

New results on the chemistry of graphite oxide.

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Graphite oxide (G.O.), also called graphitic acid, is a layer compound derived from the graphite structure. It is formed by the reaction of substances which easily give off oxygen, e.g. $\text{HClO}_3/\text{ClO}_2$, Mn_2O_7 or O_3 , on graphite salts of the type $\text{C}_{24}^+\text{X}^-\cdot 2\text{HX}$. G.O. formation proceeds the faster and the more thoroughly, the more water there is present in the oxidation mixture, up to a critical concentration. When this H_2O concentration is exceeded, the first stage of the graphite salt becomes unstable and no G.O. is formed. G.O. may be obtained by electrochemical oxidation, too. Practically no carbon is lost in the synthesis of G.O. and, hence, no vacancies are formed in the carbon network of the layers.

The properties of G.O. depend to a large extent on the method of its preparation. There are differences not only in composition but also in interlayer spacing in the dry state and in the adsorption properties. Previously, systematic errors occurred in the analyses and too high oxygen contents were found. The composition, deflagration points and other properties of G.O. samples prepared by different methods are presented in the Table. Because of the intracrystalline swelling property of G.O. and the variable water content the results (average for many samples) refer to samples which were dried extensively in a high vacuum.

Whereas G.O. prepared by the Brodie method is, after two- or threefold-oxidation, nearly white and darkens only very slowly on exposure to ultra-violet light, G.O. made by the Staudenmaier method darkens within a few hours. G.O. obtained by the Hummers and Offeman procedure is dark brown from the beginning.

The G.O. structure contains, apart from carboxyl groups at the periphery of the layers, tertiary hydroxyl groups and carbonyl groups as well as double bonds in the layers. These groups were determined by various analytical methods. The

Table: Influence of the preparation method on the properties of G.O.

Author:	Brodie ¹⁾	Staudenmaier ²⁾	Hummers and Offeman ³⁾
Oxidizing mixture	$\text{HNO}_3 + \text{NaClO}_3$	$\text{H}_2\text{SO}_4/\text{HNO}_3 + \text{KClO}_3$	$\text{H}_2\text{SO}_4 + \text{NaNO}_3 + \text{KMnO}_4$
Composition	$\text{C}_{80}^{0.3.5}\text{H}_{2.8}$	$\text{C}_{80}^{0.4.7}\text{H}_{2.9}$	$\text{C}_{80}^{0.3.7}\text{H}_{2.5}$
Deflagration point	315 - 325°	240 - 262°	200 - 228°
Interlayer spacing	5.9 ₅ Å	6.3 ₂ Å	~ 6.7 Å
Specif. surface area (BET, N ₂)	2 m ² /g	75 - 110 m ² /g	40 - 50 m ² /g

carbonyl groups can be reduced with TiCl_3 or N_2H_4 , whilst with Fe^{2+} ions only half this amount is reduced. The results indicate that about half of the carbonyl groups differ from the remainder, apparently they are able to enolize forming weakly acidic OH groups. A structure model based on the results will be discussed. The carbon layers are corrugated, some of the C-C bonds are broken and C=O bonds formed instead, the two carbonyl groups sticking out on either side of the layer.

1) R.C.Brodie, Phil.Trans.Roy.Soc.London, Ser. A 149, 249 (1859); Liebigs Ann.Chem. 114, 6 (1860).

2) L.Staudenmaier, Ber. deutsch.Chem.Ges. 31, 1481 (1899).

3) W.S.Hummers and R.E.Offeman, J.Am.Chem.Soc. 80, 1339 (1958)