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Structure of Graphite Oxide Revisited^{||}

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Graphite oxide (GO) and its derivatives have been studied using ¹³C and ¹H NMR. NMR spectra of GO derivatives confirm the assignment of the 70 ppm line to C–OH groups and allow us to propose a new structural model for GO. Thus we assign the 60 ppm line to epoxide groups (1,2-ethers) and not to 1,3-ethers, as suggested earlier, and the 130 ppm line to aromatic entities and conjugated double bonds. GO contains two kinds of regions: aromatic regions with unoxidized benzene rings and regions with aliphatic six-membered rings. The relative size of the two regions depends on the degree of oxidation. The carbon grid is nearly flat; only the carbons attached to OH groups have a slightly distorted tetrahedral configuration, resulting in some wrinkling of the layers. The formation of phenol (or aromatic diol) groups during deoxygenation indicates that the epoxide and the C–OH groups are very close to one another. The distribution of functional groups in every oxidized aromatic ring need not be identical, and both the oxidized rings and aromatic entities are distributed randomly.

Introduction

Graphite oxide (GO) was first prepared in the 1850's by oxidizing graphite with KClO₃/HNO₃.^{1,2} The various structural models of GO proposed over the years^{3–8} reflect the then current characterization methods and assume the presence of various oxygen-containing functional groups. However, because of the nearly amorphous nature of GO, its precise structure is still uncertain as diffraction methods^{3,5,7,9} are of little help in deciding which model is correct.

On the strength of solid-state NMR spectra, Mermoux et al.¹⁰ ruled out the presence of carboxyl groups in the bulk of GO. Although such groups may be present on the surface of the sample, their concentration is too low for NMR detection. To explain the spectra, Mermoux et al. went back to the model proposed by Ruess⁵ which calls for the carbon grid to be in chairlike conformation and the presence of 1,3-ether and C–OH functional groups. They assigned the ¹³C lines at 60 and 70 ppm to 1,3-ether and C–OH groups in close proximity to each other and the line at 130 ppm to double bonds.¹⁰ The resulting modified Ruess model involves isolated double bonds.⁶

However, even this most recent model leaves unanswered questions: Are the C–O–C groups really 1,3-ethers? How are the C–O–C and C–OH groups and double bonds distributed over the carbon grid? Are the double bonds aromatic or isolated? Concerning the first question, we note that ¹³C chemical shifts in ethers, including cyclic ethers, are ca. 70 ppm and above.¹¹ Only 1,2-ethers (also known as epoxides or oxiranes) have low chemical shifts such as those reported by Mermoux et al.¹¹ Also, chemical preparation of 1,3-ethers^{12,13} requires conditions which are unlikely to be realized in a solution of KMnO₄ in H₂SO₄. As to the second question, all models

proposed so far suggest a very regular distribution of the functional groups, as in an ordered unit cell. This cannot be the case, given that GO is nearly amorphous and its stoichiometry varies depending on the method of preparation (the ideal stoichiometry has never been achieved) and the kind of graphite used. As to the third question, the broad peak at 130 ppm cannot be unambiguously assigned to isolated or to aromatic double bonds, although it is unlikely that isolated double bonds, which are the easiest to oxidize, could resist the action of KMnO₄. Finally, the structural model of Mermoux et al. does not account for the strongly oxidative character of GO.

Since NMR spectra of GO itself cannot answer these questions, we have followed our initial NMR study^{14,15} by further reactions of GO with reagents specific for the different oxygen-containing C–O–C and C–OH functional groups. These reactions also involve nucleophilic or electrophilic attack and deoxygenation which could prove the existence of the epoxide groups. Some of the reagents listed in Table 1, such as NCO, have been used for the first time; others, such as iodide, have long featured in GO research.

Experimental Section

Samples. Starting Materials. The parent sample of GO was prepared by oxidation with KMnO₄/H₂SO₄ according to the method of Hummers and Offeman.¹⁶ The sample was washed with 5% aqueous HCl and dialyzed^{17,18} for 7 days in the dark (with several changes of the dialyzing water) until the solution was free of sulfate and chloride ions, dried at 40 °C in 10^{–2} Torr vacuum to remove adsorbed water, and finally pulverized and dried in 10^{–5} Torr vacuum for 2 days at room temperature. The interlayer distance of the product was 7.1 Å, corresponding to a water content of 8–15%.

Treatment of GO. Fully hydrated GO was prepared by keeping the parent sample in a desiccator over a saturated aqueous solution of NaCl. Thermal decomposition was studied on a sample of GO treated in a vacuum at 100 °C for 24 h.

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^{||} This paper is dedicated to Professor H. P. Boehm on his 70th birthday.

TABLE 1: Reactants Used for the Preparation of GO Derivatives

reactions specific for C–OH function	reactions specific for C–O–C function (epoxide)		
	deoxygenation	electrophilic attack	nucleophilic attack
acetic acid anhydride (Ac ₂ O) hexamethyldisocyanate (NCO) sodium ethoxide (NaOEt)	potassium iodide (KI) triethyl phosphite (P(OEt) ₃) triethylamine (NEt ₃) triphenylphosphine (PPh ₃) thiourea	dimethylsulfoxide (DMSO) acetic acid anhydride (Ac ₂ O) maleic acid anhydride (MAA)	pentylamine (C ₅ NH ₂) ethylenediamine (EDA) sodium ethoxide (NaOEt) sodium hydroxide (NaOH)

Dehydrated GO was prepared by drying GO over P₂O₅ for 4 weeks in order to remove as much water as possible, and then transferred to a MAS rotor in a drybox.

GO Derivatives. Separate samples of GO were soaked in aqueous solutions of KI, thiourea and NaOH, an ethanolic solution of NaOEt, a dioxane solution of MAA, or in pure reagents [P(OEt)₃, PPh₃, NEt₃, C₅NH₂, EDA, NCO, Ac₂O, and DMSO] for at least 24 h, and in some cases for 7 days (C₅NH₂ and EDA) or longer (2 weeks for Ac₂O). In the case of DMSO, the BF₃–ether complex was added as a catalyst. With the exception of aqueous solutions, the reaction mixtures were kept under argon in order to exclude water and oxygen. The reactions in aqueous solutions and amines were carried out at room temperature, other reactions at 40–50 °C, with the exception of the reaction with Ac₂O, which was carried out at 70 °C.⁵ Samples treated in aqueous solutions were washed with water and all others with ether or methylene dichloride and were finally dried in a vacuum (10^{−3} Torr) for 24 h. The reagents were used as obtained from Fluka. The solvents were distilled and stored over the 4 Å molecular sieve prior to use.

Sample Characterization. Interlayer distances were determined by Debye–Scherrer photographs with Ni-filtered Cu Kα radiation. ¹³C and ¹H magic-angle-spinning (MAS) NMR spectra were recorded using a Chemagnetics CMX-400 spectrometer operating at 100.6 and 399.9 MHz, respectively, and an MAS probehead with zirconia rotors 4 mm in diameter driven by nitrogen gas. ¹³C Bloch decay spectra with high-power (> 60 kHz) ¹H decoupling were recorded with spinning at 3.5–10 kHz, 45° pulses of 1 μs duration, and 20 s recycle delays. Conventional and short-contact-time ¹H–¹³C CP/MAS spectra (SCT-CP) were recorded with spinning at 3.5–6.5 kHz, 4 μs ¹H 90° pulses, 4 ms and 0.05 ms, contact times and 4 s recycle delays. Aware of the fact that, because of the possibly different cross-polarization efficiency for different protons, CP/MAS is in principle not quantitatively reliable, we have therefore used several delay times with each sample. Dipolar-dephased ¹H–¹³C CP/MAS spectra (DD-CP) were measured with spinning at 3.5–6.5 kHz, 4 μs ¹H 90° pulses, 4 ms contact times, 50–400 μs delays, and 4 s recycle delays. While conventional ¹³C CP/MAS spectra contain resonances from all carbons in the sample, the SCT-CP spectra show only resonances from carbons which are very close to relatively immobile, bonded and/or nonbonded protons, and the DD-CP spectra show only quaternary carbons and mobile CH₃ groups. Different spinning rates were used to distinguish central lines from sidebands. The Hartmann–Hahn condition was established using hexamethylbenzene. ¹H Bloch decay measurements were recorded with MAS at ca. 10 kHz, 45° pulses of 2 μs duration, and 4 s recycle delays. ¹³C and ¹H chemical shifts are given in ppm from external tetramethylsilane (TMS). Variable-temperature ¹H and ¹³C Bloch decay and ¹H–¹³C CP measurements were carried out in the 123–473 K temperature range.

Results and Discussion

Reaction of GO with Potassium Iodide. The ¹³C NMR spectrum of GO treated with KI for 3 days is almost identical

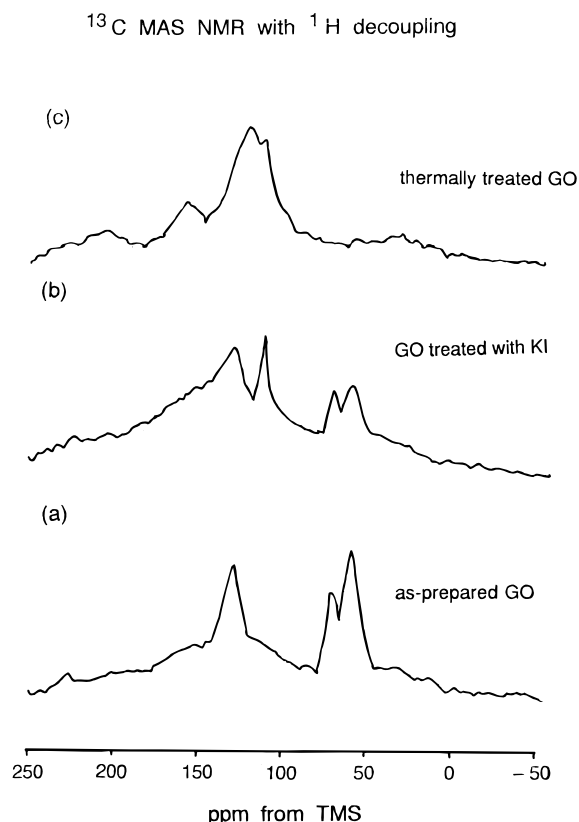


Figure 1. ¹³C MAS NMR spectra with ¹H decoupling of (a) GO, (b) GO–KI, and (c) GO calcined at 100 °C in a vacuum.

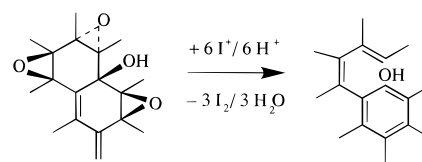


Figure 2. Reaction of GO with KI.

to that of the parent material.¹⁵ However, the intensity of the resonances at 60 and 70 ppm from a sample treated for 7 days is lower than in the parent sample (Figure 1b). A broad line centered at 130 ppm (with a shoulder to higher chemical shifts) appears, indicating major structural rearrangement, and there is a new peak at 110 ppm. We believe that the shoulder above 130 ppm and the peak at 110 ppm are due to the formation of phenol and/or aromatic diol species.^{11,15,19} Formation of such entities requires that (1) OH functional group(s) attached to the carbon ring are converted to phenols/aromatic diols, (2) at least one double bond is present in the ring or formed by deoxygenation of the epoxide, and (3) bonds are broken at the position of the OH group during “rearomatization” (see Figure 2). Iodide is capable of such deoxygenation.²⁰

The reduced intensity of the peak at 60 ppm (Figure 1b) indicates that epoxide deoxygenation by I[−] does occur. The reduced intensity of the peak from the C–OH group at 70 ppm is probably due to the transformation of C–OH to a phenol/

TABLE 2: NMR Results of the Reaction of GO with Various Reagents

reagent	interlayer distance [Å]	^{13}C NMR chemical shift ^a (ppm)		
		from GO	from reagent	other features
P(OEt) ₃	7.0	60, 70, 130	16, 62	new line: 110 SCT-CP: 60, 70
PPh ₃	9.6	60, 70, 130	130 ^b	new line: 110 SCT-CP: 70 only
NEt ₃	7.5	60, 70, 130	156, 177 ^b	new line: 110 SCT-CP: 70 only
thiourea	7.5	sample explodes during acquisition of ^{13}C MAS spectrum		
C ₅ NH ₂	13.6	60, 70, 130	14, 22, 29, 40	
EDA	9.1	60, 70, 130	41, 165	
DMSO	9.3	60, 70, 130	35, 38	new lines: 74, 110
Ac ₂ O	8.4	60, 70, 130	20, 170, 177	new line: 110 ^b
MAA	9.1	60, 70, 130	132, 167	CP: 132, 139, 168, 172 SCT-CP: 68 only
NCO	9.6	60, 70, 130	28, 40 160	SCT-CP: 70 only
NaOEt	9.1	60, 70, 130	15	

^a Only CP data of reagents and SCT-CP data of GO are shown.^b Very weak.

aromatic diol with a chemical shift of above 130 ppm. We note that GO reacts with HI thereby liberating iodine,^{21,22} which is considered by Hofmann et al. as evidence for the existence of epoxide groups.^{3,4} Authors of later publications took the reaction of GO with HI as indicating the presence of hydroperoxides. However, it is known that the ^{13}C chemical shift of a C–OOH group is 10–20 ppm higher than that of the corresponding alcohol. This interpretation can be ruled out by the absence of spectral features in the 80–90 ppm range of the GO spectrum. The only remaining explanation for the iodide reaction is epoxide deoxygenation. 1,3-ethers do not show this type of reaction.²⁰

Thermal Decomposition of GO. Upon calcination of GO at 100 °C in a vacuum, the peaks at 60 and 70 ppm in the ^{13}C NMR spectrum (Figure 1(c)) disappear, and the dominant peak is at 122 ppm. The 110–160 ppm spectral region resembles that for GO treated with KI. The resonances at 110–120 and 160 ppm are from phenolic groups, indicating deoxygenation. The reaction appears to be much more quantitative than in the case of KI. However, decomposition of GO is known not to be accompanied by a liberation of oxygen, and CO and CO₂ are the usual decomposition products.³ Hofmann explained the absence of oxygen evolution in terms of the highly reactive oxygen atom being released from the GO structure and reacting with the surface of GO to form CO and CO₂. We believe that, under the moderate conditions of vacuum and temperature used in our work, we have obtained an intermediate decomposition product of GO. When GO is treated at higher temperatures, the usual final decomposition product is highly disordered oxygen-containing graphitic carbon,³ which is not easily detected by NMR. The results from sample GO–KI and the thermally decomposed sample strongly support the existence of epoxide (1,2-ether) groups rather than 1,3-ether groups.

Other Reaction Products of GO. The results of other chemical reactions are listed in Table 2 and the ^{13}C spectra of the products are shown in Figure 3. The increased interlayer distances indicate intercalation of PPh₃, C₅NH₂, EDA, DMSO, Ac₂O, MAA, NCO, and NaOEt. Additional resonances from the intercalates in the ^{13}C NMR spectra have been observed for P(OEt)₃, C₅NH₂, EDA, DMSO, Ac₂O, MAA, NCO, and NaOEt. In the case of P(OEt)₃ and PPh₃, the results from XRD and NMR appear contradictory. In GO–P(OEt)₃ the small interlayer distance does not allow intercalation. However, chemical analysis and NMR indicate an uptake of the reagent

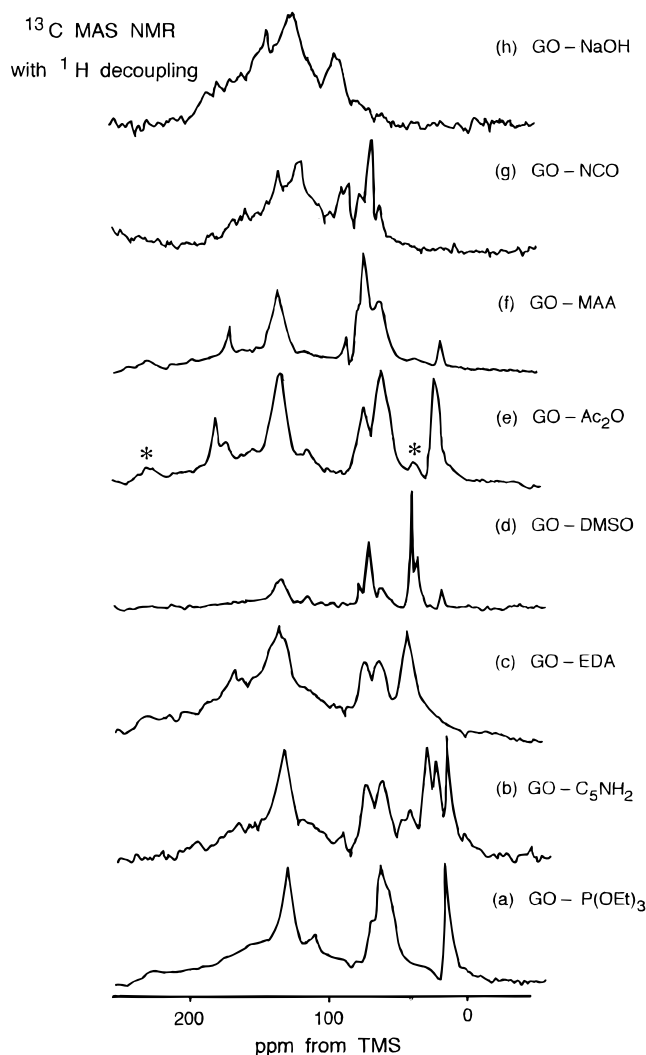


Figure 3. ^{13}C MAS NMR spectra with ^1H decoupling of (a) GO–P(OEt)₃, (b) GO–C₅NH₂, (c) GO–EDA, (d) GO–DMSO, (e) GO–Ac₂O, (f) GO–MAA, (g) GO–NCO, and (h) GO–NaOH. Asterisks denote spinning sidebands.

by the solid. The only explanation is that P(OEt)₃ or the reaction products are bound to the surface of GO. We do not know why the increased interlayer distance in GO–PPh₃ is not accompanied by a ^{13}C NMR line. As some of the intercalate lines in the NMR spectra of the products of the reaction between GO and P(OEt)₃, Ac₂O and NaOEt overlap with the GO lines at 60 and 70 ppm, the intensities of the latter resonances cannot be accurately quantified. The small intensity changes of the 60 and 70 ppm lines in most samples may be caused by insufficiently high reaction temperatures or too short a time for the reagents to react with the functional groups. This means that intercalation and reaction with functional groups are independent processes. In GO–P(OEt)₃, GO–NEt₃, GO–PPh₃, and GO–DMSO there may be a weak additional line at 110 ppm, possibly of the same origin as in the case of iodide and GO calcined in a vacuum. The first three reagents are capable of deoxygenating epoxides.²⁰

Our detailed comments on the various GO derivatives are as follows.

GO–P(OEt)₃. The main peak in the ^{31}P NMR spectrum (not shown) is at –11 ppm and a shoulder at –1 ppm. The latter peak comes from free O=P(OEt)₃ and the former from adsorbed O=P(OEt)₃ or a reaction intermediate. No P(OEt)₃, which resonates at 140 ppm, remains in the sample. The formation

of $\text{O}=\text{P}(\text{OEt})_3$ indicates oxygen release from GO. The ^{13}C peaks at 16 and 62 ppm in Figure 3a are from the $-\text{CH}_2-$ and $-\text{CH}_3$ groups in $\text{O}=\text{P}(\text{OEt})_3$. This assignment is confirmed by the presence of the same strong peaks in the SCT-CP spectrum (not shown). Because the interlayer distance of $\text{GO}-\text{P}(\text{OEt})_3$ is insufficient to accommodate $\text{P}(\text{OEt})_3$, the reaction is likely to occur on the surface of the sample. In this case the chemical reaction does not lead to the removal of the entire $\text{C}-\text{O}-\text{C}$ resonance at 60 ppm.

GO-Thiourea. Thiourea is a deoxygenating reagent.²⁰ We could not acquire ^{13}C MAS or CP/MAS spectra because the sample explodes in the MAS rotor upon applying a high-power ^1H decoupling pulse. This indirectly indicates that the oxygen of the epoxide is replaced by sulfur, forming a very unstable thiirane-like compound,^{23–25} which decomposes on application of the decoupling pulse, with a liberation of sulfur and formation of a double bond.

GO- C_5NH_2 and GO-EDA. The interlayer distance in as-prepared $\text{GO}-\text{C}_5\text{NH}_2$ is 19.6 Å, in good agreement with the literature.²⁶ After the complex was washed and dried in a vacuum, the distance decreased to 13.6 Å, indicating that a large amount of amine (0.4 mole of amine per formula unit of GO) still remained in the interlayer gap after extraction. It is interesting that the interlayer distance in $\text{GO}-\text{EDA}$ is the same when the sample is soaked in the amine solution and in the dry state, and in good agreement with literature data.^{26,27} The reactions with C_5NH_2 and EDA are mainly intercalation.^{26,28,29} In addition, nucleophilic attack probably occurs in both samples, as there is considerable loss of intensity of the peak at 60 ppm (Figure 3b and c). In $\text{GO}-\text{EDA}$ there is an additional glyoxime ^{13}C resonance at 165 ppm. Hamwi and Marchand³⁰ report an NMR spectrum of $\text{GO}-\text{NH}_3$. They interpret the decreased intensity of the 130 ppm peak and the decreased intensity of the 60 ppm peak as due to oxidation of ammonia to nitrogen and abstraction of oxygen from 1,2-epoxide groups, disregarding the fact that the currently accepted structural model of GO does not involve 1,2-ethers. The reaction is far from complete, and the changes in intensity are of similar size to that found in our samples.

GO-DMSO. DMSO reacts with epoxides to form hydroxyketones.³¹ In GO this reaction cannot occur because of the complete substitution of the epoxide carbon atoms with protons. On the other hand, it is known that DMSO is taken up by GO with a change of color from yellow to black. The intense resonance at 38 ppm in the ^{13}C NMR spectrum of $\text{GO}-\text{DMSO}$ (Figure 3d) comes from dimethylsulfone,³² the oxidation product of DMSO, and the peak at 35 ppm from unreacted DMSO. The intensities of the GO peaks at 60 and 70 ppm are low. The peak at 110 ppm probably indicates oxygen removal from GO. The sharp peaks at 15 and 70 ppm are due to the ether used for washing the sample. The latter peak is superposed on the $\text{C}-\text{OH}$ resonance of GO. We are unable to assign the peak at 74 ppm. The formation of dimethylene sulfone and the appearance of the 110 ppm peak again indicate the deoxidation of the epoxide groups of GO.

GO- Ac_2O . Given the short reaction time there is evidence only for the intercalation of Ac_2O and hydrolysis by the residual water.¹⁵ The ^{13}C spectrum is almost unchanged. However, at 70 °C and with a longer reaction time (14 days), additional reactions take place. The intensity of the peak at 70 ppm in the ^{13}C spectrum of $\text{GO}-\text{Ac}_2\text{O}$ (Figure 3e) decreases much more than that of the peak at 60 ppm. The new feature at ca. 170 ppm results from ester formation. This reaction was expected by Ruess who assumed acetylation of the $\text{C}-\text{OH}$

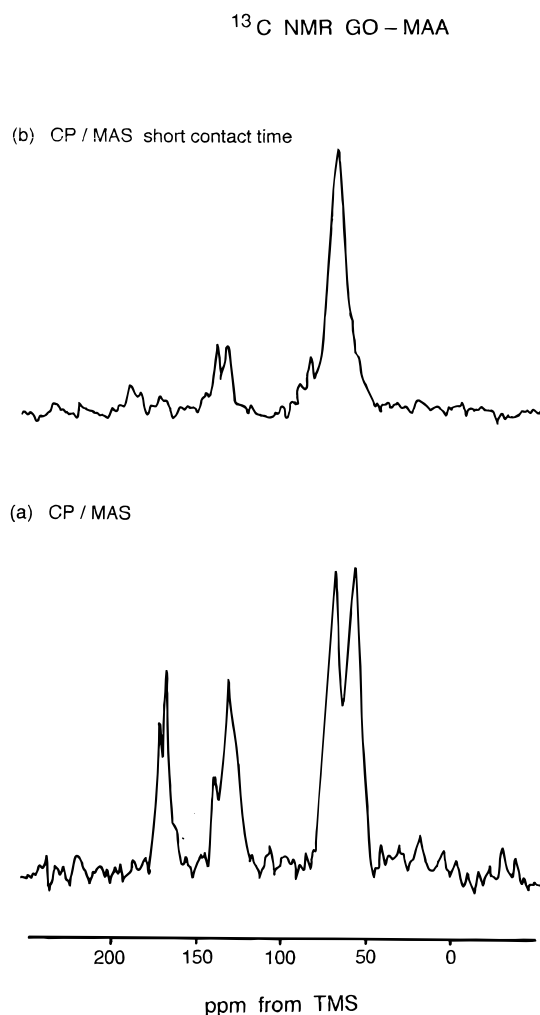


Figure 4. (a) ^{13}C CP/MAS and (b) short contact time ^{13}C CP/MAS NMR spectra of $\text{GO}-\text{MAA}$.

group.⁵ However, ring opening of the epoxide, which would also lead to acetic acid esters, cannot be excluded.³³

GO-MAA. The extent of the intercalation of MAA depends on the solvent, and proceeds in dioxane but not in toluene.¹⁴ The intensity of GO peaks at 60 and 70 ppm is reduced (see Figure 3f). We assign the 170 ppm peak to $>\text{C}=\text{O}$ groups from either MAA or a reaction product. The peak at 85 ppm could come from carbon atoms of the GO layer esterified by MAA, and the peaks at 17 and 70 ppm from the ether used for washing the sample. The CP/MAS spectrum (Figure 4a) shows there is more than one kind of $>\text{C}=\text{O}$ group (172 and 168 ppm) and $\text{C}=\text{C}$ group (132 and 139 ppm). The two peaks, at 139 and 132 ppm, in the SCT-CP spectrum (Figure 4b) provide further proof for the presence of two kinds of $\text{C}=\text{C}$ groups. We believe therefore that MAA is intercalated partly as MAA and partly as reaction products: maleic acid produced during hydrolysis or an ester formed by the reaction of MAA with $\text{C}-\text{OH}$ or epoxide groups. The Diels–Alder reaction does not occur because of the higher rate of hydrolysis of MAA or for steric reasons. It is also possible that isolated double bonds or dienes susceptible to this type of reaction are absent. The spectra of $\text{GO}-\text{MAA}$ provide further support for the presence of the $\text{C}-\text{OH}$ and $\text{C}-\text{O}-\text{C}$ functional groups.

GO-NCO. NCO, here used for the first time for the study of GO, can be expected to react with the $\text{C}-\text{OH}$ groups of GO (forming urethanes) and with residual water. One NCO group of this bifunctional molecule may react with $\text{C}-\text{OH}$ and the

other with water (with the evolution of CO_2), or both NCO groups may react with C—OH forming rings if both C—OH groups are in the same GO layer, or bridges between different layers if the C—OH groups belong to different GO layers. The partial cross linking of GO layers is supported by the intercalation of C_5NH_2 in GO—NCO: the interlayer distance of GO—NCO intercalated with liquid C_5NH_2 is about 5 Å smaller than that of GO— C_5NH_2 . The intensities of the peaks at 60 and 70 ppm (particularly the latter) decrease strongly (Figure 3g), which means that the reaction of NCO with C—OH does occur. This reaction leads to urethanes containing $>\text{C}=\text{O}$ groups responsible for the peak at 160 ppm.

GO—NaOEt. The ^1H spectrum of GO treated with NaOEt contains a single peak at ca. 1 ppm, and the peak from residual water is absent (see Figure 7 in ref 14). The high intensity of the 1 ppm peak indicates that NaOEt is unable to remove protons from the C—OH groups, which is consistent with the $\text{p}K_a$ values of tertiary alcohols. On the other hand, NMR confirms that the EtO^- groups are not removed by washing the sample, indicating that they are bonded to GO more strongly than is usual in adsorption processes. One possible explanation is a nucleophilic attack of EtO^- on the epoxide groups with the formation of an ether and $\text{C}=\text{O}^-$. Since, given the steric restrictions in GO, such nucleophilic attack would be slow, only some of the epoxide rings would be opened. Repeated treatments with NaOEt are therefore required to complete the reaction. Hence subsequent treatment of GO—NaOEt (termed GO—base in ref 14) with another nucleophile will attack the remaining epoxide groups. The transformation of GO—base into GO—ether is thus easily explained.

Role of Water in GO. The DD-CP spectra show that all carbon atoms in GO and all its derivatives are quaternary, while the SCT-CP spectra demonstrate that there are protons close to the carbon atoms of the C—O—C and the C—OH groups. The C—OH groups and water are the only sources of such protons. ^{13}C nuclei may experience different dipolar interactions with different ^1H sources, and the intensity of CP signals is related to the distance between ^1H and ^{13}C nuclei and the motion of ^1H . In GO there are only two kinds of proton sources, and the low intensity of the SCT-CP spectra of GO dried over P_2O_5 indicates that, for short CP contact times, the ^{13}C signal is enhanced almost exclusively by protons belonging to the water molecules. Since we believe that the motion of protons in intercalated water is slow (see Figure 5) and will not significantly reduce the dipolar interaction, the ^1H — ^{13}C CP/MAS spectra of GO may be discussed simply in terms of the $\text{H}\cdots\text{C}$ distances. The SCT-CP results thus indicate that the distance from all carbons to protons in water is smaller than the distance to protons in the —COH groups. Our earlier explanation of the SCT-CP spectra¹⁴ was based on the assumption that the $\text{C}\cdots\text{H}$ distances to the C—OH and C—O—C groups are very similar. If this is not the case, the spectral intensities from carbons in the two groups will be different, given their $1/r^3$ dependence on the $\text{C}\cdots\text{H}$ distance, making our previous assignment of the ^{13}C spectra¹⁴ incorrect. We now have the following evidence that the strength of the interaction between protons and the two kinds of functional groups in question is indeed unequal: (1) The C—OH/C—O—C intensity ratio in the DD-CP spectra at $< 100\ \mu\text{s}$ delay times is constant, in agreement with Mermoux et al.,¹⁰ but changes for longer delay times. (2) The 60 ppm/70 ppm intensity ratios in the SCT-CP and CP/MAS spectra are different. (3) The SCT-CP spectra of the sample exchanged with D_2O contain only the 70 ppm peak.¹⁴ The SCT-CP spectra of some GO derivatives (Table 2) also

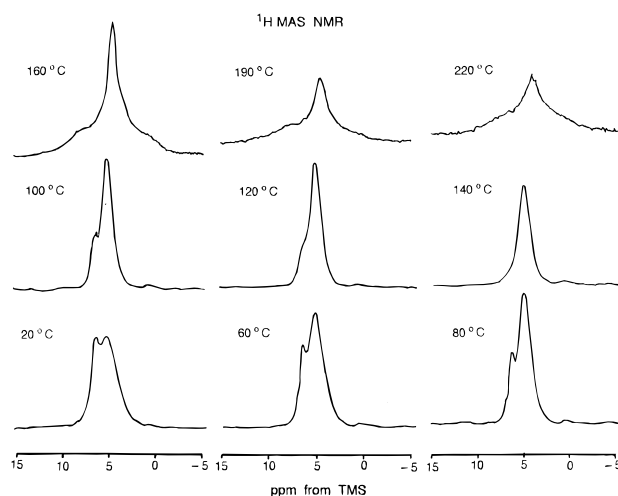


Figure 5. Variable-temperature ^1H MAS NMR spectra of fully hydrated GO. The relative intensity scales for the spectra in the 20–140 °C and 160–220 °C temperature ranges are 13 and 1, respectively.

contain only the 70 ppm peak. Their formation has led to the removal of most of the water as in the case of treatment with D_2O .

These results show that the protons are closer to the C—OH groups than to the C—O—C groups. We have proposed¹⁴ contributions from the protons both across the GO layers and within the same layer. However, as the 60 ppm/70 ppm intensity ratio in the SCT-CP spectrum of the sample intercalated with Ac_2O is the same as in the parent sample of GO, there appears to be no cross-layer interaction. This means that the strongly bound water molecules, locked in the “defects” in the layers of oxygen atoms from the C—O—C and C—OH groups, are an integral part of the GO structure.⁹

We have performed further experiments in order to elucidate the role of water in GO. The ^1H NMR spectra of fully hydrated GO (Figure 5) contain two resonances from water, at 6.6 and 5.4 ppm, corresponding to two different kinds of water molecules. Because of the high water content of this sample, the line from the C—OH group is insufficiently intense to be seen. The line at 6.6 ppm decreases in intensity with increased temperature and completely disappears above 140 °C. The peak at 5.4 ppm maintains its position and intensity until 160 °C, when it decreases significantly in intensity and shifts to ca. 6 ppm. The intensity decreases further as the temperature increases to 220 °C. Our results are in agreement with those of Yazami et al.,³⁴ although their experiments were performed in a vacuum before the structure of GO collapsed and thus at lower temperatures than described here. We assign the peaks at 6.6 and 5.4 ppm to mobile water and strongly bound water, respectively. The considerable line width of the ^1H NMR resonances from “structural” water at high temperatures (Figure 5) indicates its low mobility. XRD (pattern not shown) shows that upon high-temperature treatment, which involves removal of the strongly intercalated water, the structure of GO becomes significantly less ordered.

New Structural Model. On the basis of the evidence from NMR experiments on additional GO derivatives, we confirm the assignment of the 70 ppm line to C—OH groups.¹⁰ NMR spectra of GO treated with iodide, as well as the course of the thermal decomposition of GO, strongly argue for the presence of epoxides. We note that the formation of 1,3-ethers requires a complex sequence of reactions, unlikely to be realized in $\text{KMnO}_4/\text{H}_2\text{SO}_4$. We therefore assign the 60 ppm line to epoxide (1,2-ether) groups, instead of 1,3-ether groups as suggested by

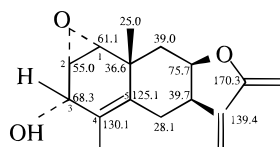


Figure 6. Model compound for the assignment of the ^{13}C NMR spectra of GO. Carbons 1 and 2, carbon 3 and carbons 4 and 5 correspond to C—O—C, C—OH, and double bonds in the structure of GO, respectively.

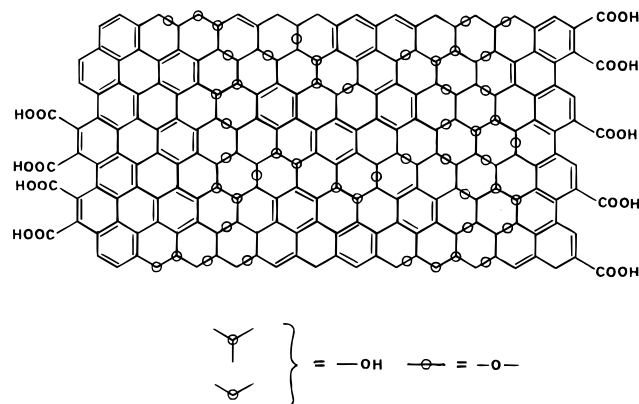


Figure 7. New structural model of GO.

Mermoux et al.¹⁰ The main contribution to the 130 ppm peak is from aromatic entities and conjugated double bonds. This assignment is supported by the ^{13}C chemical shifts found in a natural sesquiterpenoid compound (Figure 6).³⁵ The concentration of isolated C=C double bonds is likely to be very low, as they are easy to oxidize, and varies with the degree of oxidation of GO.

The formation of phenol (or aromatic diol) groups during deoxygenation indicates that the epoxide and the C—OH groups are very close to one another. Apart from the double bonds, the “oxidized” benzene rings contain epoxide and C—OH groups. It is not necessary for the distribution of functional groups in every oxidized aromatic ring to be identical, and both the oxidized rings and aromatic entities are distributed randomly. The layers of GO terminate with C—OH and —COOH groups, consistent with infrared spectroscopic results.^{7,22,36}

Having considered the information discussed above, we arrive at the following picture. The structure of GO involves two kinds of regions: aromatic regions with unoxidized benzene rings and regions containing aliphatic six-membered rings (Figure 7). The relative size of the two regions depends on the degree of oxidation. Aromatic entities, double bonds and epoxide groups give rise to a nearly flat carbon grid, a conclusion supported by the structure of smaller molecules containing epoxide groups.^{37–39} Only the carbons attached to OH groups are in a slightly distorted tetrahedral configuration, resulting in some wrinkling of the layers. The functional groups lie above and below the carbon grid forming a layer of oxygen atoms of variable concentration. This arrangement of negatively charged oxygen layers could prevent nucleophilic attack on carbon atoms, explaining the relative chemical inactivity of the epoxide groups in GO.³⁹

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