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Graphite Oxide Story – From the Beginning Till the Graphene Hype

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1.1 Introduction

The formation of graphite oxide (GO) was described for the first time by Brodie in a short note that appeared in 1855 in *Annales de Chimie* in French [1]. Another preparation method – the reaction of graphite with potassium chlorate in fuming nitric acid, now known as the “Brodie method” – and a detailed description of the composition and the chemical properties of the new compound were published in 1859 in the *Philosophical Transactions of the Royal Society of London* [2]. One year later this paper was published in both French and German translations [3, 4]. The titles of all these papers [1–4] do not give any hint of a new carbon compound. The title of the English version is as follows: “On the atomic weight of graphite”. The new compound was called “oxyde de graphite” in the first publication, and “graphitic acid” in the later papers. It is also worth mentioning that Brodie himself did not cite his first work on the new compound.

The actual aim of Brodie’s scientific work presented in his publications was to differentiate by means of chemical methods various forms of carbon with dissimilar properties but all called graphite. Among the reactions described in the second paper, there was also the treatment of graphite with a mixture of concentrated nitric and sulfuric acids, leading to the graphite sulfate intercalation compound. The graphite intercalation compound was described for the first time by Schafhäütl [5] (pp. 155–157) in 1840, but it was hidden in two other publications devoted almost exclusively to iron–carbon steels. This might be the reason why Brodie was not aware of this data, and did not cite it. On the other hand, the

content of the first paper had been presented before in the *London and Edinburgh Philosophical Magazine*. In the paper of 1859, Schaffhäutl [6] (pp. 300–301) complained that nobody took notice of his result.

The circumstances of the beginning of the GO story have been outlined *in extenso* because of their curiousness. In 1865 Gottschalk [7] reproduced and confirmed the results of Brodie. In his publication the term “graphitic acid” appeared for the first time in the title: “Beiträge zur Kenntnis der Graphitsäure” (“Contributions to the knowledge of graphitic acid”). GO received greater attention only due to the publication of Berthelot [8] in 1870 in which he proclaimed Brodie’s procedure for the preparation of GO as a method to distinguish different forms of graphitic carbon, although Brodie had already described the different behavior of various graphite forms toward oxidation reactions earlier.

In 1898 Staudenmaier [9] discussed in detail the problems and disadvantages of the various preparation methods existing up to the end of the nineteenth century. He also described his trials to find more convenient and less dangerous preparation methods, and presented the new preparation method which is named after him to the present day.

Of utmost importance is the publication of Kohlschütter and Haenni in 1919 [10]. It marks the end of the classical research on GO, which was based on classical chemical analysis and a careful description of the reaction behavior. On the one hand, it carefully reviews and evaluates all the previous publications on the topic. Based on crystallographic considerations, reproducing the results of Brodie [2] and Weinschenk [11], the authors consider the close structural correlation between graphite and GO as evidence for a “topotactic” relation. This paper presents new data for the formation of GO, its thermal decomposition and chemical reduction, and the products of chemical reduction. Also, in this publication, the authors discarded their own previous pessimistic view that GO could be nothing other than an adsorption of CO and CO₂ at graphite surfaces.

A new period of GO research was opened by Hofmann in 1928 [12] and by Hofmann and Frenzel in 1930 [13] by applying for the first time powder X-ray diffraction (XRD) to GO. Based on these investigations and chemical considerations, Hofmann and his school of researchers gave the first structural model of GO to find general acceptance. This period of research started in 1928, continued through 1930 and 1934 with the first structural models by Thiele [14] and Hofmann *et al.* [15], and ended in 1969 with a new structural model proposed by Scholz and Boehm [16]. During this period, GO structural models were modified several times, mainly due to the debate between Hofmann and Thiele, and due to the application of new spectroscopy methods allowing the proof of assumptions about the functional groups playing a role in the chemistry of GO.

The third period of activity on GO was initiated by the first application of magic angle spinning nuclear magnetic resonance (MAS NMR) on ¹³C by Mermoux *et al.* in 1989–1991 [17, 18]. In the extended publication [18], the authors questioned the structural model of Scholz and Boehm [16] and credited the model of Ruess [19] as the one that best fitted their data. However, later this interpretation was questioned again [20]. The interpretation of the 60 ppm signal as originating from epoxide functions revitalized the first model of Hofmann *et al.* [15], with some modifications [20]. This model has been confirmed in various studies [21], but is now again questioned by a two-component model [22].

Graphite oxide was a laboratory curiosity [23] till the discovery of graphene by Geim and Novoselov [24]. Soon after this discovery, the easy reduction of graphite oxide was considered as a cheap method to obtain graphene layers. This idea started a hype of research

on GO, which has lasted up to now. Looking at many modern publications from a historical perspective, one cannot avoid the impression that many groups have fallen into traps, which previous generations of scientists have learned to circumvent. And, vice versa, reading the previous publications from the actual point of view, one discovers a lot of interesting aspects that have been described with scrutiny, later considered as unimportant, still later forgotten completely, but can now be re-evaluated on the basis of recent research.

The aim of this chapter is to sketch the storylines of various aspects of GO-related studies, which were important for understanding the peculiarities of GO. These topics include GO preparation and purification, the development of structural models, the problem of stability and decomposition, the swelling to a colloid, the acidity of GO, and the ability to intercalate very different chemical species. Some of these aspects have been on the agenda since the discovery of GO, and others came to attention triggered by progress in neighboring fields of research. This chapter is restricted mostly to the historical retrospective of GO studies. *My own thoughts and conclusions from the historical material, colored by my own experience in the field, are written in italic.*

1.2 Preparation of Graphite Oxide

1.2.1 Trials for Improving and Simplifying GO Preparation

In his paper of 1855 Brodie achieved the oxidation of graphite by adding concentrated sulfuric acid to a mixture of graphite and KClO_3 [1]. The subsequent treatment with water led to disintegration of the solid and a strong extension of the volume. Calcination of the dry product resulted in graphite, which was contaminated with sulfates and chlorates. At the end of the short paper, Brodie mentioned as alternative oxidants nitric acid and bichromate.

In his publication of 1859 Brodie described first the treatment of graphite with a mixture of concentrated nitric and sulfuric acids [2]. The product obtained can be assigned in modern terms as the graphite intercalation compound of sulfuric acid, as one can conclude from the described properties of the sample, especially the exfoliation phenomena (observed earlier by Schafhäütl [5, 6]). Then Brodie stresses that replacing nitric acid by potassium chlorate or potassium bichromate leads to a different product that is bright yellow or brown and decomposes easily to a graphite-like material.

The procedure given in this paper for the new compound has been used to the present day and is called “Brodie’s method” [2]:

The details of this process are as follows:—A portion of graphite is intimately mixed with three times its weight of chlorate of potash, and the mixture placed in a retort. A sufficient quantity of the strongest fuming nitric acid is added, to render the whole fluid. The retort is placed in a water-bath, and kept for three or four days at a temperature of 60°C until yellow vapours cease to be evolved. The substance is then thrown into a large quantity of water, and washed by decantation nearly free from acid and salts. It is dried in a water-bath, and the oxidizing operation repeated with the same proportion of nitric acid and of chlorate until no further change is observed: this is usually after the fourth time of oxidation. The substance is ultimately dried, first in vacuo, and then at 100°C . A modification of the process which may be advantageously adopted, consist in placing the substance with the oxidizing mixture in flasks exposed to sunlight. Under these circumstances the change takes place more rapidly, and without the application of heat.

The note at the end of this paragraph, that sunlight can favor the formation of GO, sounds very interesting, but seems to have been overlooked up to now.

From that time there were many trials to replace the used reagents (fuming nitric acid, concentrated sulfuric acid and potassium chlorate) by less dangerous and more convenient oxidizing reagents. Staudenmaier [9] and Kohlschütter and Haenni [10] mention explicitly the dangerous reaction of chlorate with concentrated sulfuric acid leading to ClO_2 , which decomposes at temperature above 45°C in explosions. *Is that fact the reason why Brodie did not mention this procedure in his second paper?*

Luzi [25] and later Charpy [26] applied KMnO_4 and HCrO_4 (“acide chromique”) in sulfuric acid, both mentioning the tendency to decompose graphite (see section 1.1.2). Kohlschütter and Haenni [10] mentioned unsuccessful trials of oxidation with persulfuric acid, Caro’s acid and ozone. Boehm *et al.* [27] studied Ce(IV) nitrate, Co(III) sulfate, NaOCl , $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and OsO_4 . Hofmann and Frenzel [13] and later Boehm *et al.* [27] obtained GO by the reaction of graphite suspended in a mixture of concentrated nitric and sulfuric acids with gaseous ClO_2 . Boehm *et al.* [27] also obtained GO by oxidation of graphite suspended in concentrated sulfuric acid with Mn_2O_7 and by reaction of a suspension of graphite in fuming nitric acid with an O_2/O_3 mixture for 10 days.

Despite these efforts, at the present day only two further methods are of importance, the procedures described by Staudenmaier [9] and Hummers and Offeman [28], respectively.

Staudenmaier [9] used (as Luzi [25] did) exfoliated (“aufgeblähten”) graphite, adding it to the mixture of concentrated nitric and sulfuric acids when the mixture was cooled to room temperature after mixing. He mentioned explicitly that the oxidation is faster the faster the KClO_3 has been added, but more KClO_3 is then necessary because of the temperature increase leading to stronger decomposition of the chlorate. Whereas he used up to 25 g of graphite for one procedure, he never observed an explosion. The green product obtained after washing and drying can then be transferred to the yellow product by a reaction with a solution of potassium permanganate in diluted sulfuric acid. *Interestingly, Staudenmaier commented on the procedure used by Luzi, but did not mention Luzi’s trials with permanganate.*

Kohlschütter and Haenni [10], Hofmann and Frenzel [13] and Hamdi [29] used the “Staudenmaier method”, but with some modifications, as follows. Instead of exfoliated graphite, they used powdered graphite; hence, the reaction afforded longer reaction times. At least three oxidation cycles were necessary to get a reasonable degree of oxidation. The oxidation with permanganate solution was dropped without giving an explicit reason. Hofmann and Frenzel [13] and Hamdi [29] also found the process hazardous.

Hummers and Offeman [28] for the first time successfully applied permanganate as an oxidant for the formation of GO: powdered graphite flakes and solid sodium nitrate were suspended in concentrated sulfuric acid and then the permanganate added in portions, so that the temperature can be kept below 20°C . Then the temperature of the suspension was brought to 35°C , and kept at that temperature for 30 minutes. The now pasty suspension was then diluted by adding water, causing a temperature increase up to 98°C . After 15 minutes the mixture was diluted with more water and the residual permanganate reduced with hydrogen peroxide.

Boehm and Scholz [30] discussed for the first time the drawbacks and advantages of the three preparation methods for GO. *(Almost no attention has been paid (only 11*

citations in 50 years) to this important paper.) The following most important conclusions should be mentioned:

The GO samples obtained via “Brodie’s method” are the purest and the most stable ones (see section 1.4.1).

The purification of GO samples prepared according to the “Staudenmaier method” and the “Hummers–Offeman method” is much more tedious; especially, the Hummers–Offeman samples are contaminated with a considerable amount of sulfur, probably bound to carbon as sulfonic acid or as esters of sulfuric acid.

Replacing KClO_3 by NaClO_3 prevents the formation of insoluble KClO_4 , which is hard to remove by washing with water.

Warning is mentioned to allow temperature increase during pouring the sample into water at the end of the oxidation reaction because of decomposition.

The chemical composition of the various samples shows a great variation, but there is a trend in the degree of oxidations: the C/O ratio decreases in the order Brodie > Staudenmaier > Hummers–Offeman.

The principal routes of work-up have been established since the early days of GO research. It is a tedious process, which can lead to changes in samples exposed to light or to water for too long. The work-up always starts with a strong dilution of the acids. In the first step, it is recommended to pour the reaction mixture into a huge amount of excess water to keep the temperature as low as possible. Since the particles of GO are very small, the sedimentation takes some time. During the washing process, the sediment volume increases strongly and the time for sedimentation becomes longer. In order to shorten the process, the GO is precipitated after some dilution/sedimentation cycles by adding dilute HCl. The obtained precipitate can be separated from the solvent by filtration or centrifugation. For the cleaning steps, dialysis or electrodialysis [29] has also been applied.

A very strange purification was recommended by Thiele [14]: he removed the oxidation mixture ($\text{KClO}_3/\text{H}_2\text{SO}_4/\text{HNO}_3$) by repeated boiling with concentrated nitric acid; the nitric acid is then removed by washing with acetic acid/acetic acid anhydride, and at the end with alcohol or ether.

Obtaining dry GO is also a tricky business. It is almost impossible to remove the solvent water completely. The minimum water content (5–10%) can be achieved without decomposition at room temperature in vacuum and in the presence of P_2O_5 . An alternative method is freeze-drying [30].

Apart from these chemical preparation methods, it is possible to obtain graphite oxide also by electrochemical oxidation. This was shown for the first time by Thiele [31] in 1934. He applied a very high current density and obtained in concentrated sulfuric acid first the blue phase, which is the sulfuric acid intercalation compound, and then a so-called primary oxide, graphite oxide and perhaps humic acid. Later Boehm *et al.* [27] and Besenhard and Fritz [32] obtained GO under controlled conditions in 70% perchloric acid. However, the degree of oxidation is considerably lower than for GO samples prepared via chemical oxidation. In the case of the concentrated sulfuric acid, beyond the first-stage phase $\text{C}_{24}(\text{HSO}_4)(\text{H}_2\text{SO}_4)_2$, there is a two-phase region in which there is a superposition of GO formation and O_2 evolution. The processes in this range depend strongly on the current density, indicating that the processes involved are much slower than the formation of the graphite sulfate intercalation [33].

1.2.2 Over-Oxidation of Graphite

Whereas graphite treated with boiling sulfuric acid loses only a small quantity of carbon as CO_2 [7, 34], most of it is lost when oxidizing agents such as nitric acid or $\text{K}_2\text{Cr}_2\text{O}_7$ are added to the boiling mixture [7]. Even Schafhäütl observed that repeated treatment of a piece of graphite with boiling sulfuric acid and the addition of nitric acid leads to a continuous loss of the material and finally to a complete disappearance [6].

Gottschalk [7] showed that the graphite-like carbon obtained by thermal decomposition of GO (prepared via the “Brodie method”) reacted faster during the Brodie reaction the more oxidation/decomposition cycles had been carried out: after the third oxidation, only traces of GO were found. In every oxidation cycle the quantity of graphite is reduced, and after the fourth oxidation step the graphite is gone completely.

Charpy [26] showed later that pristine graphite can be transferred to GO by bichromate or permanganate in sulfuric acid, but these reactions lead easily to over-oxidation: at room temperature one can get GO with nearly no loss of graphite. By oxidation with permanganate at 45°C , a small part of the graphite is lost, whereas at 100°C already 50% is oxidized to CO_2 . In the case of chromate, 50% is lost at 45°C and all graphite is transferred to CO_2 at 100°C .

In their GO preparation experiments in which they used a modified “Staudenmaier method”, Kohlschütter and Haenni [10] described that the amount of GO obtained decreases with every step of oxidation (the yield of GO being 95% after the first oxidation and only 54% after the fifth repetition of oxidation) till nothing is left. The amount of GO obtained decreases also with the time that graphite or graphite oxide is in contact with the oxidizing medium.

Hofmann and Frenzel [13] found that the C/O ratio of the obtained GO decreases (thus the oxygen content increases) with decreasing size of the graphite crystallites. Very interesting are the results of Luzi [25]. He demonstrated that, besides the insoluble GO, some soluble by-products, especially mellitic acid, are formed, even in chlorate/nitric acid mixtures. The quantity of this by-product increases with subsequent oxidation steps. According to Thiele [14], up to 50% of mellitic acid is formed when GO is prepared via the procedure of Staudenmaier. To avoid it, the portions of chlorate should be small, the time intervals of additions longer, and the reaction temperature should be kept below 20°C . Thiele [14] stated also that GO can be transformed to humic acid. In a later paper Thiele [35] mentioned that under special circumstances (*not formulated*) humic acids can be obtained as an intermediate state of the total oxidation of graphite to CO_2 by application of alkaline oxidation agents. In the same paper [35] he stated that humic acid is formed when an aqueous suspension of GO is left in air.

Ruess [19] remarked upon an increasing tendency to form mellitic acid or to destroy the graphite structure with decreasing particle size of the starting graphite. *This tendency is confirmed by my own experience. We have obtained mostly mellitic acid with the Hummers–Offeman method, when we applied the optimal reaction conditions for getting GO from crystalline graphite (particle size $500\mu\text{m}$) to a graphite powder with particle diameters of $<100\mu\text{m}$ (unpublished results).* And even Hummers and Offeman [28] recommended in their work-up process to filter the suspension while it is still warm to avoid precipitation of mellitic acid. In their GO preparation Hummers and Offeman used powdered graphite flakes with particle size 325 mesh ($44\mu\text{m}$).

On the basis of these very early results in GO research, I have the feeling that Rourke et al. [22] do not really present a new structural model, but investigate intermediate states between the formation of GO and mellitic acid.

1.2.3 Formation Mechanism – First Approximation

Already in 1919 Kohlschütter and Haenni [10] (p. 125) had recognized the essential role of nitric acid to open the graphite interior for the access of oxidants without acting as an oxidant for the formation of GO.

In 1930 Hofmann and Frenzel [13] showed for the first time by the application of XRD that the layer distance increases from 3.4 Å to 8 Å when graphite reacts with a mixture of sulfuric acid and nitric acid. *Thus, they confirmed the suggestion of Kohlschütter and Haenni [10] that nitric acid supports the opening of the interlayer space in graphite.* The product obtained is the “blue phase” described first by Schafhäütl [5, 6] and Brodie [2–4] and has been identified as a graphite sulfate [36]. Since this compound is highly sensitive to water, the pure first-stage compound (intercalation in every interlayer space) $C_{24}^+(HSO_4)^-(H_2SO_4)_2$ with the maximum content of sulfuric acid can be obtained by chemical or electrochemical oxidation of graphite in concentrated sulfuric acid [36, 37]. In a chemical oxidation with nitric acid in sulfuric acid (water content of 20%), the redox potential of the nitric acid allows only the preparation of a second-stage intercalation compound [37]. Although nitric acid is a strong oxidant, it is hard to get a pure first-stage nitric acid intercalation compound. In concentrated nitric acid (66 wt.%), only a mixture of higher stages can be obtained, and even in fuming nitric acid only a second-stage phase [36]. Only the addition of a small amount of permanganate allows the formation of the first-stage compound [38].

Thiele [39] as well as Rüdorff and Hofmann [36] mention that other oxidants such as $KClO_3$ or $KMnO_4$ or CrO_3 could take over the role of nitrate in the formation of graphite salts. However, they do not give experimental details. In 1992 Avdeev *et al.* [40] gave a physicochemical basis for the rational choice of oxidants allowing the formation of graphite sulfate salts. A detailed study of the system $KMnO_4/H_2SO_4/C$ was presented only in 2005 by Sorokina *et al.* [41]. They showed that the graphite sulfate salt is only formed when the $MnO_4^- : C$ molar ratio is $\leq 1 : 1$ [41]. The formation of a CrO_3/H_2SO_4 graphite salt is even more complex [42].

Thus, the unfortunate experiences of Brodie [1–4], Gottschalk [7], Charpy [26], Luzi [25] and Kohlschütter and Haenni [10] are not surprising (see section 1.2.1). From these experiences one can conclude that it seems to be unfortunate when the oxidant for the formation of GO has to act also as the oxidant for the formation of the graphite salt. In that case the opening of the interlayer galleries and the oxidation to GO start simultaneously and can, thus, lead to over-oxidation. The original formulation of Kohlschütter and Haenni [10] (p. 126) sounds, therefore, very modern:

setzung der Graphitsäurebildung erfüllen. Nur wenn die Oxydation gewissermaßen aus dem Innern heraus bzw. in der ganzen Masse zugleich ansetzt, kommt es zur Bildung von Graphitsäure. Greift das Oxydationsmittel von außen her an, so geht die Oxydation bis zu den einfachsten Produkten, da die Einwirkungsdauer für eine kleine Menge Graphitsubstanz verhältnismäßig lang ist, wenn die Reaktion nur Schicht um Schicht fortschreiten kann, und der schließliche Effekt immer — auch bei der Chloratmischung! — von der Zeit abhängt, während deren das Reagens wirkt. Infolgedessen bleibt bei Oxydationsmitteln, die weniger leicht als Salpetersäure in die Substanz eindringen, die Oxydation vielfach nicht bei Graphitsäure stehen, und wird ander-

(English translation: “Only when the oxidation starts simultaneously in the total mass from the interior does the formation of graphitic acid occur. If the oxidizing agent attacks [the graphite] from outside, the oxidation continues to the simplest products, since the time of action for the small amount of graphite is too long, when the reaction can proceed only layer by layer ...”)

To get optimal access of the oxidant to the interlayer space and to get GO monolayers in the colloidal state, it must be guaranteed that a pure first-stage intercalation compound has been obtained. This corresponds quite well with the statement of Boehm et al. [27] that the water content in sulfuric acid should not exceed 15% for the preparation of GO of high quality. However, it is hard to recognize the ideal endpoint of the intercalation reaction because of inter-stratification phenomena. Looking at the modern preparation methods of GO, I get the feeling that the importance of the intercalation process for optimal GO formation is mostly overlooked and the time before the addition of the oxidants is too short for optimal intercalation.

If the interlayer space is free for the access of the oxidizing agent, two questions arise: What are the oxidizing species? And how do they enter into the interlayer space? It is generally assumed that ClO_2 and Mn_2O_7 formed in concentrated sulfuric/nitric acid mixtures from KClO_3 and KMnO_4 are the active species. In the case of KMnO_4 in concentrated sulfuric acid, the reactive species could also be the MnO_3^+ cation [43]. However, it is hard to imagine that this cation enters the interlayer space constrained by two positively charged carbon layers. To enter into the interlayer space, ClO_2 and Mn_2O_7 have to replace the sulfuric acid molecules that form together with the HSO_4^- ions a densely packed arrangement in the interlayer space in the precursor intercalation compound. This exchange process has to occur against a huge excess of sulfuric acid in the surroundings of the graphite salt. Therefore, it seems to me more probable that the ion exchange of the monovalent chlorate and the permanganate ion against the HSO_4^- ion is the essential next step in the GO formation. (The possibility of ion exchange in the graphite salts was mentioned by Boehm et al. [27] and demonstrated by Rüdorff and Hofmann [36].) Both ions could be present to some extent since the pK_a values of sulfuric acid, chloric acid and permanganate acid are almost of the same order of magnitude ($\text{H}_2\text{SO}_4/\text{HSO}_4^-$, -3 ; $\text{HMnO}_4/\text{MnO}_4^-$, -2.25 ; $\text{HClO}_3/\text{ClO}_3^-$, -2.7 ; provided these values have any meaning under conditions in which the pH scale is not really valid). However, one essential problem is left: permanganate and chlorate act differently on organic compounds; but in the case of GO formation both must act very similarly.

1.3 Discovery of Essential Functional O-Containing Groups and its Relation to the Development of Structural Models

1.3.1 Analytical Composition of Graphite Oxide

Throughout the history of GO research, the composition of GO was determined by combustion analysis to determine the C and H contents. The oxygen content corresponds to the difference from 100%. Only Thiele [14] carried out reduction reactions of GO to determine the amount of reducing agent necessary for full reduction, to get the C/O ratio. However, there was general agreement at that time that the reduction is never complete even under strong conditions (e.g. up to 800°C). To get the correct C/O ratio one has to make a correction for the ash left after burning. A serious problem for the determination of the correct

C/O ratio is the amount of hydration water left in the sample after careful drying without the risk of deterioration. Boehm and Scholz [30] recommend using samples for analysis with 10–17% residual water because this corresponds to the water content of GO in the normal water vapor pressure in the laboratory atmosphere; thus, the samples do not change the weight so much during weighing.

For samples prepared via “Brodie’s method”, the carbon and hydrogen contents are fairly constant over the time of GO research. Brodie reported a carbon content of 60–61% and a hydrogen content of 1.75–1.91%; Gottschalk [7] reported similar values, but questioned whether these values mark an endpoint of drying. However, Boehm and Scholz [30] confirmed, despite some scatter, the values of Brodie [2].

For their GO prepared via the modified “Staudenmaier method”, Kohlschütter and Haenni [10] found after the first oxidation a carbon content of 59% and a hydrogen content of 1.91%. The carbon content decreases with the number of oxidation/purification cycles to 55%. Such strong alterations have not been reported since. Boehm and Scholz [30] reported values between 56% and 58% with an average of 57%.

Hummers and Offeman [28] reported a carbon content of 47% for their product and a carbon content of 52% for the sample prepared according to the “Staudenmaier method”. These values are the lowest to be found in publications. Boehm and Scholz [30] found the carbon content in the range from 56% to 63.7% for the Hummers–Offeman GO product.

Boehm and Scholz [30] stated that there is always a large scatter in the analytical results of various samples, but they are convinced that there is a trend in the degree of oxidation: the value of the C/O ratio is highest for the Brodie samples ($C/O=3.5$), slightly lower for the Hummers–Offeman samples (3.3) and lowest for the Staudenmaier materials (2.9). In contrast, Thiele [14] stated (*without giving experimental proof*) that the number of oxidation cycles and the method of preparation have no serious influence on the analytical results. On the other hand, he gave the ratio of C : O : H of 2 : 1 : 1 for his own samples prepared via the “Staudenmaier method”. This would correspond to the full oxidation of all aromatic double bonds.

Summing up all the analytical data in the Boehm and Scholz publication [30] and the analytical work done by all scientists working on GO since Brodie, I conclude that carbon contents lower than 55% (corresponding to a C/O ratio below 2.5) indicate over-oxidation of GO, and that carbon contents higher than 63% (C/O ratio above 3.3) are caused by incipient decomposition due to drying the samples at about 100 °C.

1.3.2 Creation of the Structural Model from 1930 till 2006

Based on his analytical result and especially on the unusually high hydrogen content, in 1930 Thiele proposed that oxygen is attached to the carbon grid in the form of OH groups [14]. Since the carbon atoms form a honeycomb arrangement, he gave a sum formula $C_6O_3H_3$. To be in agreement with this sum formula, Thiele had to assume that the OH functions are covalently bound to every second C atom on both sites of a carbon bilayer, which are interconnected by covalent C–C bonds. A sketch of this structural model is shown in Figure 1.1. Thiele considered the possibility to transform GO into humic acid as an additional hint for the presence of OH groups in GO.

Almost 60 years after Thiele, Nakajima *et al.* [44, 45] presented a very similar structural model of GO (see Figure 1.1, right), without giving any reference to Thiele’s paper. Nakajima

et al. proposed a slightly different sum formula ($C_8(OH)_4$) instead of $C_6(OH)_3$) and based their model on the similarity of XRD data to those of a carbon fluoride compound with the same composition. Neither of these models found attention in the community.

An alternative model for the structure of GO was presented by Hofmann *et al.* [15] in 1934. The starting point of the model construction was based on the following considerations. As a maximum, all three double bonds per carbon hexagon could be replaced by three oxygen atoms bridging two neighboring carbon atoms (forming epoxide units). Since the most frequently found C/O ratio is 3, some double bonds have to be left unoxidized. In the oxygen removal from some ethylene oxide compounds under re-formation of a double bond via HI treatment, Hofmann *et al.* [15] saw an analogy to the ease of oxygen removal in GO. This analogy was considered as a hint for the presence of epoxide functions in GO. From the fact that the heat of combustion of GO is quite similar to that of graphite, Hofmann *et al.* concluded that the oxygen is only weakly bound to the carbon layers in GO [15]. An additional proof is presented by the authors via the first single-crystal XRD analysis of GO.

For the calculation of the intensities of the reflections, four different arrangements of oxygen atoms has been considered (Figure 1.2, top, a–d). The observed intensities agree best with the calculated intensities for model a) under the additional assumptions that every third C layer is at the same position, and that the oxygen atoms are statistically distributed between the possible sites. This arrangement is only possible if the carbon grid remains flat

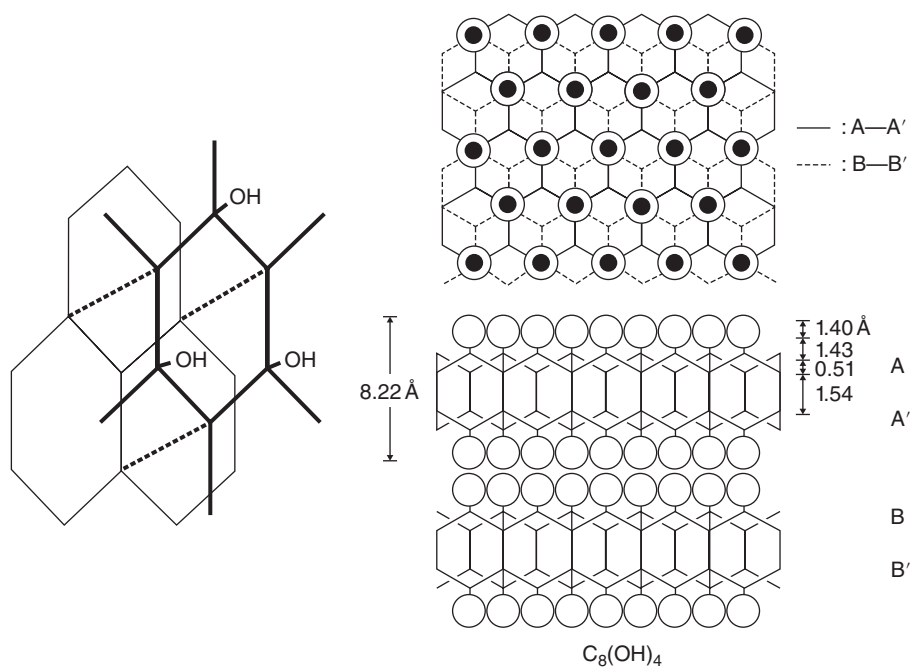


Figure 1.1 The structural models of Thiele [14] (left) and Nakajima et al. [44, 45] (right). (left) Reproduced from [14] with permission of Wiley-VCH. (right) Reproduced from [44] with permission of Elsevier

as in graphite. The authors did not see any evidence for the presence of OH groups covalently attached to the carbon grid. They ascribe the hydrogen exclusively to residual “bound” water, without specifying the nature of this bonding state [15]. *The unusually high hydrogen content in Thiele’s samples can be explained by the retention of the organic solvents (acetic acid, acetic anhydride, ether) used by Thiele in his work-up process (described in section 1.2.1).* In a subsequent paper, Hofmann and König [46] devoted a small section to sum the formula of Thiele, which they discarded again. This conclusion has been confirmed also by a very thorough study of Thiele’s purification method carried out by Ruess [47]. In his experiments Ruess observed some evidence for a covalent attachment of the acetyl groups from the acetic acid anhydride to the OH groups (see section 1.4.6).

In the 1937 paper of Hofmann and König [46] there is an interesting turn. They confirm the cation exchange capacity in slightly basic medium determined by Thiele [35] and conclude that the amount of carboxyl groups in GO will not be enough to explain the acidity of GO. Thus, OH groups like those in humic acid may fill the gap. In addition, they suggest that the OH groups may be formed by hydrolysis of the epoxide groups.

In 1947 Ruess pointed out in his paper [19] that GO is not as reactive as organic epoxides and does not show the typical ring opening reactions with ammonia, HBr or HCl forming vicinal hydroxyamines or halogenohydroxides. He questioned also the idea that hydroxyl groups can be formed by hydrolysis of the epoxide functions. Based on these chemical arguments, the covalent bonding of OH to the carbon grid and a re-evaluation of Hofmann *et al.*’s [15] and his own XRD data, Ruess [19] presented a new structural model. He claimed the best fit between the observed and calculated structure factors he had obtained, shown in Figure 1.3.

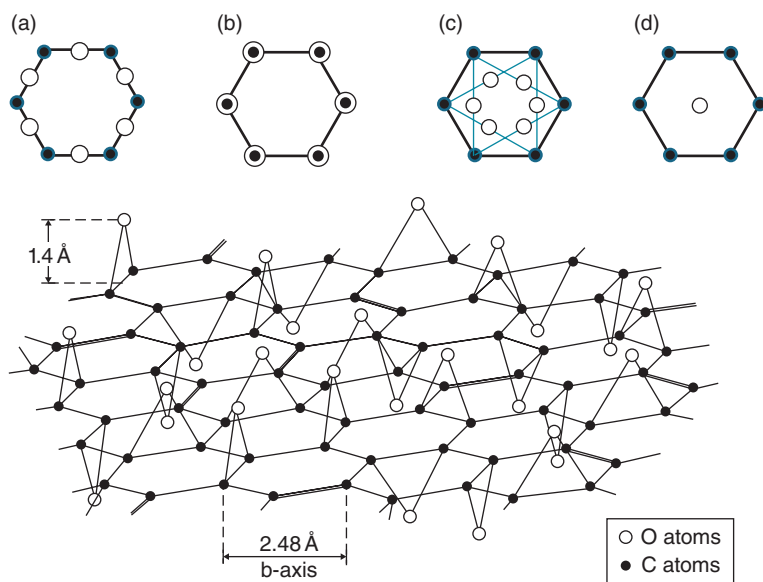


Figure 1.2 The structural model of Hofmann *et al.* [15]. Reproduced from [15] with permission of Wiley-VCH

The carbon grid is now corrugated in a form typical for an arrangement of cycloalkanes with sp^3 -hybridized carbon atoms. This structure no longer allows epoxide functions, and is therefore replaced by 1,3-ether functions. According to Ruess's determination of non-removable hydrogen atoms, there is about one OH group per six carbon atoms in the structure. The remaining oxygen atoms form the ether bridges. Their number and the number of double bonds vary with the degree of oxidation.

However, a single type of OH groups – particularly tertiary OH functions – is hardly compatible with the variety of reactions of the GO hydroxyl functions (see section 1.4.5) [16, 46, 48, 49]. Therefore, Clauss *et al.* [48] suggested that an OH function in the neighborhood of a C–C double bond (enols) could be much more acidic. However, in that case C–C bonds must have been broken, and the arrangements shown in Figure 1.4 (left) could be present in GO.

The transition from an enol to a keto function could explain the transition from the bright to the dark state of GO. However, this tautomerism could not be clearly established by the authors in an infrared (IR) spectrum. IR spectra by Clauss *et al.* [48] and earlier by Hadži and Novak [50] clearly confirmed the presence of carboxyl and hydroxyl groups but gave no indications for the 1,3-ether functions. Trials to split these ethers were unsuccessful also [16, 48]. Hadži and Novak assigned a weak feature at a wavenumber of 980 cm^{-1} as a hint for the presence of epoxide functions. In a later paper Scholz and Boehm [16] assigned the signal at 1720 cm^{-1} to a carbonyl function, which in alkaline solution undergoes a keto–enol tautomerism or forms a geminal diol. Another vibration mode at 1620 cm^{-1} was interpreted as originating from a carbonyl function of an extended quinonoid system. This assignment was the basis of the new structural model of Scholz and Boehm [16] shown in Figure 1.4 (right). Note that this assignment was later shown to be incorrect [51]. *I think that the model published by Szabó et al. [51] combines structural elements of both Scholz and Boehm [16] (broken C–C bonds, quinone groups) and Ruess [19] (1,3-ethers).*

In 1962 Aragon de la Cruz and Cowley [52] found the intensity distribution of the spots in their electron diffraction pattern to be compatible with epoxide functions over C–C double bonds and OH groups on top of carbon atoms in a random distribution, in agreement with a modified Hofmann model. However, the authors conceded that this interpretation

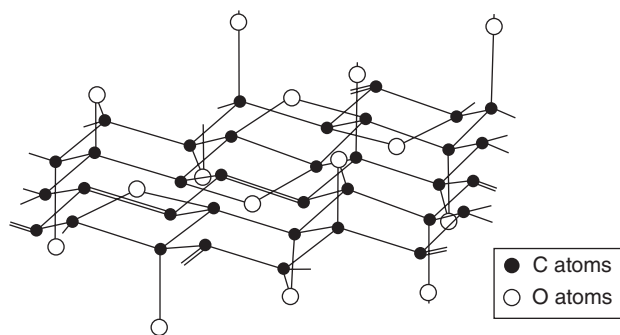


Figure 1.3 The structural GO model according to Ruess [19]. However, this figure is taken from Ref. [48] because it shows clearly the double bonds left unoxidized. Reproduced from [48] with permission of Wiley-VCH

suffers from some uncertainty. And, indeed, Scholz and Boehm [16] stated that a similar electron density distribution would be found for carbonyl functions in neighboring carbon layers lying on top of each other. The electron density distribution could also originate when the layers were built up from small areas oriented in all three *a*-directions [16].

Summing up the results of this era of investigation, it is disappointing that the application of the most modern methods at that time did not allow the structure of GO to be unambiguously clarified. With respect to the XRD, this is mainly due to the fact that, for GO, one can observe only two 001 reflections and a few *hk*0 reflections, but no *hkl* reflections.

A new era in GO studies started with the possibilities offered by MAS NMR. NMR monitors mainly the electronic structure of the first coordination sphere and is, therefore, less sensitive to the long-range order in a crystal. Thus, it is the ideal method for investigating almost amorphous materials. The first NMR experiments on GO were published by Mermoux *et al.* in 1989 and 1991 [17, 18]. The ^{13}C NMR spectrum shows just three dominant signals, as shown later in Figure 1.6(a), with chemical shifts of 60, 70 and ~ 130 ppm. The three signals of an as-prepared GO have been assigned to ether functions, to alcohol functions and to aromatic or conjugated double bonds, respectively. Therefore, Mermoux *et al.* [18] ruled out the structural models of Thiele [14], Nakajima *et al.* [44, 45] and Scholz and Boehm [16]. Whereas in their first paper [17] Mermoux and Chabre assigned the 60 ppm signal to epoxide functions, in the following paper [18] they did not differentiate between epoxide (1,2-ether) and 1,3-ether functions and considered their spectra as confirmation of Hofmann *et al.*'s [15] and Ruess's models [19]. At the end the authors preferred

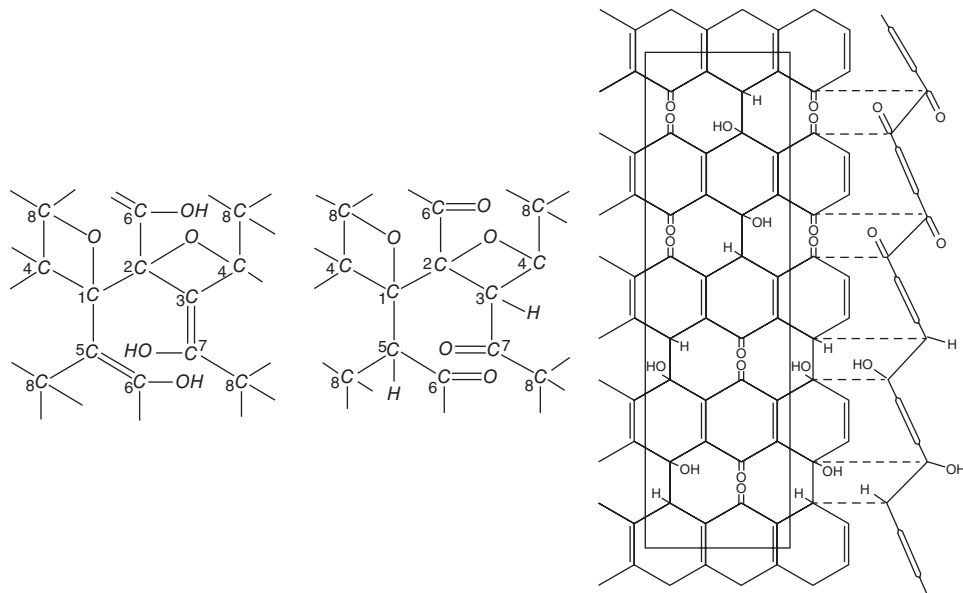


Figure 1.4 Possible keto–enol tautomerism in graphite oxide (left) according to Clauss *et al.* [48], and the new structural model (right) of Scholz and Boehm [16]. (left) Reproduced from [48] with permission of Wiley-VCH. (right) Reproduced from [16] with permission of Wiley-VCH

a Ruess-type model, but name the 1,3-ethers as epoxides as well. In subsequent papers [53, 54] the position of the authors is not clear. On the one hand they assign the 60 ppm peak to epoxides, but on the other hand they argue only based on the model of Ruess, despite Ruess [19] clearly stating that epoxides are not compatible with corrugated layers of sp^3 carbons.

The assignment of the 60 ppm signal to epoxide groups in our studies signifies the return to the structural model of Hofmann with some modifications [20, 55]. Part of the epoxide groups must be replaced by tertiary OH groups; and the two functional groups are more or less randomly distributed over both sites of the carbon grid. Since the signal at 130 ppm can be ascribed to aromatic carbon atoms, patches of aromatic rings of varying size are distributed between the oxygen-carrying areas. These aromatic areas and the epoxide groups keep the carbon grid almost flat; some deviations may result from the sp^3 -hybridized carbon atoms carrying the OH groups. A sketch of the resulting structure is shown in Figure 1.5.

To be honest, one should be aware that the interpretation of the NMR spectra might not be the end of the story. We cannot differentiate if isolated or conjugated double bonds contribute to the signal at 130 ppm. In addition, NMR is a local probe and, thus, we do not know whether this signal is caused by isolated aromatic rings or by polycyclic arrangements as we have shown it in the sketch of our model. Thus, the NMR data could also be compatible with a distribution of aromatic rings following Clar's concept of aromaticity (as shown in figure 1 of Ref. [56]). The signals at 60 and 70 ppm overlap partially. A deconvolution analysis showed that perhaps four signals are hidden in the experimental peak. Going through NMR data collections (e.g. Ref. [57]), one can find structural features that could be compatible with the structural models discussed with almost similar chemical shifts, i.e. allylic alcohol. However, it is clear that in pristine GO there is little evidence for the presence of enol or phenol functions.

1.3.3 Considerations for the Formation Mechanism – Second Approximation

As discussed in section 1.2.3, the intercalation of sulfuric acid and/or nitric acid into graphite is the first step of GO formation [10, 13, 16]. Recently, Dimiev and Tour [58] confirmed elegantly by means of modern scientific methods (XRD, Raman spectroscopy) all the observations on GO formation described from the early days of GO research by Brodie [2], Gottschalk [7], Staudenmaier [9], Luzi [25], Kohlschütter and Haenni [10] and Hofmann and Frenzel [13], just to mention the most important workers.

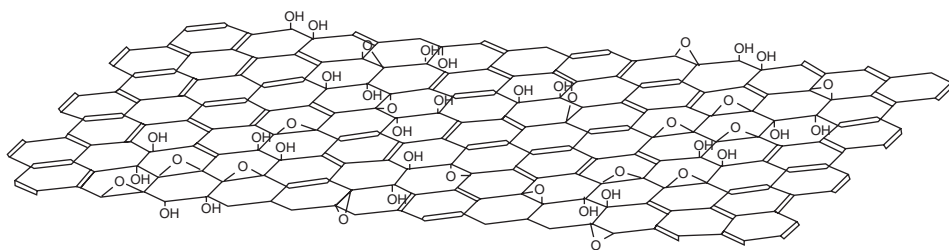


Figure 1.5 Lerf-Klinowski model of the as-prepared GO structure [55]. Reproduced from [55] with permission of Elsevier

Since it is hard to guarantee a pure first-stage phase throughout the intercalated graphite particles, it cannot be ruled out that there are multi-layer assemblies of a second-stage phase. In that case the oxidation could occur only in any second interlayer gallery, resulting in an assembly according to Thiele's model [14]. The real arrangement must not follow the ideal and very regular arrangement in Thiele's model, but there could be some covalent linkages of C atoms (carrying OH groups) between the neighboring C layers. Besides the OH groups, there could also be epoxides or other functional groups.

Hofmann *et al.* [15], Boehm *et al.* [16, 48] as well as Dimiev and Tour [58] refrain from discussing the molecular mechanism of graphite oxidation. This is understandable because there are no low-molecular-weight model systems with large polycyclic aromatic hydrocarbons (PAHs) where the reaction behavior of hydrogen-free carbon atoms has been investigated. Therefore, considerations on the mechanism of GO formation must start from knowledge of the reaction behavior of low-molecular-weight PAHs.

Assuming epoxides as an important structural element in GO, one is faced with the fact that neither ClO_3^- nor MnO_4^- are known to oxidize PAHs to epoxides [59]. MnO_4^- reacts with isolated double bonds to form *cis*-diols [59, 60]. This sort of reaction could happen only at the peripheral carbon atoms of the graphite layers, and the subsequent reaction from diols to ketones could occur with breaking of C–C bonds. Whether isolated double bonds can undergo the same reactions is not clear. The proposed mechanism of diol formation has been proved experimentally only for permanganate oxidation in neutral or basic solutions [60]. However, it cannot be ruled out completely that this diol–ketone reaction can happen also in concentrated sulfuric acid, as has been discussed for the unzipping of carbon nanotubes [61].

In the destructive oxidation of PAHs, the permanganate ion is bound via an oxide ion to the carbon under abstraction of a proton, the formation of a carbonium ion and the reduction of manganese to the Mn(v) state [62]. At the end of the reaction, the manganese is liberated and a quinone is formed. This process could work again only for peripheral carbon atoms or at defect sites in the graphite layers. Such defect sites could be the nuclei for the subsequent oxidation of the whole layers. The product of this reaction would be compatible with the structural model of Scholz and Boehm [16] and Szabó *et al.* [51]. However, according to the NMR spectra, quinones are at best minority species in pristine GO (*I guess less than 10%*).

If one assumes that *cis*-diols are formed, then there is no mechanism explaining their transformation to 1,3-ethers postulated by Ruess [19]; the water abstraction to epoxide groups by concentrated sulfuric acid can also be questioned. Whether these reactions can occur in the interlayer space of GO is also unclear. Even less clear is how these functional groups could be formed with the other important oxidant ClO_2 (or ClO_3^- , HClO_3 ?). Their oxidation power is so high that low-molecular-weight compounds are completely destroyed. In addition, when oxidants diffuse from outside into the interior of graphite salt crystals, one would expect that oxidation occurs at the site of entry. The removal of the reaction by-products and the different chemical nature of the carbon surfaces could obstruct the progress of oxidation toward the center of the crystals.

Therefore, it seems necessary to think about a common mechanism for both oxidants. If in the case of the chlorate and permanganate ions the ion exchange process were faster than the oxygen liberation, the process of oxidation could start in the interior of the graphite salt crystals. If this liberated oxygen is in the $^1\text{O}_2$ state and cyclohexadiene units exist due to the disturbances in the graphite π -electron system (positive electron holes or the carbocations), it could be attached to the graphite sheets as peroxide functions, which can

thermally rearrange to diepoxides in analogy to reactions discussed in Ref. [63]. Starting from these oxidized nuclei, new sites would be created to continue the reaction. The epoxides could be hydrolyzed to hydroxyl groups. It should be recalled that Boehm postulated that some residual water in the concentrated acids is necessary for GO formation [27].

However, one should keep in mind that these considerations are deduced from the solution chemistry of PAHs, and it is not clear whether these reactions can occur in the same way in the constrained space of the interlayer galleries and in an electrostatic field created by the interaction of the intercalated anions with the positively charged graphite planes. In addition, there is a highly protic solvent in the surrounding of the crystals which is also present as a solvent in the interlayer space.

1.4 Properties of Graphite Oxide

1.4.1 Thermal Degradation and its Products

In the 1850s Brodie [2] described the vigorous decomposition of GO during heating. To control the process better, he carried out the decomposition reactions in purified naphtha. In the temperature range of 100–200 °C considerable amounts of water and CO₂ are liberated. The black residue obtained after heating GO in this fluid for a few hours at 240 °C still contains some oxygen, and Brodie determined its composition as C₂₂H₂O₄. By heating this sample in a stream of nitrogen, more CO₂ and CO were liberated, but even after heating the sample to red heat some oxygen and hydrogen was left in the sample.

Kohlschütter and Haenni [10] as well as other workers before (e.g. Gottschalk [7], Berthelot [8] and Staudenmaier [9]) confirmed the observations of Brodie and stated that the form of the black decomposition products is in close correlation with the form of the graphitic acid and the starting graphite materials. The decomposition residues become more voluminous the more often the oxidation and cleaning cycle is repeated [10]. Kohlschütter and Haenni [10] found also that the temperature of deflagration is the lower the slower the materials are heated up. Decomposition under pressure resulted in a more graphite-like residual compound with higher density. When the samples are heated in concentrated sulfuric acid, the samples decompose again to graphite-like material, but do not deflagrate. Hofmann found by XRD investigation (*this is the first application of XRD in the GO research carried out in 1928*) that the decomposition products obtained under pressure or in sulfuric acid are more crystalline than the soot-like decomposition products obtained in decomposition products at normal pressure [12].

Hofmann *et al.* [15] stressed later that no oxygen can be detected in the gaseous decomposition products and concluded that the liberated oxygen had reacted with carbon at the crystal edges, forming CO₂ and CO. Later De Boer *et al.* [64] reported that they discovered a considerable amount of oxygen due to the decomposition of the proposed peroxides present in GO. This conflicting result was not confirmed by Boehm and coworkers [16, 65]. Boehm and Scholz [66] showed in addition that the deflagration point of GO decreases in the order GO_{Brodie} > GO_{Staudenmaier} > GO_{Hummers–Offeman}. The low decomposition temperature of the Hummers and Offeman samples could be caused by catalysis from residual manganese ions. This conclusion is based on the observation that a GO sample soaked in an aqueous FeCl₃ solution explodes under fire. In general, any impurity leads to lowering of the deflagration point [66].

Hofmann *et al.* [15] found that the interlayer distance decreases almost continuously during decomposition. At a temperature slightly above the temperature of deflagration (320 °C), the layer distance amounts to 4.05 Å, and after heating up to 850 °C, it is 3.38 Å, almost identical to the layer distance of graphite. This can be explained only when the gaseous decomposition products leave the interlayer spaces almost randomly and when there is an almost random interstratification of completely empty and partially oxygen-loaded interlayer spaces.

Decomposition of GO can occur at 70 °C [66]. Very slow decomposition of GO with the liberation of CO₂ and CO can be observed already at 50 °C [67]. Hofmann and Holst [49] showed that the ion exchange capacity decreases irreversibly when the samples have been dried at 130 °C.

To the best of my knowledge, Matuyama carried out the first thermogravimetric and differential thermal analysis (TG-DTA) measurement in 1954 [68]. He chose a heating rate of 42 °C h⁻¹ to avoid deflagration. The weight loss starts slightly below 50 °C and reaches a plateau at ~100 °C. This weight loss is mainly caused by dehydration. The greatest weight loss occurs in the range 150–200 °C and amounts to about 40%. Up to 300 °C the weight loss continues smoothly. Martín-Rodríguez and Valerga-Jiménez [69] extended the TG-DTA analysis up to 800 °C and determined the evolved gases by gas chromatography. They confirmed the results of the previous works. In a most recent TG-DTA study of the thermal decomposition of GO coupled with a mass spectroscopic analysis of the evolved gases, new (up to now unknown) gaseous species with molar masses of 43, 46, 59 and 60 have been detected [70]. Hofmann *et al.* had already mentioned the liberation of “carbon like oxygen containing compounds” beside CO₂ and CO as decomposition products [15].

1.4.2 Chemical Reduction Reactions

Again, Brodie [2] was the first to describe that the treatment of GO with reducing agents such as potassium or ammonium sulfide, Cu(I) chloride or Sn(II) chloride leads to a black residue with the appearance of graphite. However, he could not purify the obtained solids and, thus, a further study was given up. Gottschalk [7], Staudenmaier [9] and Kohlschütter and Haenni [10] using Cu(I) chloride and Fe(II) sulfate confirmed the graphite-like appearance of the reduction products. These authors stated also that the reduction product can be transferred again to GO.

Thiele's conclusion [14] that GO can be quantitatively reduced to graphite was not confirmed by Hofmann *et al.* [15]. They found that the amount of oxygen that can be removed depends on the reducing agent used: with Fe(II) chloride, ~68% oxygen can be removed; with hydrazine hydrate in aqueous medium, 82%; and with H₂S in water, 91%. In the latter case Hofmann and Frenzel assumed that sulfur replaces oxygen by forming the sulfur analog of the epoxides, which decompose already at room temperature [71]. Lerf *et al.* treated GO with thiourea, an agent sensitive to epoxides; however, they could not get an NMR spectrum because the sample exploded in the rotator after starting the measurement [20]. Only more recently, in 2003, have Bourlinos *et al.* [72] introduced new reducing agents: NaBH₄ and hydroquinone. Especially the latter is of interest because the graphite obtained shows a higher crystallinity.

When GO is reduced with hydrazine, first mentioned by Thiele [73], the residual solid retains a lot of water (>30%) although the layer distance of 3.5 Å is only slightly larger than that of the graphite [46]. Most of the water can be removed by application of

mechanical pressure on the sample. More water can be removed then by heating the sample to 110 °C, and it requires temperatures up to 350 °C to remove all the water. Hofmann and König [46] explained this surprising fact in the following way: since an aqueous solution of hydrazine is alkaline, GO disperses to piles with a few GO monolayers and these piles are further propped apart by the reduction processes; after reduction the lamellae are deposited randomly to a dense felt where the water is occluded in hollow spaces. The loss of water during heating is again a continuous process and is accompanied by a decrease of the linewidth of the 001 Bragg peaks indicating an increased ordering of the graphite layers in the direction of the crystallographic *c*-axis. Thiele reported that the specific conductivity is in the order of that of graphite [35].

Whereas Hofmann *et al.* [15] considered the deoxygenation of molecular epoxides with hydrogen iodide under the formation of double bonds as a model case for the deoxygenation of GO, Ruess [19] and later Scholz and Boehm [16] mentioned that hydrogen iodide does not react with the epoxide or the 1,3-ethers in GO. However, De Boer and van Doorn [74] observed a reduction of GO with sodium iodide and ascribed the amount of liberated iodine to the reduction of a hydroperoxide function and to a ketone function which is involved in a keto–enol equilibrium.

By means of ^{13}C NMR spectroscopy it has been shown that iodide treatment affects GO considerably (see Figure 1.6). Following the suggestion of Hofmann *et al.* [15], Lerf *et al.* [20] assumed that iodide could lead to a selective abstraction of the epoxide oxygen. However, the intensity of the peak assigned to epoxide groups (60 ppm) decreased simultaneously with the intensity of the 70 ppm signal (Figure 1.6a). Simultaneously, new features appear

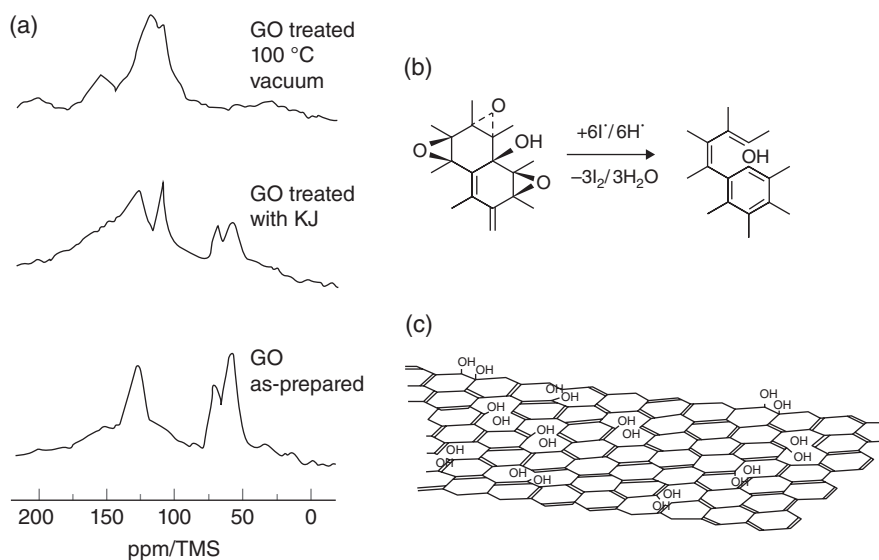


Figure 1.6 (a) ^{13}C MAS NMR spectra of GO modified by thermal treatment and reduction with KI [20, 55]. (b) Proposed reorganization of the double bond system after liberation of oxygen [20, 55]. (c) Modified structure of GO containing only phenols and double bonds after complete removal of epoxide groups [55]. Reproduced from [55] with permission of Elsevier

in the NMR spectrum: a peak at ~110 ppm and another at ~160 ppm. The simultaneous appearance of these signals has been interpreted as the formation of phenols in GO.

A complete disappearance of the epoxide and OH functions and a still higher portion of signals typical of phenols were observed when GO was treated at 100 °C in vacuum. The transformation of OH functions can only occur when the electron system has been reorganized completely after removal of oxygen and breaking of some C–C single bonds (Figure 1.6c). In an extreme case, only phenol groups and the rearranged π electron system could be left (Figure 1.6c).

These results demonstrate a relation between the structural models of Hofmann et al. [15] and Lerf and Klinowski [20, 55] and the slightly modified model of Scholz and Boehm [16] and Szabó et al. [51] due to the proposed chemical transformations. The Scholz–Boehm model can now be considered as a verification of Thiele’s suggestion that oxygen could enter the carbon grid as a first step of GO transformation to humic acid [14, 35]. Pallmann [75] and Hamdi [29] compared the colloidal dispersion, the ion exchange capacity and the acidity of GO, humic acid and different forms of lignin (see section 1.4.5) and found that lignin takes an intermediate state between humic acid and GO.

1.4.3 Reactions with Acids and Bases

GO was shown to be very stable against acids, at least against oxidizing acids. In his cleaning process Thiele treated GO with boiling concentrated nitric acid without evidence for destruction [14]. Several authors added ClO_2 or nitric acid to aqueous suspensions of GO to keep the samples bright-colored [7, 9, 30, 48].

Aqueous alkali/alkaline earth–alkali hydroxide solutions can interact with GO in different ways:

- Dilute NaOH solutions are essential for the redispersion of acid-precipitated GO or to cause osmotic swelling of GO (see section 1.4.4).
- Alkali and alkaline earth acetate solutions deprotonate GO, leading to GO–alkali salts (see section 1.4.5) and these neutralization reactions seem to be reversible.
- OH^- ions can initiate more or less reversible alterations of GO.

Only the latter phenomenon will be discussed here. GO suspensions in dilute alkaline solutions (<0.1 M) turn black within minutes, but NMR spectra do not show significant changes even when the samples are exposed to the solution for a day at room temperature (unpublished results). In contrast, Dimiev *et al.* [76] found a significant decrease of the peak intensity of the alcohol and epoxide peaks, but no other significant changes in the spectrum. When a GO–ethylate sample is treated with a 1 M NaOH solution at 70 °C for 3 h, the NMR spectrum looks similar to the NMR spectrum of the thermally treated sample shown in Figure 1.6(a) [20]. The only difference is that the sharp signals are superimposed on a very broad background with a maximum at about 130 ppm, perhaps indicating that the changes of the samples are more serious than in the case of the thermally treated sample. Fan *et al.* [77] observed, by treating GO with 18 M NaOH solution at 80 °C, a spectrum similar to ours, which we have obtained for a sample treated at 100 °C in vacuum.

Therefore, I think that Fan et al. observed a “base-assisted thermal decomposition”. Recently, Dimiev et al. [76] proposed chemical rearrangements in the GO structure,

triggered by the nucleophilic attack of OH^- ions. The proposed mechanism explains for the first time the liberation of CO_2 during the slow decomposition of GO in basic solutions. It is also a model process to explain the lack of oxygen liberation during thermal deflagration of GO [15, 65] as well as the evolution of CO_2 in the thermal decomposition of GO at 50°C [66], if one assumes that the strongly bound water can act as a nucleophile, perhaps after deprotonation. In that case it could be that the changes of GO caused by soaking GO in water [35] or by exposure to sunlight [67] follow the same mechanism. The presence of Ba salts, which can act as a trap of the liberated CO_2 due to the formation of insoluble BaCO_3 , may enhance the rate of decomposition [35, 49].

The iodide reaction [20] leads to very similar products as the thermal decomposition, but it acts as a reducing agent. Therefore, the question arises how it can be combined with the reaction scheme of Dimiev et al. [76].

1.4.4 “Osmotic Swelling”: Hydration Behavior and Colloid Formation

The hygroscopic properties of GO have been described already by Brodie [2]. Gottschalk [7] mentioned the presence of “Hydratwasser” casually. Kohlschütter and Haenni [10] mentioned the weight gain of dried GO exposed to air and that the water taken up can be removed easily during mild heating. They mentioned also that the water is liberated in vacuum or by keeping the samples over concentrated sulfuric acid, but that it is hard to get constancy in weight even for long time runs.

Hofmann and Frenzel [13] found by means of powder XRD that the water taken up in GO props open the graphite oxide sheets. A sample containing about 95% water showed a layer distance of $11.3\text{\AA}$; an air-dried sample with $\sim 15\%$ water, a distance of $7.84\text{\AA}$; and a thoroughly dried sample with 7–8% water, a distance of $6.4\text{\AA}$. The uptake and the release of water is a reversible process. From the layer expansion of $\sim 6\text{\AA}$ the authors assumed that two layers of water are inserted between the GO monolayers when GO is soaked in water. Since the $hk0$ reflections are not changed by the water uptake, the authors call the phenomenon a “one-dimensional swelling”.

Hofmann *et al.* [15] demonstrated for the first time the correlation between the water vapor pressure in the air with the percentage of water taken up and with the layer distances of the hydrated product. This correlation was later confirmed by Derksen and Katz [78] and Ruess [19]. Derksen and Katz [78] as well as Hofmann *et al.* [15] found that the isotherm of water adsorption shows a sigmoidal curve as for other known water adsorption processes. The maximum layer distance in fully hydrated GO decreases with temperature from $11.3\text{\AA}$ to $9.95\text{\AA}$ at 80°C [78]. They found also, like Hofmann *et al.*, that the layer distance increases almost linearly with the amount of water taken up during hydration. This effect has been confirmed later several times [79, 80]. It can be explained only in terms of random interstratification [15, 81, 82]. Hofmann *et al.* [15] mentioned that partially decomposed GO samples with C/O ratios up to 5 do not lose their swelling behavior in water.

According to the latter authors [15], shaking the fully hydrated GO in alkaline and ammonia solutions leads to a complete delamination of GO. Derksen and Katz [78] gave the layer distance of GO as a function of the pH. They showed the increase of the layer distance from $10.7\text{\AA}$ to $11.4\text{\AA}$ with decreasing proton concentration and a layer distance of $12.5\text{\AA}$ at pH 13. In the range $6 < \text{pH} < 13$ no layer distances are given because of the colloidal

dispersion of GO. Clauss *et al.* [48] showed that the layer distance in 0.05 M and 0.03 M NaOH solution increases from 11.3 Å to 12.5 Å. In 0.02 M NaOH solutions the colloidal dispersion of the GO occurs discontinuously. The authors mentioned also that disintegration occurs at the same layer charge density (1–2 sodium ions per 100 Å²) as for montmorillonites [48, 83].

Whereas the swelling behavior during the work-up of GO has been well known since the discovery of GO by Brodie, Kohlschütter and Haenni [10] described this process as colloidal dispersion (“Kolloidisierung”) of GO for the first time and mentioned the precipitation with strong acids. Thiele was then the first who described the fundamental colloidal properties of GO [84], e.g. the movement of the colloidal particles towards the anode in an electrophoresis experiment, and the increase of the flocculation tendency according to the Hardy–Schulze rule in the series of flocculants $H < K < Ca < Al < Ce$.

Hofmann *et al.* used colloidal dispersions of GO to prepare membranes and measured their properties [85, 86]. These membranes were permeable for water and cations but not for oxygen and nitrogen. An application is difficult because of their instability due to the strong swelling. The fractal dimension of such “membranes” (*single- or multi-layer aggregates*) determined by light scattering has been determined to be 2.5. This has been interpreted by crumpling of the GO layers [87, 88]. Other workers disproved this finding and corrected the value of the fractal dimension to 2.15, indicating flat GO monolayers [89].

Boehm *et al.* [90, 91] succeeded in preparing extremely thin graphite lamellae by reducing dispersed GO via reduction with hydrazine or by thermal treatment (Thiele mentioned this possibility [84]). They found monolayers and aggregates up to four layers. Reduced samples in suspension have a specific surface area of $\sim 800 \text{ m}^2 \text{ g}^{-1}$ determined by means of the methylene blue method, and only $\sim 100 \text{ m}^2 \text{ g}^{-1}$ when measured with the Brunauer–Emmett–Teller (BET) method. Thus, Boehm *et al.* were the first to prepare graphene layers. In the new era, Stankovich *et al.* [92] simply used this method in the context of graphene formation. They showed also that hydrazine attacks the epoxide functions and transfers them to the nitrogen analog (aziridine), which then splits off the nitrogen.

Colloidal dispersions of GO have been used by Matsuo *et al.* to prepare GO–polyethylene oxide nanocomposites by flocculation of GO with the polymer [93, 94]. Later, synthesis of other nanocomposites, e.g. poly(vinyl acetate), polyacrylamide, poly(vinyl alcohol) [95–97] (and references therein) were reported. Almost at the same time Kotov *et al.* [98] described highly organized GO–polymer nanocomposites by means of layer-by-layer deposition using GO colloidal dispersions. Only a few research groups have used this elegant method [99–101].

1.4.5 GO Acidity

Again, Brodie [2] in 1859 as well as Gottschalk [7] in 1865 described the acidic properties of GO by the reaction with litmus. Thiele was the first to start a thorough investigation of the acidic properties of GO in 1937 [35]. He found that an aqueous NaCl solution becomes strongly acidic when GO is soaked in it. Thiele explained this observation by a release of protons from GO and a simultaneous uptake of sodium ions with the formation of a graphitic acid sodium salt. In sodium hydroxide solutions, Thiele determined a reversible uptake of sodium up to 800 mval/100 g of GO (mval is the same as mmol).

Almost simultaneously Hofmann and König [46] found that the cation exchange capacity from sodium acetate solutions of increasing concentrations approaches a limit of $\sim 150 \text{ mval}/100 \text{ g GO}$. The most obvious explanation for the acidity would be that there are COOH groups at the external edges of the GO particles. A rough estimate of the possible number of such acidic groups would result in an uptake of sodium in the order of $1 \text{ mval}/100 \text{ g GO}$ [46]. The assumption of a partial destruction of the graphite layers during exhaustive oxidation could lead to a strong increase in the number of COOH groups when the edges of the interior holes are also fully covered with them, as shown in Figure 1.7. Even in such a case, the high cation exchange capacity cannot be explained. Therefore, Hofmann and König concluded that, apart from the carboxylic groups, some acidic OH groups must be present in GO.

Hofmann and Holst [49] observed later that the cation exchange capacity determined with sodium and calcium acetate varies strongly in the range of $27\text{--}184 \text{ mval}/100 \text{ g GO}$ depending on the degree of oxidation. GOs with higher C/O ratios show lower values of the exchange capacity, but there is no systematic correlation. The exchange capacity of GO is much higher when the experiments are carried out with sodium hydroxide. The limiting value is scattered in the range $500\text{--}600 \text{ mval}/100 \text{ g GO}$ depending on the nature of the GO samples used, in fair agreement with the data of Thiele [35].

To get more insight into the acidic properties of GO, Hofmann and Holst [49] carried out methylation reactions. The methylation with methanol and HCl is known to be sensitive for carboxyl groups, whereas diazomethane reacts with different OH groups including carboxyl OH and phenolic OH groups. Only $\sim 30 \text{ mval}$ of $\text{CH}_3\text{O}/100 \text{ g GO}$ have been obtained for the first reaction independent of the pretreatment of GO (wet, dried at 100 , 130 or 180°C). Thus, only the carboxyl groups at the edges have been methylated with this method. The methylation of GO dried at 100°C with diazomethane in ether leads to $\sim 500 \text{ mval CH}_3\text{O}/100 \text{ g GO}$, in fair agreement with the values of the sodium ion exchange

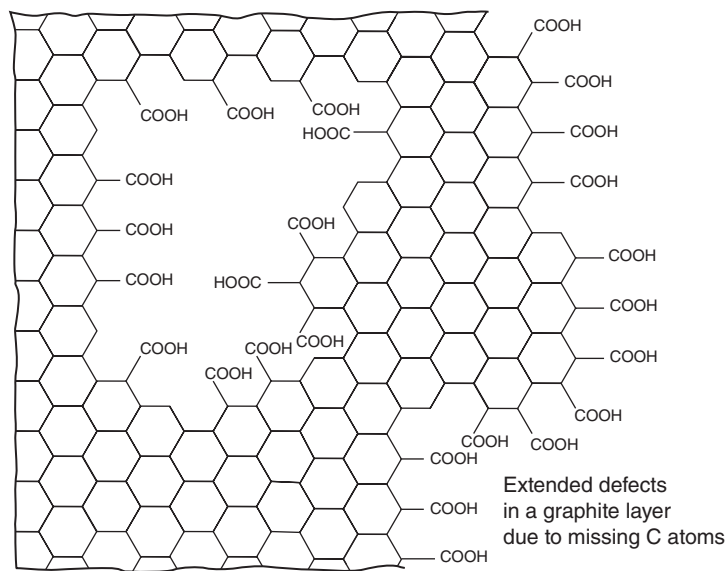


Figure 1.7 Defective graphite layer [46]. Reproduced from [46] with permission of Wiley-VCH

capacity. This value is strongly reduced for a GO dried at 180 °C. Ruess [19] carried out acetylation reactions to transfer carboxyl and acidic OH groups into acetic esters by treating GO with acetic acid anhydride and a trace of sulfuric acid in closed ampoules at 70 °C. The amount of acetic acid bound to OH groups in GO is again in the range 500–600 mval/100 g GO. When he carried out the acetylation reaction in a dioxane solution, the amount of inserted acetate was in the order of 800 mval/100 g GO, the highest values of the cation exchange capacity (CEC) found by Thiele [35]. Ruess explained the difference between the two methods by the enhanced diffusion of the reactant to the acidic sites, because dioxane is co-intercalated and props up the interlayer expansion to 9–10 Å. He suggests that the acetylation reaction without an additional solvent and the methylation reaction with diazomethane in ether were not finished because of retarded diffusion in the constrained interlayer space; in these cases the layer expansion amounts only 3–4 Å.

Pallmann [75] and Hamdi [29] confirmed the values of the exchange capacity determined by Hofmann and Holst [49]. Pallmann as well as Hamdi compared the cation exchange capacity of GO with those of humic acid, lignin and oxidized lignin, and they found a correlation between the C/O ratio and the cation exchange capacity: it decreases the higher the carbon content. The partially destroyed samples of Hofmann and Holst [49] fit quite well into this correlation.

Hamdi [29] carried out also the first titration experiments monitoring the pH change in the supernatant solution versus the applied quantity of mval NaOH/g of GO (Figure 1.8, left). The titration curve shows two well-pronounced inflection points. If they are not just experimental artifacts, the one at a pH of 10.5 corresponds to the number of OH groups that can be deprotonated with NaOH solutions, with methylation or esterification. The pH of the other inflection point is in the order of the pK_a values of phenols. The maximum deprotonation that can be achieved with acetate solutions (~100 mval/100 g GO) leaves no trace in the pH curve. Of the recently published titration experiments [76, 102, 103], one [103] seems to be compatible with the previous data of Hamdi [29], whereas the other two show a continuous featureless increase of pH with increasing amounts of NaOH. All four titration curves start at a pH of ~4.

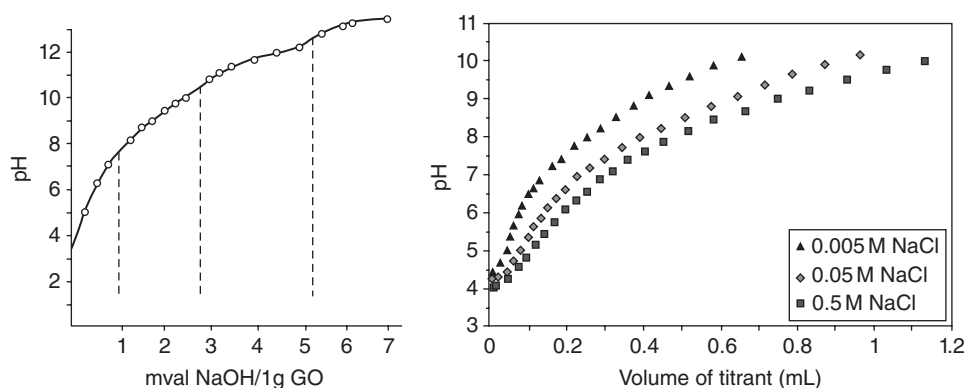


Figure 1.8 Titration curves of Hamdi [29] (left) and Szabó et al. [102] (right). (left) Reproduced from [29] with permission of Springer (right). Reproduced from [102] with permission of Elsevier

The amount of exchangeable protons is roughly half of the expected value when one assumes that all hydrogen determined by chemical analysis (including the hydrogen of not extractable water, which amounts to 7–8%) is bound as OH to the carbon grid. When the carefully dried GO samples are treated with sodium ethylate, it is possible to deprotonate also those OH groups which cannot be exchanged by highly concentrated NaOH solutions [16, 48].

Scholz and Boehm [16] collected all information available about deprotonation (titration) experiments for the three different types of GOs (Brodie, Staudenmaier and Hummers–Offeman), showing no clear distinction between them. The scatter of available data could be due to the properties of the GOs (particle size, degree of oxidation and degree of decomposition), the equilibration time, the deprotonation methods applied and the skill of the workers. The results of the exchange experiments of Thiele, Hofmann and Boehm indicate that there are four different types of OH groups with differing acidities:

- OH deprotonated with Na ethylate
 pK_a values 14–17 tertiary alcohols (sp^3 C)
- OH deprotonated with NaOH
 pK_a values 10–12 enols, vicinal diols
 pK_a values 7–9 phenols
- OH deprotonated with Na acetate
 pK_a values < 8 carboxyl groups, phenols, water (?)

For $pH < 12$, this division seems to be in fair agreement with the inflection points of the titration experiments of Hamdi and the most recent ones of Konkena and Vasudevan [103]. The titration curves found by Szabó et al. [102] were greatly affected by the solution conditions: increasing the pH and the ionic strength promotes the dissociation of acidic surface sites as weaker functional groups progressively participate in the ion exchange process, and the electrolyte provides an effective shielding for the surface charge. The acidity and surface charge characteristics were also found to depend on the degree of oxidation. Thus, their study points out that additives such as acids, bases and salts affect the surface charge behavior, which, in turn, may reflect the colloidal stability of their aqueous dispersions.

In addition, the question arises whether it is really possible to define discrete pK_a values for OH groups in the constrained space of the interlayer galleries in which an increasing electric field is created by the deprotonation of the OH groups and the concomitant charging of the GO layers partially shielded by the uptake of cations. In addition, the NMR experiments (dipolar dephasing, short contact time measurements) of Mermoux et al. [18] and He et al. [104] show that the protons of the OH groups and of the bound water molecules are in strong van der Waals interactions to the neighboring O atoms and to the carbons on which the atoms are attached. This may enhance their acidity so that they take part also in the deprotonation reactions.

1.4.6 Intercalation and Functionalization Reactions

In 1962, Slabaugh and Seiler intercalated ammonia into GO for the first time [105]. They carried out the reaction at temperatures between -25 and -45°C and they found an exceptionally high ammonia uptake of ~ 170 mg/g GO, which corresponds to the total amount of OH groups determined by Clauss *et al.* [48]. Later Seredych and Badosz found an ammonia uptake of ~ 18 mg/g GO prepared by the “Brodie method”. These authors explained the

uptake by the neutralization of the carboxylic groups and the deprotonation of interlamellar weakly acidic OH groups [106]. The $\text{GO}_{\text{Hummers-Offeman}}$ takes up even more NH_3 (~60 mg/g GO) because it forms $(\text{NH}_4)_2\text{SO}_4$ with the sulfate groups covalently bound to GO (first proposed by Boehm and Scholz [30] and later by Titelman *et al.* [107]) and detached from the GO by the action of the superoxide radical anion present in GO [108].

Whereas Kohlschütter and Haenni [10] and earlier authors discussed the solubility and insolubility of GO, Hofmann *et al.* [15] described for the first time reactions of solvents with GO in terms of swelling. Kohlschütter and Haenni mentioned the insolubility of GO in alcohols, ether, benzene, toluene, xylol, acetone, carbon disulfide and chloroform. Hofmann *et al.* [15] stated that GO swells in many polar liquids, e.g. ethanol, acetic acid, acetone and red fuming nitric acid, but they do not give layer distances. Derksen and Katz [78] gave for the first time the layer distance of GO swollen in ethanol, which is 9.3 Å. These authors show also that the admixture of ethanol or tannin to water reduces the layer distance with respect to the fully hydrated GO.

Ruess [19] discovered that dioxane is the only swelling agent that leads to some ordering in the GO compound, as indicated by the appearance of up to six 00 l reflections (normally only one or two 00 l reflections are observed). Therefore, he used this intercalation compound to improve his structural analysis.

“Interlamellar sorption complexes” of a great number of organic compounds were studied for the first time by Cano-Ruiz and MacEwan [109, 110] following the research program of MacEwan first applied to montmorillonite and halloysite [111]. They showed that non-polar molecules like alkanes, PAHs, CS_2 or long-chain alcohols are not taken up in the interlayer space. For various other molecules, the insertion into the interlayer galleries can be questioned. If the so calculated expansions are ≤ 3 Å, an uptake of organic molecules in the interlayer space is highly improbable because it affords an expansion of at least 3.5 Å, the smallest possible dimension for an organic molecule. Layer expansions of 4–5 Å have been found for various aliphatic alcohols, glycol, glycerol, other diols, phenol, aliphatic and aromatic amines, and aliphatic and aromatic nitro-compounds. Significantly higher layer expansions have been described for aniline or pyridine and long-chain aliphatic alcohols and amines. Intercalation of amines is preferred with respect to the uptake of other molecules because they undergo acid–base reactions like ammonia with particular OH groups in the interlayer space forming ammonium cations. This effect leads to a higher uptake of amines over that of the alcohols. Recently, Bourlinos *et al.* have shown that amines are intercalated easily in GO, but not ammonium ions [72]. They show also that tertiary amines are hardly inserted in GO [72].

Subsequent papers were exclusively devoted to the uptake of long-chain alkyl alcohols and amines (up to 16 C atoms) [112, 113] (and references therein). These compounds found increased attention after their discovery by MacEwan [111] and Jordan [114, 115] in 1948–1959, because of the membrane-like arrangements of the alkyl compounds in the interlayer space. Krüger-Grasser continued this work, but used a sodium-loaded GO for her studies; thus she transferred GO to a montmorillonite-like system [116]. Correspondingly, she found much higher layer distances (up to 50 Å) and could also insert long-chain alkyl alcohols. In addition, mixtures of alcohols and amines have been intercalated. These systems allow the selective adsorption of hydrophobic solvents from their mixtures [117]. Matsuo *et al.* [118] used the sodium salt of GO to insert quaternary ammonium surfactants $[\text{R}_3\text{NC}_n\text{H}_{2n+1}]^+$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5; n = 12, 14, 16$)

and $[C_{16}H_{33}NC_5H_5]^+$. In subsequent papers they used them for selective adsorption of PAHs (e.g. [119, 120]).

Due to the reactive oxygen atoms in the interlayer space of GO, the uptake of organic molecules (intercalation) can be accompanied by the reaction of some of the reactive species taken up. The first examples of this functionalization were realized with two very reactive organic species – diazomethane and acetic acid anhydride – both reacting with the OH groups with the formation of a methyl ether and an acetic acid ester, respectively [19, 47, 49]. Both reactions have been used to determine acidic sites on GO (see section 1.4.5). Aragón de la Cruz and MacEwan [113] and later Krüger-Grasser [116] intercalated long-chain alkyl compounds into these functionalized GO. However, the functionalization leads to a reduced uptake of these compounds.

Later the functionalization was used to identify the functional groups on GO by specific reactions [20, 55, 104, 121]. While in the cases of acetylation, ethylation and the reaction with an isocyanate, the specific functionalization could be confirmed by NMR, most of the other reagents studied did not lead to detectable changes in the NMR spectrum. *In all the studies a new peak at about 110 ppm has been assigned to the formation of phenols. Protonation/deprotonation reactions and additions of water or OH groups like those proposed by Dimiev et al. [76] could also induce phenol formation near defect sites apart from epoxide ring opening reactions.*

Bourlinos *et al.* [72] suggested that nucleophilic attack on epoxides and covalent bonding is the main mechanism for the uptake of primary aliphatic amines by GO. This conclusion has been drawn mainly from the observation that the treatment of amine–GO complexes with hot ethanol or aqueous NaOH solution does not reduce the layer distance significantly.

Bourlinos *et al.* [72] and Matsuo *et al.* [121] were able to silylate the hydroxyl groups of GO, forming C–O–Si bonds. The product is stable up to 300 °C. Since that time the functionalization of GO has become a new field of research.

1.4.7 Functional Groups, their Reactions and their Relation to GO Formation and Destruction

The thermal decomposition behavior of GO is indicative of a reactive oxygen function. The 1,3-ethers of Ruess are not as reactive as the 1,2-ethers. Peroxide groups would be even more reactive, but the evidence for peroxides in GO is weak. The H_2S , the thiourea and probably the iodide reactions seem to be indicative for epoxide functions.

The argument of Ruess that typical nucleophilic addition reactions do not occur in GO is not a convincing argument against epoxides. Nucleophilic ring opening reactions on epoxides start with the addition of the nucleophile from the opposite site of the epoxide oxygen. But both sites of the carbon grid are covered with a more or less densely packed oxygen layer, which is negatively polarized. So the access of the nucleophiles to the carbon atoms is restricted to defects in the oxygen coverage. This may retard the reaction considerably. And indeed steric hindrance by bulky substituents on the opposite site of the epoxide oxygen prevents any nucleophilic reaction [122].

Hydronium ions in the interlayer space could induce ring opening of epoxides via a proton transfer to the epoxide oxygen followed by the covalent bonding of a hydroxyl group to the carbocation [59, 60, 123]. Electrophilic reactions induced by protons can also induce

the transformation of epoxides to phenols, at least for low-molecular-weight PAHs. The transformation to phenols in GO would afford C–C bond breaking, which seems improbable, but it could happen at defects in the carbon grid. Protons could also induce an oxygen walk on the carbon surface, another interesting aspect for GO chemistry [59]. Perhaps electrophilic reactions could be of much more importance in GO than nucleophilic reactions.

1.5 Epilogue

Going through the publications of 150 years or so, it is interesting to see how the mode of scientific work and the style of writing publications have changed, what has been cited in later generations, what has been omitted consciously or subconsciously, and what has been neglected because it could not be understood in later times. These topics would be an interesting case for a study in the sociology of science. I would like to give just a few comments for such a study.

Knowledge of the chemical properties of GO was highly developed by 1919, and it was excellently reviewed by Kohlschütter and Haenni [10]. This remarkable paper and all the previous publications had practically no figures. The experimental conditions were not described separately. The manipulations done were integrated in the very precise and detailed description of the observations made. The experiments were focused on the reaction behavior with respect to other chemical substances, temperature or in vacuum. The observations were mostly qualitative in nature. Analytical results were restricted to the determination of the C/H contents via combustion analysis, as in organic chemistry. The procedure applied was a standard method and not further described.

Worth noting is the debate between Thiele [14, 31, 35, 39] and Hofmann [12, 13, 15, 46, 49]. Thiele was the first to make a statement concerning the functional groups in GO and presented the first structural model. He carried out for the first time the ion exchange reactions, the electrochemical intercalation of sulfuric acid and the electrochemical preparation of GO, and discussed the relation to humic acids. Hofmann in 1934 presented an alternative structural model and criticized Thiele's model with a few pejorative remarks. In 1937, shortly after the paper by Thiele, he presented a confirmation of Thiele's data concerning the ion exchange and admitted the existence of OH groups in GO besides the epoxide functions. He never corrected his structural model; modifications of it were given by his young coworkers, first Ruess [19] and later Boehm [16, 27, 30, 48], maybe because his scientific interests shifted towards clay minerals. It is interesting to look at the style of the publications. Thiele published in the style of previous workers; his publications are narrative and many important experimental details are not reported; exceptions from this attitude were the description of his reduction and his ion exchange experiments. Hofmann was more modern; although he was also narrative in large parts of his publications, he gave the experimental details in a separate part of the publications; one can also recognize in his arguing the influence of physical chemistry.

The research on GO received some stimuli from other fields of research: the invention of XRD, colloid chemistry, ion exchange processes and soil science (i.e. the relation between GO and humic acids). An important aspect was the phenomenon of swelling. In the 1920s macromolecular chemistry was established and it was found that especially biological

macromolecules show a remarkable swelling behavior, which was investigated with XRD [78]. This triggered the corresponding work of Hofmann and his coworkers. In at least one of his publications he called the isolated graphite oxide layers “macromolecules”. Because these macromolecules were layered materials, the swelling could occur in just one dimension. This one-dimensional swelling was also discovered by Hofmann almost simultaneously for the low-charged clay minerals.

The research on GO was for a long time a specialty of solid-state chemists. The most important work was done by researchers in France and Germany. Therefore, many important publications on GO were written in German. This is a problem for estimating the value of previous work in the field today.

In 2015 one can say the following about GO from the point of view of scientific activities over the 150 years from 1855 to 2005: GO is a metastable non-stoichiometric solid carbon compound whose structure has not been fully established. It is a tricky intermediate state between over-oxidation and self-destruction. While all the information was available, nobody had drawn this conclusion in 1970. Only under careful adjustment of the preparation conditions, starting with the choice of the graphite (crystalline, powders, particle size), the control of the water content of the acids applied, the temperature and time regime, exclusion of sunlight during work-up, and the drying conditions, can one obtain GO with reproducible properties. A useful guide for the choice of the reaction conditions is the almost neglected publication of Boehm and Scholz [30]. The sample with a residual water content of about ~8% should have a C/O ratio of 3 ± 0.3 and in the NMR spectrum there should be only three peaks at ~60 ppm, ~70 ppm and ~130 ppm.

Comparing recent work on GO and the historical material, a statement of an older colleague of mine came to my mind: “You can redo the same thing in 25 years, and almost nobody will recognize it.” I also feel I should mention a statement by the English mathematician and philosopher, A.N. Whitehead, who wrote in a footnote of his most famous book *Process and Reality*: “All philosophical concepts are just footnotes to Plato.” So, in a manner of speaking, most workers active in the field of GO research since 2005 are just preparing footnotes to the seminal works of Kohlschütter, Hofmann and Boehm, and I must confess that my own work is also nothing else. I realized that I have overlooked also many interesting aspects in the previous works when we wrote our own papers. I fear this is quite normal, because you can recognize and understand the importance of details in publications only when you have your own experimental experience in a new field into which you have jumped.

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