

GRAPHITE INSERTION COMPOUNDS AS CHEMICAL REAGENTS IN ORGANIC CHEMISTRY

HENRI B. KAGAN

Université de Paris-Sud, Orsay, France

Abstract—The main properties of graphite and graphite compounds will be summarized. Special attention will be devoted to lamellar compounds, since many derivatives are known or were recently discovered.

It is interesting to investigate the chemical behaviour of graphite intercalated molecules for several reasons. It should be possible to make heterogeneous reactions in various solvents where the substrate is dissolved. Selective reactions can be expected since they occur on the surface. It would be interesting, too, to perform reactions in the interlamellar space.

Some examples will be given to illustrate or discuss these points. Reduction with potassium-graphite, halogenations with graphite-bromine or graphite SbCl_3 , are examples of reactions performed by lamellar compounds. The behaviour of graphite electrolytic lamellar reagents will be presented, with the more recent results obtained in our laboratory. Strong inorganic acids such as H_2SO_4 , HClO_4 , H_3PO_4 , may be intercalated under oxidizing conditions and give rise to electrolytic lamellar compounds. The deep blue compound $\text{C}_2\text{SO}_4\cdot\text{H}_2\text{SO}_4$ is particularly interesting. It allows esterification of a carboxylic acid at room temperature in cyclohexane solution. It plays two combined roles: that of an acid catalyst by activating the carboxylic acid and that of a dehydrating agent by reacting with water. Thus this graphite compound is not merely a catalyst. Some other of its reactions will be presented.

It is clear that the chemical behaviour of graphite intercalated molecules may differ in various ways from that of the non-intercalated reagents, giving reagents of potential interest in organic chemistry.

INTRODUCTION

The preference of organic chemists to carry out a reaction in an homogeneous medium is well known. However, during these last ten years there has been an increasing interest in reactions occurring between two phases, especially when one phase is a solid one.

The main advantage is the ability to recover by filtration one of the components of the system after reaction, as in the Merrifield synthesis of peptides. In some cases it can be interesting to have a small or null concentration of an aggressive reagent in the reaction medium. This can be realized if the reagent is more or less tightly bound to a solid support. In other cases it can be expected that reactions occurring at the surface of a solid could be more selective than in an homogeneous medium.

I will present some results that we obtained by using lamellar graphite compounds. This work was possible thanks to a fruitful collaboration in Orsay between my laboratory and the laboratory of Inorganic Physical Chemistry (Pr Mazières, Dr Setton).

We can expect several consequences of this type of research. Graphite should be useful as a solid carrier for a reagent, especially if it is very reactive. Heterogeneous reactions can be made in many kinds of solvents. If the reaction occurs at the surface some specificity should be expected. Last point: is it possible to carry out reactions in the interlamellar space? Before discussing our main results, I will briefly introduce the area of interstitial compounds in graphite. Several reviews have appeared on the subject.¹⁻⁴

GRAPHITE STRUCTURE

The structure of graphite is well known. Graphite crystallises in a layer structure. In each layer carbon atoms are tightly bound to three other atoms. These bonds are shorter than carbon single bonds. The layers are bound together by weak forces, with a separation of 3.35 Å (Fig. 1). Alternate layers are displaced relative to

each other. Two kinds of graphite are known. The hexagonal modification is such that every second layer is superimposable (stacking sequences A B A B . . .). In rhombohedral graphite the stacking sequences are ABC ABC . . .

Graphite can give rise to two kinds of derivatives. Some *non-conducting compounds of graphite* are known. Oxidation gives graphite oxide in which the aromatic character is lost. The structure of these polymers is not well defined. Graphite monofluoride CF was prepared too and its structure recently established.⁵ The second kind of graphite derivatives are the *lamellar compounds* which retain electrical properties of graphite. A layer of reactant can be intercalated between two carbon layers. A number n of carbon layers can indeed separate two reactant layers. This number n is usually called the stage of the lamellar compound. For example, the insertion of potassium in graphite was carefully studied by Rudorff and Schulze and five stages were observed. Stage 1, which is the most concentrated, can be obtained with potassium. For other compounds such a high concentration cannot be

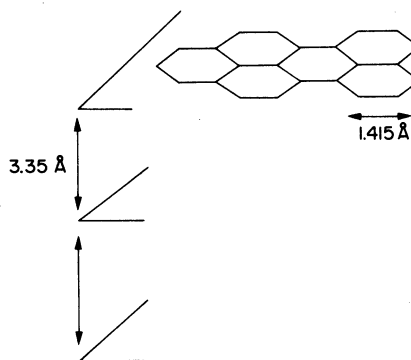


Fig. 1.

obtained and it is the second or even higher stages which are the most concentrated forms.

The structure of the reactant layer can be inferred from electrical and X-ray measurements. In general the monolayer does not retain the structure of the solid reactant nor does it assume a random arrangement as in the liquid state. The molecules or atoms R are arranged on a lattice which is closely related to the vicinal graphite lattice. The triangular or hexagonal arrays are known,¹ giving a $C_{12}R$ or C_6R stoichiometry at stage 1. The spatial orientation of molecules between the layers was studied too. It is interesting to point out that the distance between two carbon layers can change according to the nature of the inserted compound.

INTERSTITIAL COMPOUNDS

What are the compounds which can be intercalated in graphite? There is a large number of inorganic or organic substances which can be placed between carbon layers. The intercalation can be effected spontaneously or by electrolysis. In Fig. 2 are reported some spontaneous graphite compounds. Halogens, metals, salts or oxides can be intercalated. There are some exceptions: for example $SbCl_3$ is inserted but not $SbCl_5$, $SmCl_3$ but not $PrCl_3$, ... It is quite evident that the list of lamellar compounds is of great interest to the organic chemist. Some cases of interest are pointed out on Fig. 2. Mixed lamellar graphite derivatives are known too, for example graphite, $FeCl_3$, N_2O_5 .⁵ The electrolytic compounds are prepared by electrolysis and have the general formula indicated in Fig. 3. This graphite has been oxidized and reacted with one mole of reactant RH. The modified graphite incorporates additional intact RH molecules. Many inorganic or organic acids are able to form lamellar compounds as well as some amines.

This introduction shows the great potential of graphite derivatives for organic chemistry. When we started to investigate this field, several years ago, we looked on what was done. The main results had been obtained by the use of potassium-graphite as catalyst or reagent in several reactions.⁴

Recently, Lalancette *et al.*⁷ used potassium-graphite for reduction of some ketones. It found that the stereochemistry of reduction of camphor in THF is reversed by respect to the metal reduction. It was interpreted as the result of specific absorption of the

Spontaneous insertion in graphite

Li, Na, K, Rb, Cs, Sr, Ba, Sm.

Br₂, ICl.

CrO₂Cl₂, CrO₂F₂, UO₂Cl₂, UCl₄, FeCl₃

AlCl₃, ErCl₄, CuBr₂, AlBr₃, SbF₅.

CrO₃, Sb₂O₄, MoO₃,

Sb₂S₃, CuS, Fe S₂, WS₂.

No spontaneous insertion in graphite

TiCl₄, SnCl₄, SOCl₂, PrCl₃, SbCl₃, NiCl₂, PtCl₂.

PCL₃, PCL₅, POCL₃, NO, NOCL.

Fig. 2.

Graphite electrolytic lamellar compounds

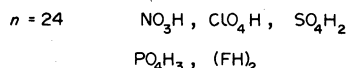
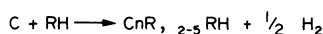


Fig. 3.

ketone on the surface. The reduction then occurs by a two-electron transfer from the potassium-graphite, as in an electrolytic process.

HALOGENATING REAGENTS

Our initial idea was to perform bromination on a small scale with a reagent easy to handle. We worked⁸ on samples of C_8Br , $C_{24}Br$, $C_{48}Br$. In the vial appear some bromine vapours above the solid. Nevertheless it is very easy to weigh, especially after cooling, since vapour pressure decreases strongly. First we performed brominations on small amount of ketosteroids by using acetic acid as solvent. The treatment is easy, there is only a filtration and an extraction to recover the bromosteroid. Other cases were studied, for example cyclopentene gives trans 1,2-dibromo cyclopentane with good yield. We used this reagent to solve a monobromination problem (Fig. 4). This is an example where a specificity is associated with a graphite reagent. It is possible that the bromination occurs mainly on the surface of the graphite and is related to the observation of Pincock *et al.*⁹ about the catalytic effect of graphite on binaphthyl racemization.

We prepared several samples of graphite-bromine and we studied the release of bromine in a solvent such as chloroform.⁸ The bromine is never quantitatively recovered. There is always residual bromine, a known phenomenon. We found that the residual bromine increases with time. In addition an aged sample is much more selective. This was investigated with 1,1'-binaphthyl. We could prepare selective reagents more rapidly by washing out with CCl_4 . The superficial bromine is then

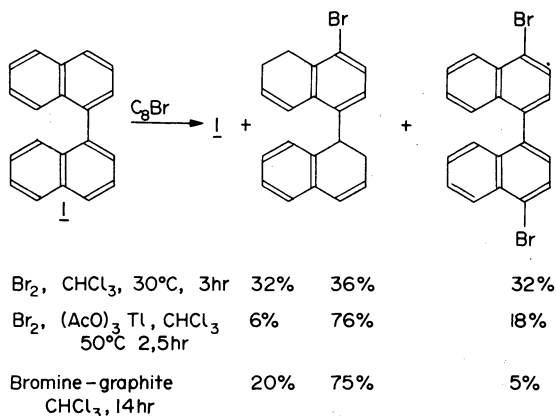
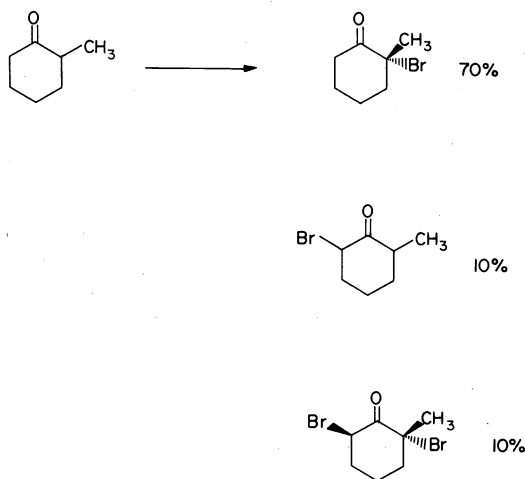


Fig. 4. From Ref. 8.

removed from the fresh sample. For example, the monobromination of 2-methyl cyclohexanone is not perfect (Fig. 5). But if we first wash the bromine-graphite we can obtain almost pure monobromoketone with a high conversion yield (Fig. 6). We have not further explored this area but it seems that some synthetic applications can be expected. As chlorinating reagent we looked for $C_{24}SbCl_5$ which is a compound easy to make and very stable. We wanted to compare its behaviour with free $SbCl_5$, since we found unexpectedly¹⁰ that it is very easy to chlorinate bromocycloalkanes stereospecifically by $SbCl_5$. Secondary and tertiary bromides react easily at room temperature. In the acyclic series there is no stereospecificity.¹⁰ We observed a transposition in the halogenation of the tertiary bromides in the cases where we could demonstrate it. The structure of the dihalides could be established by ^{13}C spectroscopy.

Now what about the properties of the lamellar compound? (Fig. 7). If we stir it¹¹ in chloroform or CCl_4 solution with an organic substrate we always have a slow reaction. With acyclic bromides we observed only halogen exchange, the chlorine derivative being obtained. This is very different from what we obtained in homogeneous conditions. In one case, with a tertiary halide the α -chlorination was the predominant reaction (Fig. 7).



Br_2 (1 equiv.), CCl_4
or
 C_6Br fresh, CCl_4

Fig. 5.

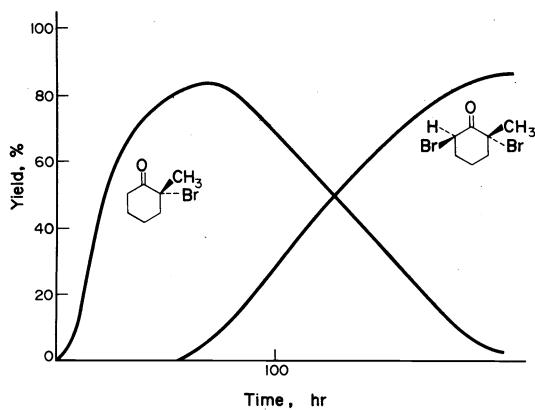


Fig. 6.

	Substrate RX	RCl	RX	Dihalide	
1	$n-C_6H_{13}CH_2-CH_2-Br$	$n-C_6H_{13}-CH_2-CH_2-Cl$	98%	2%	—
2			60%	5%	35%
3			62%	20%	18%
4			25%	—	75%
5	$C_6H_5-CH_2-CH_2-Br$	$C_6H_5-CH_2-CH_2-Cl$	30%	70%	—
6	$C_6H_5-CH-CH_3$ Br	$C_6H_5-CH-CH_3$ Cl	98%	2%	—
7			86%	14%	—
8	$n-C_6H_{13}CH_2-CH_2-OTs$	$n-C_6H_{13}-CH_2-CH_2-Cl$	15%	85%	—
9			5%	90%	5%
10			22%	78%	—

Fig. 7. From Ref. 11.

It appears then that the behaviour of inserted $SbCl_5$ is very different from free $SbCl_5$. This is an important conclusion; $C_{24}SbCl_5$ acts not only as carrier but also by its electronic or physical properties. This fact can be useful for other interstitial reagents.

When $C_{24}SbCl_5$ performs substitution on bromocyclohexane we are sure that the reaction does not occur via cyclohexene, which gives different products. An ionic step seems reasonable.

CrO_3 -graphite. Several years ago we tried to prepare and study CrO_3 -graphite, but a publication of Lalancette⁷ appeared, describing interesting results. It is possible by heating with a primary alcohol in toluene to obtain aldehydes selectively. Secondary alcohols are not attacked. The reagent is now commercialized under the trade name of Seloxcette.

Recently the true nature of the reagent was questioned by Ebert *et al.*¹² who showed that the procedure used to intercalate CrO_3 gives in fact a superficial deposit of Cr_2O_3 . It remains to investigate the chemical properties of intercalated chromium trioxide which can indeed be obtained by working in the presence of acetic acid.¹²

Cl_3Al -graphite. The compound was used as a Friedel-Crafts catalyst and compared with Cl_3Al .¹³ The alkylation of aromatic systems is more selective with the graphite catalyst. It gives less polysubstituted reaction products.

Electrolytic lamellar derivatives. Sulfuric acid has many catalytic properties. It is a strong acid which can be dangerous for labile organic molecules, and we were curious to see what would be the behaviour of the sulfuric acid-graphite. The preparation is described in Fig. 8. Each block of 24 carbon atoms loses one electron in the electrolysis. The positive ion is neutralized by SO_4H^- coupled with the reduction of a proton. Two sulfuric acid molecules are then inserted. This blue graphite compound is easy to handle and to store.

We investigated it for esterification, and we were surprised to see its good and smooth catalytic properties. We worked in cyclohexane at room temperature¹⁴ and

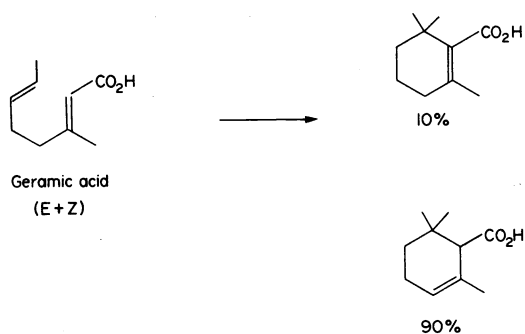


Fig. 10.

should be found. The question of performing reactions inside the layers is left open. However, it must be noted that organic molecules can be intercalated in some cases.

A catalytic activity of intercalated graphite compounds with transition metal derivatives would be of great interest; first results have been recently published.¹⁶

Graphite is not the only family giving rise to insertion. Many inorganic materials are able to intercalate organic or inorganic molecules,¹⁷ and interesting developments should also be expected in such systems.

Acknowledgements—I thank Drs. Mazière, Setton, Luche, Bertin, Colli, Page and Alazard for their collaboration and DGRST for financial support.

REFERENCES

- ¹G.R.Hennig, *Progr. Inorg. Chem.* **1**, 184 (1959).
- ²A. Herold, N. Platzer and R. Setton, *Les Carbones*. Tome II, Masson et Cie 458–646 (1965).
- ³P. Pascal, *Nouveau Traité de Chimie Minérale*, Vol. VIII, Masson et Cie, p. 388 (1968).
- ⁴M. A. M. Boersma, *Cat. Rev. Sci. Eng.* **10**(2), 243 (1974).
- ⁵L. B. Ebert, J. I. Brauman and R. A. Huggins, *J. Amer. Chem. Soc.* **96**, 7841 (1974).
- ⁶A. G. Freeman, *J. C. S. Chem. Comm.* 746 (1974).
- ⁷J. M. Lalancette, G. Rollin and P. Dumas, *Can. J. Chem.* **30**, 3058 (1972).
- ⁸A. Page-Lecuyer, J. L. Luche, H. B. Kagan and C. Mazieres, *Bull. Soc. Chim.* 1690 (1973).
- ⁹R. E. Pincock, W. M. Johnson, K. R. Wilson and J. H. Farmer, *J. Amer. Chem. Soc.* **95**, 6477 (1973).
- ¹⁰J. L. Luche, J. Bertin and H. B. Kagan, *Tet. Letters*, **9**, 759 (1974).
- ¹¹J. Bertin, J. L. Luche, H. B. Kagan and R. Setton, *Tet. Letters* **9**, 763 (1974).
- ¹²L. B. Ebert, R. A. Huggins and J. J. Brauman, *Carbon*, **12**, 199 (1974).
- ¹³L. M. Lalancette, M. J. Fournier-Breault and R. Thiffault, *Can. J. Chem.* **52**, 589 (1974).
- ¹⁴J. Bertin, H. B. Kagan, J. L. Luche and R. Setton, *J. Amer. Chem. Soc.* **96**, 8113 (1974).
- ¹⁵Alazard, R. Setton and H. B. Kagan, unpublished results.
- ¹⁶A. A. Slinkin, Y. Novikov, N. A. Pribytkova, L. J. Leznover, A. M. Rubinstein and M. E. Vol'pin, *Kinet. Kata*, **14**, 633 (1973); *Chem. Abstr.* **79**, 104348 (1973).
- ¹⁷M. B. Dines, *J. Chem. Educ.* **51**, 221 (1974).