection of these findings: he argued that they were either obtained by using flawed methodology or, at the very least, in themselves inconclusive. This perspective finds support by Mazé (1920); Rouge (1924) and Sachs (1862).

[49] Cf. Manning (1938, p. 272).

[50] See on Mill’s methods and their application in nineteenth century science, e.g., Scholl (2013).

[51] See on this method of experimental design Graßhoff et al. (2000); Baumgartner and Graßhoff (2004); Weber (2005, 2012); Graßhoff (2011). On the condition of homogeneity given in the two situations, see also Hofman and Baumgartner (2011).

an additional supply of formaldehyde was provided.[52] What was found was that without formaldehyde, the rate of photosynthesis remained normal, which was not surprising; yet, even with a surplus of formaldehyde the rate did not change.

An allegedly obvious conclusion from this experiment would be that formaldehyde had no relevant influence on the rate of photosynthesis and the formaldehyde hypothesis ought to be dropped. However, this would have been a fallacy. It is one of the uncomfortable features of causal reasoning that it is impossible to conclusively infer the *causal irrelevance* of any factor.[53] If the result of an experiment is negative—in the sense that the situations with or without the testing factor do not differ in outcome—then the following conclusions are possible: (1) formaldehyde is, indeed, causally irrelevant; (2) the detection method is flawed or inappropriate; (3) formaldehyde is causally relevant but was unable to exert its influence, because at least one necessary cofactor was not realised in the test situation. From this follows that even if all the aspects of the experimentation were carefully designed, set-up and carried out, one could not conclude from an indifferent result, not even from a consistently indifferent one, that the respective test factor was irrelevant. This explains why the (few) pieces of positive evidence were considered so much more important. Notably Fischer's in vitro experiments of 1890 seemed to provide good reason to believe in the existence of a pathway from carbon dioxide to carbohydrates via formaldehyde. At the same time, of course, chemists felt the need to account for their failure to either detect the alleged key intermediate or demonstrate its relevance. Thus, it was soon agreed among nineteenth-century chemists that formaldehyde was, most probably, processed very swiftly by plants: too swiftly to be captured by the chemists' crude methods. This was made even more plausible by the fact that formaldehyde was such a strong cell poison; surely, plants would have developed mechanisms to prevent it from freely floating about.[54] The Swiss chemist Walter Löb even suggested that formaldehyde was perhaps never actually released as such; he surmised instead that the formaldehyde's constituents (C, OH_2) immediately condensed to sugar.[55]

2.3 Reconciling the First Approaches

While these attempts to account for the formaldehyde problem left many questions open, the majority of chemists still chose to include the formaldehyde pathway into their model suggestions, albeit in a modified version and contextualised in a different

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[52] This general approach was practised by Baker (1913); Boitreux (1920); Grafe and Vieser (1909, 1911); Jacoby (1919, 1922); Moore and Webster (1913); Sachs (1862).

[53] See Nickelsen and Graßhoff (2011) for more details.

[54] See Schroeder (1917, pp. 8–12). Manning (1938, p. 122) underlined this point, stating that, even if photosynthesis was running at a maximum rate, formaldehyde "concentrations higher than a few hundredths of a per cent are distinctly toxic".

[55] Löb (1906).

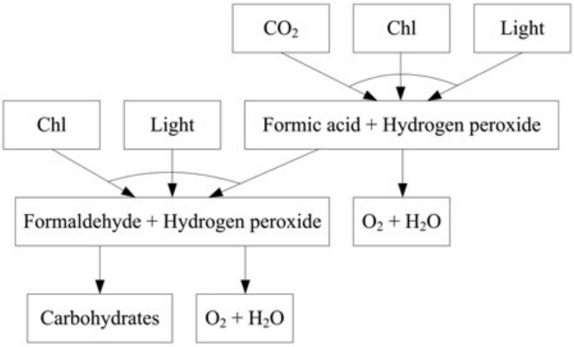

Fig. 2.5 The processes involved in photosynthesis according to the formic acid hypothesis, which was proposed by Erlenmeyer (1877).

manner. The aim of the following sections is to introduce the four most important attempts to reconcile the approaches to the photosynthesis mechanism put forward by Liebig and Baeyer.

2.3.1 The Formic Acid Model

One of the attempts to integrate the advantages of the earlier models by Liebig and Baeyer, while at the same trying to avoid their shortcomings, was the assumption that the first reduction product was formic acid, which scientists believed could be further reduced to formaldehyde—the supposed precursor of carbohydrate formation. The earliest proponent of this point of view was the German chemist Emil Erlenmeyer. He suggested, in 1877, that, in the process of photosynthesis, carbonic acid was first reduced to formic acid; this would yield hydrogen peroxide as a by-product, which would then be immediately decomposed into water and molecular oxygen.[56] A graphical reconstruction is given in Fig. 2.5. This proposal was mainly based on experiments that Erlenmeyer had carried out with glycolic and lactic acids: both these acids were readily decomposed following the pattern described above, so that Erlenmeyer believed he could postulate that carbonic acid reacted in the same way (although he had not been able to test it in the laboratory). As Erlenmeyer wrote, he was convinced that, in view of the ready decomposition of hydrogen peroxide, this path was the most obvious way to explain the liberation of free oxygen in photosynthesis. In subsequent steps, Erlenmeyer assumed that formic acid would, under the influence of light and chlorophyll, be further reduced to formaldehyde and then polymerise to form carbohydrates.[57] (Unfortunately, along with formaldehyde,

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[56] Erlenmeyer (1877).

[57] Erlenmeyer (1877, p. 634).

the presence of formic acid and hydrogen peroxide was also never detected in the green parts of plants to any substantial extent.[58])

2.3.2 The Organic Acid–Formaldehyde Hypothesis

An alternative hybrid model that tried to combine the advantages of Liebig's and Baeyer's approaches was proposed in 1913 by the Swiss physical chemist Emil Baur.[59] A graphical reconstruction is given in Fig. 2.6. In line with Liebig's hypothesis, Baur argued that it was highly improbable that the reduction of carbon dioxide or, rather, carbonic acid, was accomplished in one single step, as Baeyer had postulated. Considering the respective oxidation states of the carbon atom, Baur thought that several potential intermediates might be formed on the path from carbon dioxide to carbohydrates; and since chemical processes almost always include the formation of intermediates, as Baur pointed out, he preferred to assume that they did, in fact, occur.[60]

Baur was convinced that oxalic acid was the first product of photosynthesis, and that it was produced after the carbon dioxide had interacted with the pigment, which then absorbed and utilised the light energy—two different processes, neither of which Baur discussed in any detail.[61] In the later stages of the gradual reduction of carbonic acid, which, most probably, involved the formation of glycolic and formic acids, oxygen would be released. And, although Baur found it highly improbable that formaldehyde was the first reduction product, he nevertheless believed that the final stage of photosynthesis in which carbohydrates are formed was reached via formaldehyde.

2.3.3 The Water Cleavage Model

A third hybrid variant was proposed by the German physical chemist Georg Bredig in 1914,[62] while this suggestion was subsequently supported and elaborated by the (less prominent) chemists Karl August Hofmann and Karl Schumpelt.[63] A reconstruction

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[58] See Stiles (1925, p. 199).

[59] Emil Baur is not to be confused with the German geneticist *Erwin* Baur, who was one of the three co-authors of a notorious German textbook of genetics and race hygiene in the 1920s.

[60] See Baur (1913, p. 474). To substantiate this point, Baur also cited H. Euler, *Pflanzenchemie*, 1909, 3rd part, p. 183 and 266; as well as his own monograph, *Cosmografia Chimica*, Milan, 1908, p. 207.

[61] Baur (1913, p. 475).

[62] Bredig (1914b); see also Bredig (1914a) and Bredig (1915). See also Czapek (1913), p. 524, for a review of this theory in the standard plant physiology textbook of the time.

[63] See Hofmann and Schumpelt (1916).

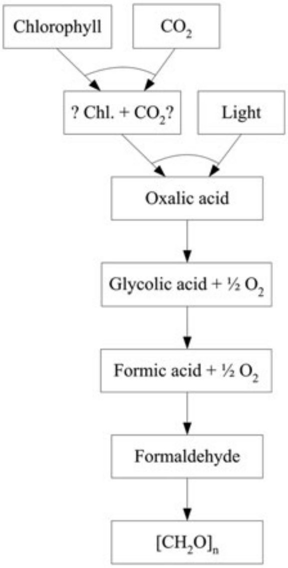

Fig. 2.6 The processes involved in photosynthesis according to the organic acid hypothesis, which was advanced by Baur (1913).

is given in Fig. 2.7. In line with Erlenmeyer, Bredig proposed that formic acid was the first product to be formed, which was supported, he believed, by his recent finding that, under moderate pressure, the salts of formic acid were produced from the salts of carbonic acid in the presence of a surface-providing catalyst, such as palladium. This also tallied with his earlier discovery that, under the influence of surface-providing catalysts, hydrogen was removed from organic substances and transferred to other molecules.

Bredig suggested that in nature the catalytic function could be ascribed to the chlorophyll, while the hydrogen came from water cleavage: it had been observed, after all, that, under the influence of ultraviolet light, water decomposed into an explosive mixture of molecular oxygen and hydrogen (oxyhydrogen gas, in German called *Knallgas*, i.e. detonating gas). In plants, the catalysing agent took the hydrogen from the decomposition of water and used it in the reduction of carbonic acid, whereby oxygen was released. Thus, Bredig was one of the few scientists of these decades to address explicitly the question of the origin of the reducing hydrogen equivalents; and he was one of the few scientists at the time to consider water as a possible source of hydrogen and, at the same time, oxygen. (Walter Löb and some other contemporary chemists also cautiously held this view, which turned out to be correct.) However, Bredig admitted that water might be replaced as the source of hydrogen in plants by other substances that would remove the hydrogen under the influence of sunlight.

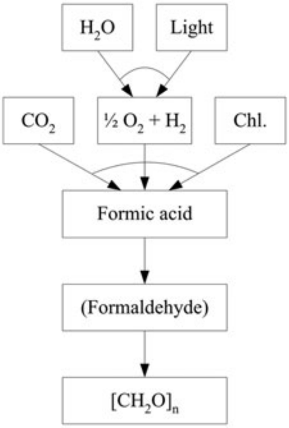

Fig. 2.7 The processes involved in photosynthesis according to the water-cleavage hypothesis, which was proposed by Bredig (1914) and Hofmann and Schumpelt (1916). While Bredig doubted the role of formaldehyde, it was reinserted by his successors; therefore the factor is put in *brackets*.

Bredig seriously doubted the validity of the formaldehyde hypothesis: apart from the fact that there was no convincing evidence that formaldehyde occurred in green plants, he pointed out that "the formaldehyde, in any event, is the one reduction product of carbonic acid, the production of which would require *the highest energy input* by light; and for this reason alone it is not very likely that nature should have chosen this detour".[64] Yet, no alternative explanation was given by Bredig to account for the subsequent stages from formic acid to carbohydrates—so that Hofmann and Schumpelt tried to amend this gap by the suggestion that formic acid was further reduced to formaldehyde (even without the presence of hydrogen peroxide), which then served as a starting point for the synthesis of carbohydrates following the well-known sequence.

2.3.4 The Chlorophyll Complex Model

The last model that should be presented in this context is the sophisticated suggestion advanced by Richard Willstätter and Arthur Stoll, which emerged as a result of their comprehensive 1918 monograph on the role of chlorophyll in photosynthetic assimilation.[65] A reconstruction of this model is given in Fig. 2.8. From their experimental findings, Willstätter and Stoll concluded that, once carbon dioxide had found its way into the plant's green cells, the first stage of photosynthesis consisted of a dissociable

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[64] Bredig (1914b, p. 363); emphasis in the original.

[65] Willstätter and Stoll (1918).

binding of the gas to unknown, organic constituents of the plant cell, presumably plant proteins or amino acids. It was by this means that the concentration of carbon dioxide within the plant cells was thought to increase, so that photosynthesis operated more efficiently. (After all, the concentration of carbon dioxide in the air is rather low.) Willstätter and Stoll surmised that the carbon dioxide was probably chemically altered in the course of these events, converted either into carbonic acid or into one of the latter's derivatives. The product of this absorption process, which was considered to be a purely chemical, light-independent process, is symbolised in the figure as the (CO_2*–Cell complex), where the asterisk indicates that the original carbon dioxide was added to this complex in a modified form. Willstätter and Stoll believed that the modified carbon compound was then passed to the chlorophyll. From their experimental findings, they postulated that an additive compound of the bicarbonate type was formed by chlorophyll and either carbonic acid or one of its derivatives. This intermediate substance is symbolised in the figure as [Chl–CO_2**], indicating that the original carbon dioxide had undergone a second conversion. The actual photochemical step of the process was believed to be the chemical rearrangement of the carbonic moiety of this intermediate, additive product into an isomer, which was higher in energy and was then reduced in the process that followed (indicated in the figure as [Chl–CO_2***]). Willstätter and Stoll assumed that this product was a kind of peroxide, most probably formylhydroperoxide.

It was thought that the further decomposition and reduction of this compound was effected by an enzyme, which Willstätter and Stoll assumed was the mysterious "living cell" factor (see above). They surmised that, in the course of this catalysed reduction process, oxygen was released and formaldehyde synthesised, and that subsequently carbohydrates were produced via condensation reactions: we have seen this pattern in most of the models discussed so far. However, Willstätter and Stoll found it highly probable that no intermediate product was released before the reduction process of the carbon had been completed, so that the stages of this reduction process were very hard to establish. In Fig. 2.8, the result of these reactions is, therefore, symbolised only vaguely by the expression [Chl + 'C' + O_2], which is the last intermediate before the final carbohydrate stage $[CH_2O]_n$ is reached.

In contrast to the other scientists mentioned so far, Willstätter and Stoll considered chlorophyll to be the central factor in the whole process of photosynthesis: in addition to its capacity to absorb light and make it chemically available, chlorophyll was also assumed to be the actual *site* of carbon reduction, which involved the formation of an intermediate additive compound. The action of light was thought to be effective only in interaction with this additive compound; that is, the light did not act on the chlorophyll, as one might assume, but on the carbonic moiety, which was thereby converted into one of its isomers. This differed sharply from the widely held view at the time that chlorophyll only acted as a sensitiser in photosynthesis, in that it transformed rays of shorter wavelengths into more efficient rays of longer

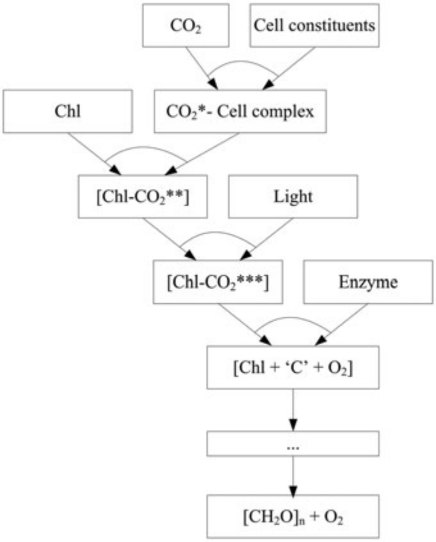

Fig. 2.8 The processes involved in photosynthesis as conceptualised by Willstätter and Stoll (1918).

wavelengths—although it was unclear which effects these rays would then bring about.[66]

2.4 Features Common to the Models

The previous sections had the purpose to introduce the range of models that were under debate by 1918. Despite their divergences in terms of content, all these models shared a number of structural features. The aim of the following sections is, therefore, to spell out these common features, reflect on the type of mechanism that was being suggested and the evidence that was invoked. This will provide us with a reasonable basis from which then the chemists' strategies and methodology of model building in this period will be discussed.

2.4.1 Simplicity and Simplification

The most obvious feature that all the photosynthesis models had in common was their simplicity: none of them included more than a very limited number of factors and

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[66] See, e.g., Czapek (1913, p. 614), for a review and emphatic endorsement of the "sensitiser" position.

reaction steps. The conscious simplification of the process to be explained is a typical, well-known and even indispensable aspect of the construction of scientific models.[67] In the case of photosynthesis, it is striking, for instance, that almost all the scientists limited their choice of "root" factors, that is, the raw materials but also the chlorophyll and other preconditions, to those of the previously discussed one-step model. There were only two exceptions: *first*, Liebig, who postulated the involvement of the vital force and of some alkaline bases, both of which were immediately dropped by his successors; *second*, Willstätter and Stoll, who believed that an unknown enzyme was an additional root factor, which, they assumed, catalysed the final reduction steps. Along with the root factors, the actors also limited the range of end products under consideration—these were taken to be quite definite, as one could read in a review of 1916 by the plant physiologists Ingvar Jörgensen and Walter Stiles: "The substances which are known to be produced as a result of carbon assimilation are oxygen and carbohydrates".[68] It is remarkable that hardly anyone played with the option that some of the many other compounds which by then were known to be synthesised in plants came out of photosynthesis. The widespread argument for this restriction was that the "assimilatory coefficient" of plants, that is, the quotient of carbon dioxide absorbed and oxygen released, in most cases approached unity, which corresponded well to the assumption that only molecular oxygen and carbohydrates were produced. The formation of, for example, proteins or fats would have favoured different coefficient values. However, one could have constructed scenarios that might have included the formation of a mixture of substances, which would still have produced an assimilatory coefficient of unity. It seems that for those parts of the process that were reasonably established even the chemists were inclined not to introduce additional speculations. (As we shall see in later sections, they were far less scrupulous when it came to the modelling of intermediate stages of the process).

In addition to the selection of factors also the number of reaction steps was minimised to the extreme; this holds true even for the most sophisticated variant by Willstätter and Stoll. And, finally, all the chemists in this chapter shared the implicit assumption that the same mechanism of photosynthesis operated in all species of higher plants. None of the actors mentioned above considered the possibility that in the leaves of trees, for example, the process of photosynthesis might differ from the process of photosynthesis in the leaves of grass. In his widely read textbook on photosynthesis of 1917, also the plant physiologist Heinrich Schroeder believed that one

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[67] This has been underlined in many accounts of models and model building heuristics, such as Bailer Jones (2009) or Frigg and Hartmann (2012), although the latter rather speaks of "idealization", which partly, but not fully coincides with the "simplification" in our case.

[68] Jörgensen and Stiles (1916a, p. 186). One may want to add, however, that a wide range of different carbohydrates was considered as potential photosynthetic products, including polysaccharides, disaccharides, hexoses and pentoses; see, e.g., the synopsis given in the cited review. The authors also maintained: "We do not wish it to be supposed that we [. . .] support the view that glucose is the first sugar of carbon assimilation. We hold that the data so far produced from analyses of carbohydrates in leaves and from microchemical examination provide insufficient evidence in favour of or against either theory".

could safely assume that the same mechanism was valid for all higher plants, because "given the same raw materials (CO_2 und H_2O), the same products are found, while the circumstances as well as other resources of the transformation are also the same".[69] Given the many morphological and physiological differences that were known to distinguish different species of plants from each other this declaration of like circumstances was not entirely beyond doubt. (In fact, as it turned out much later, in the 1960s, the assumption was inaccurate: grasses do have a different photosynthesis mechanism).

Resorting to assumptions like these, however, was inevitable. The mechanism of photosynthesis was so complicated that none of the scientists working around 1900 could possibly have hoped to achieve more than a rudimentary understanding of it. (Although they unquestioningly shared the principal assumption that there was a linear, decomposable pathway to be elucidated.[70]) In view of this situation, they seemed to have agreed that it was inadvisable to make things even more difficult by taking into consideration more factors than was absolutely necessary, not to mention possible detours of the pathway or variants in different plant species. Methodologically speaking, the chemists (and even most plant physiologists) shared the working hypothesis that photosynthesis acted as a mechanism of the same type in all higher plants; thus, if the causal relationships were established in one instance, the same should be true of all others. "Construction assumptions" of this type, as I would suggest to call them, were an essential part of the modelling process: for the sake of constructing the model, the chemists assumed that the process had certain properties, even if they knew, or strongly suspected, that this was not actually the case (which certainly was true for the number of reactions steps involved). Whether these assumptions were deemed permissible or not, however, was dependent on the context—in the aforementioned, plant physiological review of 1916 by Jörgensen and Stiles, for instance, the authors expressed their astonishment that most of the chemists so easily restricted the range of internal factors to the plant's chlorophyll: recent findings in plant physiology had demonstrated, they thought, that there were significant influences connected with the properties of the cell and their structural environment that deserved closer inspection.[71] The contrast between the different communities will become even more conspicuous in a later section of this chapter, when I turn to the heuristic strategies that chemists utilised in their work.

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[69] Schroeder (1917, p. 58).

[70] See Bechtel (1986a) on the underlying conception of metabolism, which was the dominant view up to the 1930s.

[71] Jörgensen and Stiles (1916a, p. 176).

2.4.2 Incomplete Empirical Support

The second common feature of the chemical models that I wish to highlight is the fact that all the photosynthesis models were dramatically underdetermined by empirical data. In stark contrast to the conservative attitude towards introducing new root and end factors to their models of the mechanism, the chemists in the period under study apparently did not mind postulating completely new *intermediate* factors. This is true, for example, not only of all the assumptions about the products of the gradual or immediate reduction of carbon dioxide but also of the formation of a complex made of chlorophyll and either carbon dioxide (Baeyer) or an unknown derivative of carbonic acid (Willstätter and Stoll). None of the actors seemed too concerned about invoking either unheard-of reaction mechanisms or the occurrence of reverse reactions the existence of which was yet unknown. Still, none of these models was discarded on the grounds of incomplete experimental foundation—at least not by their chemical colleagues; while the plant physiologist Hermann Spoehr sarcastically commented this situation in a review, when he wrote: "It can safely be said at the outset that, when critically considered from a physiological view point, none of the existing theories [on the mechanism of photosynthesis] is even moderately well established by observations of facts".[72]

Take the formaldehyde model as an example. Baeyer's assumption that carbon dioxide formed a complex binding with chlorophyll was exclusively based on the observation that chlorophyll was structurally similar to haemoglobin; and since the latter was known to bind carbon dioxide, the former was assumed to do the same. All inherent differences were silently considered irrelevant. On the other hand, the hypothesis that formaldehyde was formed in living leaves and that the formaldehyde molecules subsequently combined to larger units was based on the observation of an artificial system, that dramatically differed from the conditions in real plants. Likewise, the evidence for the formic acid hypothesis was solely based on the observation of test tube experiments, which were then transferred, by Erlenmeyer and others, to specific life processes. This type of reasoning was omnipresent: the chemists tended to back up their models with evidence that had been taken from observations outside the organism.[73] Even Willstätter and Stoll who actually measured the gas exchanges of living material used empirical data that were unrelated to their physiological observations when it came down to the mechanism. Again, this was a practice which appears to have been perfectly acceptable among the chemists, but was sharply criticised by plant physiologists: "So long as our knowledge of the heterogeneous system in which these [processes] take place is so incomplete, it is impossible to draw conclusions from experiments in which the conditions are clearly so different", Jörgensen and Stiles underlined in their review.[74]

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[72] Spoehr (1916, p. 2).

[73] The in vitro vs. in vivo debate has vexed biochemistry ever since. See Jacob (2002) for a philosophical perspective on this point.

[74] Jörgensen and Stiles (1916b, pp. 79–80).

2.4.3 Selected Focus and Modules

Closely related to the principle of simplicity is the third observation which I would like to draw attention to: all the chemical models, to a greater or lesser extent, were inherently inconsistent in their level of detail and explanatory scope. All of them treated at length one specific aspect or one particular process of photosynthesis, while other, equally relevant, sequences of events were merely summarised or even totally ignored. Take, for instance, Liebig's model. The key feature was the assumption that the formation of carbohydrates occurred through the formation of organic acids that became increasingly poor in oxygen and rich in hydrogen. Liebig failed, however, to explain how these acids were thought to be then converted into carbohydrates. This neither implies that he considered this reaction step unimportant, nor that he thought that this step had been adequately treated in the model. The synthesis of carbohydrates simply lay outside Liebig's focus of investigation. Baeyer's focus was the introduction of formaldehyde as the central intermediate on the path of carbon from carbon dioxide to carbohydrates. He also hypothesised about the complex of chlorophyll and carbon monoxide, yet remained silent on all the details. Willstätter and Stoll concentrated on the first stages of photosynthesis, which involved the function of chlorophyll, although when it came to the actual carbon reduction they vaguely postulated that some intermediate substance, which was peroxide in nature, was formed, and that it would eventually pass through the stage of formaldehyde and polymerise, as in Baeyer's model.

To some extent, incompleteness is a consequence of simplification: if one chooses to model only those aspects of a problem that are considered of central importance, one will inevitably present an incomplete account of the whole—yet, from this perspective one would expect the same level of simplification for all parts of the mechanism, while simplification alone does not explain the fact that selected aspects were treated in considerably more detail. Additionally, one might argue that different models frequently are constructed to cover one and the same phenomenon in view of different aspects of the phenomenon and different explanatory functions of the model. This is well-known to have happened in physics quite regularly, for example, in the case of the wave–particle dualism, when more than one model was found to be necessary to cover the different aspects of the phenomenon.[75] However, in the case of photosynthesis the function and intended scope of the models were fairly similar to each other, yet the scientists still presented widely divergent accounts. It is significant in this context that the chosen focus of research corresponded so closely to the authors' general knowledge and skills: Willstätter and Stoll, for example, were experts in the field of chlorophyll research, while they had only a limited knowledge of the chemistry of carbohydrates. I shall come back to this observation in a later section of this chapter.

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[75] See on this case Wheaton (1983). Daniela Bailer-Jones coined the term "*Aspekthaftigkeit*" ("aspectivity") for this wide-spread feature of models; Bailer-Jones (2009).

2.5 Model-Building Heuristics

In summing up the observations made so far, it would seem that the process of modelling the mechanism of photosynthesis had taken a quite peculiar path: even the most promising models dealt with a highly simplified notion of photosynthesis; all the models were strikingly incomplete and focused on selected aspects only; and, finally, none of the available models was more than partially supported by empirical evidence, while even the available data were mostly gathered from artificial systems, which had little in common with the living plant. It is easy to understand that these deficiencies were sharply criticised by plant physiologists. However, within the group of chemists that form the focus of this chapter these procedures seem to have been part of the generally accepted practice. In the following sections I shall try to extract from the available evidence some of the principles of model-building heuristics that nineteenth-century chemists in search of a photosynthetic mechanism applied.

2.5.1 Extending a Prototype

At the beginning of the chapter, I gave an outline of the body of generally accepted knowledge of photosynthesis. The standard raw materials and end products of the process had been well established by earlier generations of scientists and were never seriously questioned—this is why I referred to this early, phenomenological description of the process as the "prototype model", although as such it was never defended by one particular person. One then could interpret the photosynthesis models introduced in this chapter as extensions and modifications of this first model into different directions.[76] This does include local condensation of model suggestions, as, for instance, the dropping of the vital force and the alkalis as factors from Liebig's model. Baur's version, for example, at the same time extended Liebig's proposal (by adding the synthesis of carbohydrates via formaldehyde) and modified it (by introducing a different sequence of acids). The important observation here is that the modelling always took off from existing knowledge that served as a starting point.[77] Yet, according to which lines of reasoning was this prototype extended? Given the fact that the actual empirical knowledge was scant, owing to a lack of appropriate methods, other criteria and strategies had to be followed. One of the most important among them was the transfer of (mostly: causal) knowledge from one subject to another, which the following section is concerned with.

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[76] See Graßhoff (1998) for a discussion of how models can be extended, condensed or modified at the example of the modelling of the astrophysical object SS433.

[77] This is a typical procedure for any kind of causal reasoning; see on this point Graßhoff (2011).

2.5.2 The Transfer of Causal Knowledge

"With the development of organic chemistry it was but natural that attempts should have been made to explain the mode of reduction of carbon dioxide and the course of sugar synthesis in the green leaf", the plant physiologist Heinrich Spoehr wrote in his review of 1916. However, in doing so "some have fallen into the error of reasoning, that if they can produce sugar, or the substances closely related to sugar, from carbon dioxide and water, by almost any means, that this is necessarily also the process taking place in the leaf".[78] Spoehr found the chemists' practice to base their photosynthesis models on evidence that emerged in the test tube unacceptable. Yet, data that were gathered from the plants themselves were unavailable: more direct access to the intermediate steps of the process only became possible much later, with the introduction, in the late 1940s, of radioactive tracer molecules in metabolic studies. Thus, one could either drop the theme altogether, that is, stop thinking about the photosynthetic mechanism until more appropriate methods were developed; or try to transfer the established knowledge of biochemical reactions from test-tube situations to the photosynthesis processes in the living organism. The former was the plant physiologists' advice; the latter was what the chemists chose to do.

Take Baeyer's procedures as an example: around 1870 the polycondensation reactions of formaldehyde were the focus of his research; and he knew, from Butlerov's investigation, that, under certain circumstances, a syrup-like substance was a product of this type of reaction. Baeyer knew, too, that carbohydrates were structurally composed of a series of molecular units [CH_2O], which were identical to formaldehyde in terms of atomic composition; and although they differed in their structural arrangement, the conversion of one into the other did not seem too difficult. A similar rationale explains how Baeyer came up with the earlier stages of his model. It was well known at the time that, under certain circumstances and under the influence of strong light, carbon dioxide could be reduced to carbon monoxide. Starting from here, Baeyer then assumed that this carbon monoxide would initially form a complex with chlorophyll. In 1870, nobody knew which complexes chlorophyll was able to form because chlorophyll had proven very elusive and impossible to isolate.[79] Yet it was well-known that chlorophyll was structurally similar to haemoglobin, and that the latter easily bonded carbon monoxide. Thus, Baeyer's complex hypothesis was based on the (chemically speaking: quite reasonable) assumption that molecules which are structurally similar undergo the same chemical reactions. The resulting transfer, in this case, closely resembles Darden's notion of the instantiation of a mechanism scheme.[80]

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[78] See Spoehr (1916, pp. 1–2).

[79] "In the early years of the twentieth century the literature of the pigments of the chloroplast thus showed that knowledge of them was in a very confused state"—this is how the British botanist Walter Stiles characterised the state of affairs in his textbook on photosynthesis of 1925; cf. Stiles (1925, p. 19). Crucial parts of the long-winded history of chlorophyll research are described in Höxtermann (1991).

[80] Darden (2002).

The underlying heuristic assumption in these inferences—from haemoglobin to chlorophyll; from the test tube to the organism; and, as Schroeder explicitly stated: from one plant to another (see quote above)—can be put in a more general form, stating that similar effects under similar circumstances can be taken to be brought about by similar causes and mechanisms. In this form, it is easily recognisable as the content of Sir Isaac Newton's second Rule of Reasoning, which he formulated in his *Principia Mathematica* (1687). (Newton presents his "Rules of Reasoning" at the beginning of the Third Book of the *Principia*. The first rule states: "We are to admit no more causes of natural things than such as are both true and sufficient to explain their appearances"; to which the second rule then adds: "Therefore to the same natural effects we must, as far as possible, assign the same causes". While the first rule defines a minimising approach to the set of factors to consider, the second rule additionally postulates a minimum of explanatory schemata or mechanisms to account for natural phenomena.) Of course, this strategy is fallible; but it has a prolonged and well-established history as a useful heuristic principle. The same assumption that the (unknown) processes inside the organism should operate according to the principles that were known of the processes that occurred outside the organism had governed chemical investigation into life processes since the time of Lavoisier and others, who, for example, conceived of respiration as an ordinary combustion process.[81]

The resulting way of thinking can be categorised as "analogical reasoning", in line with Mary Hesse's classic work on models and analogies: a source system (i.e. processes in the test tube) is explored in order to get to know more about the actual target system (i.e. the organism) which is structurally similar to the source system but might not be accessible to the same degree.[82] Philosophers of science have been quite unenthusiastic about analogies and their epistemic value—not only because they are by necessity uncertain, but also because the term is so vague. However, the "analogical reasoning" in this case can be explicated by framing the situation in terms of the underlying causal reasoning: the chemists' crucial assumption was that the process under study (the reactions steps of the photosynthetic mechanism) fell into the same class of events as other, already well-known processes—that is, for example, the reactions of chlorophyll were taken to be the same as the reactions of the structurally similar haemoglobin. As the relationship of causal relevance in chemistry (and elsewhere) concerns *types* of events and their regularities, and not only individual *tokens*, the grouping together of processes into the same class implies that they are part of the same causal relationships.

Of course, this assumption hinged on the fact that not only input and output but also the conditions in the two cases were sufficiently similar. This was exactly the point most sharply criticised by plant physiologists. The aforementioned Spoehr specified his comment to the chemists' work by emphasising that, in general, they "show a lamentable lack of knowledge of the conditions under which photosynthesis takes

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[81] See Holmes (1985); Underwood (1943).

[82] Cf. Hesse (1963). For a recent treatment of analogical arguments, see, e.g., Gamboa (2008) and, in particular, Bartha (2010).

place, as well as of the physiology and structure of the chlorophyllous cells".[83] In order to make up for this lack of knowledge, but, at the same time, account for these differences, chemists had introduced additional factors for modelling the processes in the cell. Liebig had turned to "vital forces" to explain how photosynthesis operated, while Baeyer assigned a special function, perhaps of a catalytical nature, to the material constituents of the cell. These factors filled the explanatory gap (as did the assumption that water was one of the raw materials), while they did not satisfy the plant physiologists' critique. The latter asked for more than merely the causal factors; they required an explanation that referred to the cell structure and the interaction of several cell components: a *mechanistic* model that went beyond the mere existence of causal links in a chain or network.

2.5.3 The Building Block Strategy

Transferring causal knowledge from one situation to another was, to some extent, connected to a second equally widespread heuristic strategy. When one examines the different photosynthesis models it is clear that, although they diverge, most of them were not completely disparate. Rather, one finds "modules" that reappear in different combinations, such as the "formation of a chlorophyll-carbon dioxide complex", the "reducing of carbon dioxide via organic acids", the "formation of carbohydrates from formaldehyde", and so on. These were frequently interpreted as functional subunits, resulting from the (conceptual) decomposition of the of the mechanism. In the graphical notations they may correspond to one "branch" of the graph (or to one section of a longer branch).

Perhaps the most striking example of this practice is the assumption that carbohydrates were formed through the condensation of formaldehyde, which was integrated into most of the later models. Similarly widespread became the assumption, first formulated by Erlenmeyer, that a formic acid derivative and some peroxidic compounds were involved in the process, the decomposition of which gave rise to the photosynthetic oxygen. This module constantly reappeared in later model suggestions, even though the rest of the models did not resemble Erlenmeyer's original concept in other respects. Willstätter and Stoll, for example, ingeniously recombined this module with the chlorophyll complex and the formaldehyde module, added some causal hypotheses from their own field of expertise, notably the enzyme hypothesis, and thus presented a completely new amalgamation of ideas that had, in fact, been around for decades. I shall refer to this practice as the "building block strategy": the chemists carefully examined their predecessors' results and then integrated into their own work whatever they found useful and acceptable. In this respect, the chemists' procedure resembles In this case, the strategy resembles Lindley Darden's notion of

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[83] See Spoehr (1916, p. 2).

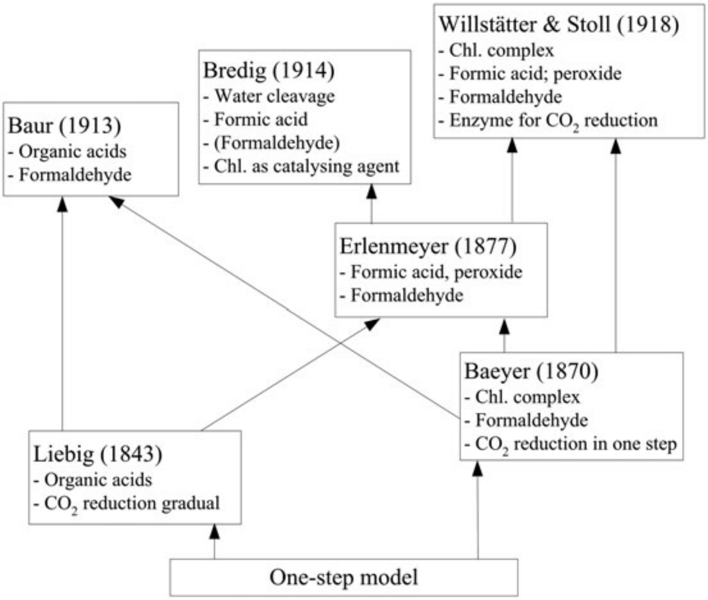

Fig. 2.9 The models and their "building blocks" shown in sequence.

"modular subassembly": one proceeds from known or suspected components of the mechanism under study and tries to rearrange them in a fruitful manner.[84]

Figure 2.9 is a schematic representation of the models discussed in this chapter and shows which modules were reused. The arrows from *x* to *y* denote the relationship "modules of model *x* were integrated into model *y*". The one-step model is taken as the starting point for the two first major alternatives that emerged in the nineteenth century: those proposed by Liebig (1843) and Baeyer (1870). Seven years later, in 1877, came Erlenmeyer's suggestion, which was influenced, on the one hand, by Liebig's proposal of a stepwise carbon reduction via acids (although Erlenmeyer believed that formic acid was the central intermediate, something that Liebig had not mentioned), and on the other hand by Baeyer's suggestion, as Erlenmeyer also included carbohydrate formation via formaldehyde in his model. In 1913, Baur published his proposal, which also attempted to synthesise the different approaches; this was followed in 1914 by the model advanced by Bredig, who, like Erlenmeyer, favoured the path via formic acid (and was rather sceptical about formaldehyde); finally, in 1918 the Willstätter–Stoll model was put forward, which was influenced both by Erlenmeyer's and Baeyer's suggestions particularly the latter's assumption that a complex of chlorophyll and carbon dioxide was formed.

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[84] Cf., e.g., Darden (2002); Darden and Craver (2002).

The building block strategy, as implemented in this case, was, arguably, at the time the most promising way to construct a model of a complex mechanism such as photosynthesis, since no single person was capable of investigating all aspects of the process to satisfactory extent.[85] As the discussion of Otto Warburg's work in chapter 3 demonstrates, the building blocks, or modules, were also taken from very different areas of science, such as photochemistry and quantum physics, which one person alone could not possibly hope to master: using "plug-ins" from other scientists' work was the only viable option. One can interpret this division of labour as a very impersonal form of "cooperation": scientists complemented their own accounts with the achievements of others. One of the advantages of reformulating the chemists' models in the form of graphs is that this aspect model dynamics becomes obvious.

2.5.4 The Principle of Plurality

Figure 2.9 could give the impression that the earlier model variants were replaced by succeeding ones during the course of this chapter's time span. However, this was by no means the case. None of the models represented in the figure was dropped until well into the 1920s—not even Liebig's and Baeyer's earliest, original ideas. After 1918, the model that Willstätter and Stoll proposed was considered by many scientists to be the most promising option—not least, because it successfully integrated a fair portion of the modules under discussion. Yet, it certainly had its weaknesses too,[86] so that none of the concurrent alternatives was completely abandoned. Every now and then selected modules of the earlier models were revived and re-examined so that at any point of time a range of different suggestions were debated. I call this practice the "principle of plurality", which is a typical feature of ongoing modelling processes.

The strategy to keep as many models as possible under investigation (even those that are thought to be less promising than others) is well-founded if one regards the model-building process as a cooperative enterprise of the whole community. The philosopher of science Philip Kitcher explored these situations from a more formal, normative perspective. The question he rose was whether there are "conditions under which, in light of our goals as an epistemic community, we ought to want to maintain cognitive diversity". Kitcher differentiated between personal and impersonal epistemic intentions, which, at times, might be in conflict: under certain conditions it could be rational for someone "to assign herself to the working out of ideas that she (and her colleagues) view as epistemically inferior".[87] Examples that seem to point in this direction include, according to Kitcher, Wegener's suggestion of continental

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[85] Comparable practices were revealed in the construction of botanical illustrations (i.e. representations of species models) around 1800, where elements from earlier images were extensively copied but at the same time modified and adapted to the new context. See Nickelsen (2000, 2006a, b).

[86] A fair number of these were pointedly exposed in Jörgensen and Stiles (1916b, pp. 84–90).

[87] See Kitcher (1990, p. 6 and 8).

drift which, initially, was discarded by the majority of geologists, while, luckily, some individuals continued to advocate and explore it—up to its "revival" in the form of plate tectonics. Hence, Kitcher argued, although the continuous pursuit of Wegener's theory might have been an irrational decision from the point of view of the individual, it turned out for the best from the point of view of the community. However, Kitcher thought that this required the existence of a special type of "altruistically rational agents" in science: "Altruistically rational scientists are those who are prepared to pursue theories that they regard as inferior when, by doing so, they will promote achievement of the goals of their own (and their colleagues') impersonal epistemic intentions". And Kitcher immediately conceded that this "raises an even more bloodless ideal of scientific rationality than that criticised by historians and sociologists of science".[88]

However, in the situation that I sketched earlier, there was no need for any individual scientist to deliberately devote herself to a clearly inferior theoretical approach. Although there were degrees of preference to one or another option, it was impossible to determine conclusively whether carbon reduction was achieved through a series of intermediates, which possibly included organic acids of one kind or another, or whether carbon dioxide was directly converted into formaldehyde or some other compound with the same oxidation state in a complex binding with chlorophyll. Concurrently pursuing alternatives, or, as Kitcher put it, stick to a broad cognitive division of labour, as long as some uncertainty prevailed (which in science is more often the case than not), seemed a reasonable course of action, without assuming any unrealistically high degree of altruism among the chemists. The philosopher of science Miriam Solomon even made a normative postulate of this, claiming that "consensus is not normatively appropriate unless theories show clear and substantial differences in degree of empirical success".[89] Under given circumstances, the plurality of approaches was not only advantageous for the community of photosynthesis research as a whole but also a useful strategy from the perspective of the individual actors: the chemists working in the period under review were struggling to establish causal relationships on the grounds of very insecure data, based on highly fallible assumptions. It was not at all improbable that an outsider module might prove, in the course of time, to be the better horse to bet on (and we know today that the water cleavage hypothesis was exactly of this kind).

It may be helpful to remember that, at the time around 1900, it was not even remotely plausible that any one of the model alternatives under discussion was "accurate" in the full sense of the word. The actors were keenly aware of this situation and repeatedly pointed to the fact that, for the time being, only preliminary hypotheses were brought forward. Willstätter and Stoll's model had some explanatory value, from the chemists' point of view, and explained relevant sets of data with recourse to established chemical knowledge; but it still seemed rather odd to assume that

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[88] Both quotes: Kitcher (1990, p. 9, Footnote 5).

[89] Solomon (1994b, p. 339).

highly poisonous compounds such as peroxides and formaldehyde could be regular intermediates of this fundamental process of life. On the other hand, given the body of knowledge of chemistry at the time, the occurrence of the whole process of photosynthesis appeared highly unlikely, if not virtually impossible: both water and carbon dioxide were known to be extremely stable, inert molecules, so that it was hard to believe that they were able to decompose at all at room temperature. Yet, since the actual existence of photosynthesis could not be disputed, the chemists felt entitled to invoke even improbable mechanisms to explain the process.

2.6 Collective Versus Individual Goals

It was mentioned earlier that each of the models discussed in this chapter had a specific focus: that is, each of them was particularly detailed in some respect, while other parts were treated more superficially. Thus, none of the models was intended to grasp the biochemical pathway of photosynthesis in all its complexity. On closer inspection, these differences in focus can be explained by turning to the chemists' individual interests and skills. It is striking that none of the actors discussed in this chapter studied the process of photosynthesis for any lengthy period of time. Rather, all of them made only a limited contribution to the field, which was frequently presented in one single paper, and they then moved on to other concerns: more precisely, they returned to their original, main, research goals. I will elaborate on this aspect in more detail in this section.

2.6.1 Photosynthesis as a Side Issue

I shall start by taking another look at Liebig. At the time that he formulated his model, Liebig was involved in the general (and rather ambitious) project to explain *all* agricultural processes from a chemical point of view, not only in order to gain fundamental knowledge but also because he had specific applied and utilitarian purposes in mind. Among other things, Liebig was concerned with enhancing crop production and, thus, of ensuring adequate food supplies.[90] This was the context in which Liebig started to think about photosynthesis. From this larger perspective, it is clear that he regarded the task of "explaining photosynthesis" at best as a lower-level goal: if one wanted to enhance crop production, for example, by developing an efficient fertiliser (which was one of Liebig's objectives) or by advising farmers how to grow their plants, it was obviously advantageous to have some knowledge about photosynthesis, the source of all plant growth.

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[90] See Brock (1997, chapter 6).

The motivation behind Baeyer's contribution was briefly mentioned earlier. Around 1870, Baeyer was studying condensation reactions, including the condensation reactions of formaldehyde; and his formaldehyde model of photosynthesis was directly related to this work. Indicative of this relation is also the title of the paper in which the model was published: "On dehydrogenation and its meaning for the life of plants and for fermentation processes".[91] Chemically speaking, the "dehydrogenation" of compounds is one of the effects of those reactions that, following Baeyer's suggestion in the paper, came to be called "condensation reactions". Indeed, Baeyer's famous and influential model of photosynthesis only appeared in this paper to illustrate one of the types of condensation reactions that Baeyer was investigating. Another type of these reactions, according to Baeyer, was central to fermentation processes. Thus, the modelling of photosynthesis was not even one of his subgoals. Rather, Baeyer probably realised that he could make a contribution to photosynthesis research only while he was working on the more general phenomena dealt with in the paper. One may call this an "incidental goal", since it was the by-product of work done while attempting to attain other superordinate goals. Typically, incidental goals of this type are very limited and specific, and can quickly be reached on the basis of immediately available knowledge and skills. Having reached the incidental goals (that is, in the case of Baeyer, having published his thoughts on how the condensation reactions of formaldehyde might help to explain photosynthesis), Baeyer immediately went back to his original work; and even though his photosynthesis model was the subject of protracted discussion, Baeyer himself never again returned to it.

The other cases examined in this chapter were very similar. Erlenmeyer was, around 1877, primarily working on the structural elucidation of organic molecules and on the chemical properties of double and triple bonds. In the one paper of relevance here, photosynthesis was mentioned only in passing, as a possible application of Erlenmeyer's thoughts on "Water as an oxidising and reducing agent" (as the title of the paper reads).[92] In 1913 on the other hand, Baur published a whole series of papers on the topic of photolysis, including the photolysis of formaldehyde. This presumably led him to think about other problems related to photoreactions and formaldehyde, including photosynthesis. As in Baeyer's case, it did not cost Baur much in terms of resources to make a quick contribution to photosynthesis before returning to his original line of research. Bredig, meanwhile, was particularly interested in the effects of surface catalysis, and since he assumed that chlorophyll acted as a surface catalyst (like palladium or platinum), he followed this approach when framing his photosynthesis model. The latter was not an obvious topic of interest for Bredig, who was, after all, a physical chemist. The findings he presented provide some indication as to how he chanced upon the subject: while working on formates (the salts of formic acid), Bredig had found that, under the influence of a catalysing

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[91] Baeyer (1870, p. 64). The original German title of the paper reads: "Über die Wasserentziehung und ihre Bedeutung für das Pflanzenleben und die Gährung".

[92] "Das Wasser als Oxydations- und Reductionsmittel"; see Erlenmeyer (1877).

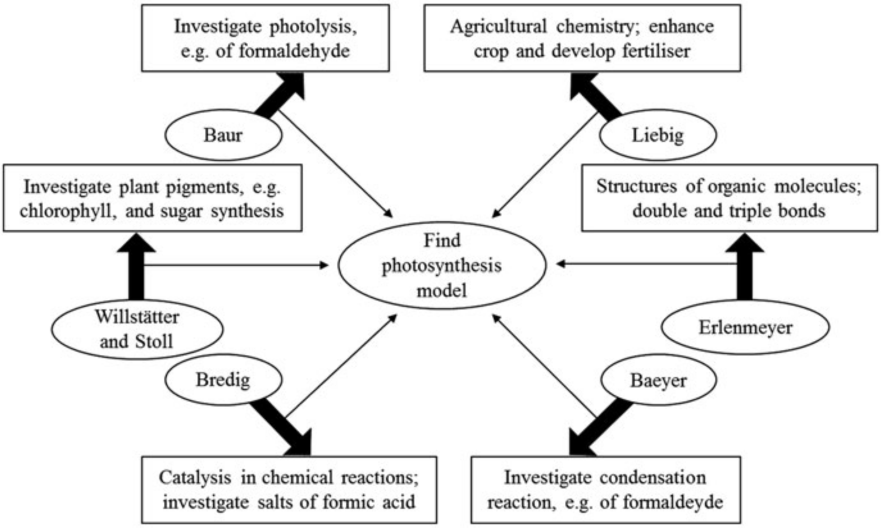

Fig. 2.10 The actors and their goals: diverging individual (superordinate) goals; and the subgoal or incidental goal of finding the photosynthesis model. The *thick arrows in bold* indicate the relationship "*X* pursues the superordinate goal *y*". The *thin arrows* indicate that, in the course of pursuing the superordinate goal, an incidental goal or, less frequently, subgoal (of contributing to finding the photosynthesis model) was reached.

agent, they could be oxidised to the salts of carbonic acid. Thus, an obvious conjecture to make from this was that this reaction might also work in reverse, that is, reduce carbonates to formates, and that this could then be assumed to be one of the processes involved in photosynthesis (Fig. 2.10).[93]

Finally, Willstätter and Stoll had already been working on the chemistry of plant pigments, in particular chlorophyll, for more than ten years when they published their model (they had, for example, established that magnesium was an integral part of chlorophyll and they had been the first to find a practicable method for isolating chlorophyll from plants).[94] It is not too surprising then that this work prompted them to make contributions to the mechanism of photosynthesis—and neither does it come as a surprise that the focus of their model was the role of chlorophyll. Yet, even then, "finding the photosynthesis model" was evidently not their first and primary goal, as the authors made clear in their introduction:

> Even though our experiments may contribute to describing more precisely the processes of [carbon dioxide] assimilation, at the same time they clearly give a negative answer to the question as to whether it is already possible to realise this assimilation outside the living cell. It is too early for experiments of artificial assimilation under the influence of chlorophyll.

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[93] See Bredig (1914a, b, 1915).

[94] See their first monograph: Willstätter and Stoll (1913).

> This is not really a negative conclusion, it is a positive finding that ought to inspire and point the way to new work.[95]

This rather defensive-sounding paragraph (in which the authors appear to be trying hard to raise their spirits in view of their failure) reveals that Willstätter and Stoll's primary goal was to realise artificial photosynthesis: to find a way of reducing carbon dioxide to carbohydrates in a light-driven reaction under the influence of chlorophyll, but without the rest of the plant cell. And it was only in order to reach this goal that Willstätter and Stoll found it necessary first to clarify how the process operated in plants. "Finding the (natural) photosynthesis mechanism" was for them, too, a subgoal in their quest to achieve artificial photosynthesis.

2.6.2 Constructive Research Opportunism

Thus, it seems that the work carried out on photosynthesis by nineteenth-century chemists, as it was presented in this chapter, can be interpreted as a by-product (or spin-off) of the scientists' work on other projects. At some point in their research, Baeyer and Erlenmeyer among others seem to have realised that, based on what they had achieved so far (in other topics), they could easily make a contribution to photosynthesis research. I shall refer to this behavioural pattern in this study, with a slight twist of irony, as the principle (or maxim) of "research opportunism".[96] Despite the term's usual negative connotation (which is by no means intended here) it nicely captures that this maxim is about taking advantage of situations if the opportunity arises. The underlying rationale seemed to be something like: "Contribute to solving an interesting research problem, whenever you can do so without being distracted for too long from the pursuit of your principal goals". The maxim can marvellously be illustrated by an episode remembered by one of the giants of twentieth-century photosynthesis research, William Arnold, whom I shall return to in later chapters of this book:

> In June [1950], Dr Bernard Strehler came to the [Oak Ridge National] Laboratory [in Tennessee]. Strehler had a brand-new Ph.D., a tremendous amount of energy, and lots of ideas about almost everything. One day he appeared in the laboratory door and said, "Arnold, how would you like to make one of the fundamental discoveries in plant physiology?" My answer was: "OK, if it won't take too long".[97]

This collaboration thus started between Arnold and Strehler would contribute to the discovery that adenosine triphosphate (ATP) is synthesised not only in the mitochondria but also in the chloroplast (for details, see Chapter 7). Here as well as in other instances, it seems that scientists are quite willing to make a contribution to an open question if the opportunity arises, even though they might never develop

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[95] Willstätter and Stoll (1918, preface, pp. III–IV).

[96] In this I am following a suggestion by Gerd Graßhoff, given in a personal communication.

[97] See Arnold (1991, p. 79).

more than a passing interest in the pertinent subject. They might provide explanatory approaches, introduce new methods or apply concepts from their actual area of research; but soon afterwards, they often return to their original field.[98] At first glance, Willstätter and Stoll seem to have been exceptions to this rule, since they spent so many years working on questions related to photosynthesis. However, if one looks at their case a little more closely, it is clear that most of the time they studied the structure of chlorophyll and its behaviour in different circumstances. It was only in the final chapter of their second book that Willstätter and Stoll turned to the mechanism of photosynthesis—which they only examined in order to find out how to synthesise sugars in the test tube (see above).[99] The "opportunistic" way of picking research problems also explains why Baeyer never turned to photosynthesis again, even though he left so many problems unsolved; and the same is true of Liebig, Erlenmeyer, Baur, Bredig, Hofmann and Schumpelt. Other eminent scientists who, at the beginning of the twentieth century, made a single contribution to photosynthesis research from their own field of expertise include Emil Fischer (see earlier in the chapter), Felix Hoppe-Seyler, Walther Nernst, Walter Noddack, Jacobus H. van't Hoff and Fritz Weigert. It was not that these men deliberately wanted to hold things back; rather, with the one shot they made they had published all they had to say on photosynthesis. Given the limited resources in terms of research time, infrastructure and money, pursuing an incidental goal is only worthwhile from the actor's perspective if it can be reached quickly and with a minimum of additional effort. This explains why all the contributions discussed in this chapter had so different foci (as was explained earlier) which closely corresponded to the chemists' individual, superordinate goals.

Thus, photosynthesis research around 1900 provides a prime example of research opportunism. Although many people were interested in photosynthesis and contributed some findings to explaining the process, hardly anybody at the time made the subject their centre of interest. As was mentioned earlier, the whole field of chemical metabolism studies was highly problematic at the time, since there were no methods through which one could gather direct information on the course of the pathways. Data were scarce and the interpretations thereof disputed. It would have been highly unreasonable to make a theme in which success was so uncertain the sole focus of one's research. Contributing to the subject in an "opportunistic" manner was the best option, both for the individual scientist, whose costs were limited while the potential gains were high, and for the collective of the chemists as a whole, since this was, after all, a viable option for keeping the topic alive until more adequate methods became available.

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[98] See Graßhoff (1998) for a case study from astrophysics in which he also discusses this phenomenon.

[99] Prompted by findings that Stoll made, however, Willstätter and Stoll both contributed once again to the field around 1932; see Stoll (1932) and Willstätter (1933).

This moment came with the rise of manometry in photosynthesis research after 1920, which fundamentally changed the field. The cumbersome and largely speculative search for potential carbonic intermediates lost its former attraction (although the approach had its comeback in the 1940s, when radioactive tracer molecules became available; remarkably, still then formaldehyde was among the products that chemists tried hard to find). Yet, even though it then became principally possible—and reasonable—to concentrate one's efforts on photosynthesis, which by this time was no longer considered a high-risk field of study with almost no hope of success, the subject remained a side issue in plant physiology (and other disciplines). The set of people that spent their professional lives on photosynthesis studies remained limited. In addition to the specialists, there always remained a substantial number of "opportunistic" contributors, in the sense outlined in this section. It will transpire in the following chapters of this book that both parties played an important role in solving the problem of how photosynthesis worked.