BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 937—938(1972)

Lamellar Reactions of Graphite with Aluminum Halides

Tadashi SASA, Yoichi TAKAHASHI, and Takashi MUKAIBO

Department of Nuclear Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

(Received July 30, 1971)

Graphite reacts with a large number of substances under suitable conditions to form lamellar compounds. Many kinds of metal chlorides are included. Few studies have been performed on the reaction of graphite with other metal halides such as bromides or iodides. The reactivity of aluminum chloride with graphite has been investigated in detail.[1,2] It was found that aluminum chloride does not react with graphite, by itself, and that the presence of another component such as chlorine, bromine or iodine is necessary for the lamellar reaction to occur. Croft[3] reported the reaction of aluminum bromide and graphite in his early systematic studies. It is doubtful, however, whether excess free bromine was thoroughly eliminated during the course of the reaction. The authors have extended the studies to investigate the reactivity of graphite with aluminum bromide and aluminum iodide.

1. Graphite-$AlBr_3$

High purity artificial graphite (heat-treated at 2400°C or 3000°C) was used for the samples. Aluminum bromide prepared by the reaction between aluminum and bromine of high purity was distilled before the reaction, and excess bromine was carefully removed. The graphite specimen was suspended by a quartz spring balance (sensitivity 20 mm/g) in an evacuated and sealed glass tube, and kept in contact with aluminum bromide vapor of saturation pressure at temperatures 100—250°C for 40 hours. No measurable gain in the weight of the graphite was observed. The electrical conductivity and X-ray diffraction measurement of the sample also showed no measurable change. It is concluded aluminum bromide alone does not react with graphite.

A small amount of gaseous bromine was added in aluminum bromide vapor at 150°C. Graphite is thought to absorb scarcely any bromine at such a high temperature.[4,5] Under these conditions, however, it started to absorb the reactants immediately. When bromine was also added to the graphite in the form of a lamellar compound and residue compound beforehand, absorption of the reactant was also observed. The optimum reaction temperature was 150°C, and the reaction terminated in 24 hours. The observed gain in the weight of the graphite by far exceeded the amounts of existing free bromine, and the existence of aluminum bromide in the graphite was actually confirmed by the decomposition of the reaction products.

It is to be noticed that release of a considerable amount of free bromine was observed at the first stage of the reaction of graphite-bromine residue compound and aluminum bromide. It is known that residue compound of artificial graphite is very stable and scarcely undergoes decomposition by heat treatment below 1000°C.[6,7] However, it was observed that some parts of bromine were released at 70°C and at the same time the reaction with aluminum bromide was initiated. As the reaction proceeded, most of the released bromine was absorbed again by the graphite. For checking the possibility of decomposition of aluminum bromide vapor, the reaction of graphite-bromine residue compound with aluminum chloride was carried out. The release of free bromine was also observed in this case. The released bromine should be attributed to the residual bromine contained in the graphite.

A quantitative investigation of aluminum bromide absorption in relation to the amount of coexisting bromine was carried out. Controlled amount of bromine was doped in graphite in the form of a residue compound or lamellar compound, and the graphite sample was allowed to react with aluminum bromide vapor. The reaction products were weighed for the determina-

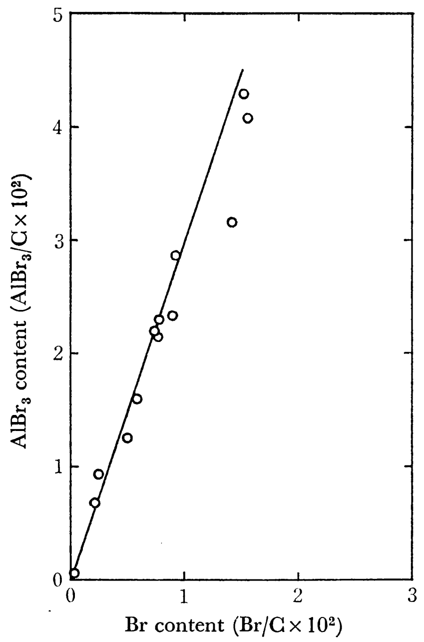

Fig. 1. Ternary lamellar compounds of graphite with aluminum bromide and bromine

1) W. Rüdorff and R. Zeller, *Z. Anorg. Allgem. Chem.*, **279**, 182 (1955).
2) M. L. Dzurus and G. R. Hennig, *J. Amer. Chem. Soc.*, **79**, 1051 (1957).
3) R. C. Croft, *Aust. J. Chem.*, **9**, 184 (1956).
4) J. G. Hooley, *Can. J. Chem.*, **37**, 899 (1959).
5) B. Bach, M. Bagouin, F. Bloc, and A. Herold, *C. R. Acad. Sci. Paris*, **257**, 681 (1963).
6) G. R. Hennig, *J. Chem. Phys.*, **20**, 1433 (1952).
7) Y. Takahashi, K. Miyauchi, and T. Mukaibo, *Tanso (Carbon)*, **1970**, (60), 8.

tion of aluminum bromide uptake. Some samples were decomposed in a vacuum at 500°C, and the released bromine and aluminum bromide were collected separately and analyzed chemically. The relation of aluminum bromide contents and bromine contents of the ternary lamellar compounds is shown in Fig. 1. Aluminum bromide contents depend entirely on the amount of coexisting bromine, and the ratio $AlBr_3$ to Br is found to be nearly three. The result coincides with that of Hennig[2] on $AlCl_3$-Cl, or $AlCl_3$-Br. The atomic composition of the ternary compound was $C_{24}AlBr_3$-$Br_{0.3}$ for the highest reactant contents investigated.

X-ray diffraction study of the reaction products of the highest reactant contents showed the formation of a 'second stage structure' compound, where every other layer spacing of graphite is invaded by the reactants and expands from 3.35 Å to 10.0 Å.

2. Graphite-AlI_3

It was found that aluminum iodide also does not react alone with graphite at temperatures up to 250°C.

When bromine was doped in graphite as the residue compound, the absorption of aluminum iodide took place. However, aluminum iodide reacts easily with bromine to form aluminum bromide and free iodine. No further quantitative studies were carried out.

Free iodine was added to graphite-aluminum iodide system to start the reaction. The intercalation of reactants in graphite was not observed in several careful runs. Thus we conclude that the aluminum iodide and iodine system does not react with graphite.

The authors are grateful to Messrs. N. Arai and K. Matsuoka for their collaboration in a part of the study.