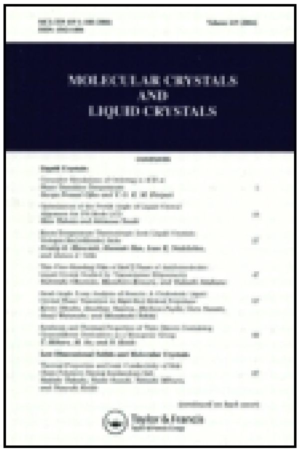

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

On the Behaviour of Potassium-Benzene-Graphite Intercalation Compounds

Hiroshi Shioyama [a], Yuichi Wakukawa [b] & Yoshihiro Sawada [a]

[a] Osaka National Research Institute, Midorigaoka 1-8-31, Ikeda, 563, Japan

[b] Osaka Electro-Communication University, Hatsucyo 18-8, Neyagawa, 572, Japan

Version of record first published: 04 Oct 2006

To cite this article: Hiroshi Shioyama, Yuichi Wakukawa & Yoshihiro Sawada (1998): On the Behaviour of Potassium-Benzene-Graphite Intercalation Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 310:1, 69-74

To link to this article: http://dx.doi.org/10.1080/10587259808045316

Mol. Cryst. Liq. Cryst., 1998, Vol. 310, pp. 69-74
Reprints available directly from the publisher
Photocopying permitted by license only

On the Behaviour of Potassium-Benzene-Graphite Intercalation Compounds

HIROSHI SHIOYAMA[a], YUICHI WAKUKAWA[b], and YOSHIHIRO SAWADA[a]
[a]Osaka National Research Institute, Midorigaoka 1-8-31, Ikeda, 563, Japan; [b]Osaka Electro-Communication University, Hatsucyo 18-8, Neyagawa, 572, Japan

KC_{24} was reacted with dehydrated benzene for a week at room temperature and then for a month at 70℃. The ternary K-Bz-GIC obtained at room temperature decomposed very slowly, when the sample was immersed in water. In case the ternary compound was heat treated at 70℃, the stability in water was very high. This unusual stability is due to the oligomerization of benzene, and hence we abbreviate the heat treated ternary compound as K-(Bz)n-GIC. The thermostability of K-(Bz)n-GIC was evaluated by XRD measurements and elemental analyses; the sample decomposed partly at 200℃ and thoroughly decomposed to graphite at 200-400℃. The reaction of K-(Bz)n-GIC with NH_3 and Cl_2 gas are also discussed.

Keywords: intercalation; graphite; potassium; benzene; stability

INTRODUCTION

It is well known that graphite intercalation compounds (GICs) of alkali metals form ternary compounds with organic molecules such as tetrahydrofuran (THF) and benzene (BZ)[1]. Especially when unsaturated hydrocarbons are co-intercalated, they are found to be oligomerized within the interlayer spacing of the alkali metal-GIC. For a few organic molecules, the oligomerization process was studied in detail[2,3], but no property of the ternary compound containing oligomerized organic molecule was reported. In this paper we report the stability and the reaction of potassium-oligomerized benzene-GIC.

EXPERIMENTAL

The slabs (5x1x0.25 mm^3) of stage 2 binary compound KC_{24} were prepared from HOPG (Union Carbide Co., ZYA grade) by the conventional two-bulb method. Samples of KC_{24} were transferred to a reaction chamber in vacuo through a glass break-seal to be exposed to dehydrated benzene for a week at room temperature and then for a month at 70℃.

Reaction products of benzene and KC_{24} before and after the heat treatment at 70℃ were characterized by recording the 00*l* reflections by means of an X-ray diffractometer. During this measurement, the sample was protected by liquid paraffin and thin polyethylene film to avoid decomposition by moisture. To evaluate the stability, products were immersed in water for any desired period and XRD measurements were repeated. Thermal stability was evaluated by XRD measurements and elemental analyses of the samples heat treated at 150, 200, 300, 400 and 1000℃.

For the estimation of the reactivity with NH_3 and Cl_2, samples were exposed to the respective gases at room temperature and 0.5 atmospheric pressure for one month, and then XRD measurements and elemental analyses were performed.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of the reaction product of benzene and KC_{24}

at room temperature (K-Bz-GIC) is shown in Fig.1(a). The diffraction lines suggest the coexistence of stage 1 binary (KC$_8$), stage 2 binary (KC$_{24}$), stage 1 ternary (K(Bz)$_{\sim2}$C$_{24}$) and stage 2 ternary (K(Bz)$_{\sim1}$C$_{24}$) compounds. The degree of co-intercalation is determined by the temperature of KC$_{24}$ and the vapour pressure of benzene[1], which might be the reason why we could not get pure stage 1 or 2 ternary compounds. When KC$_{24}$ is reacted with benzene at 60-100℃, co-intercalated benzene molecules are reported to be oligomerized in the interlayer spacing of KC$_{24}$[2]. In Fig.1(b), the X-ray diffraction pattern of the reaction product at 70℃ . (K-(Bz)n-GIC) is shown. The diffraction lines of pure stage 2 ternary compound with the c axis repeat distance of 1.260 nm were observed.

K-Bz-GIC obtained at room temperature was immersed in water to evaluate the stability. The XRD patterns are shown in Fig.2. After one-minute immersion, stage 1 binary compound (KC$_8$) disappeared and stage 3 binary (KC$_{36}$) appeared. Even after one-week immersion in water, stage 3-4 binary and stage 2 ternary compounds are retained. K-Bz-GIC is more stable than KC$_{24}$ in this manner. This is due to benzene molecules in the interlayer, which retard the reaction of

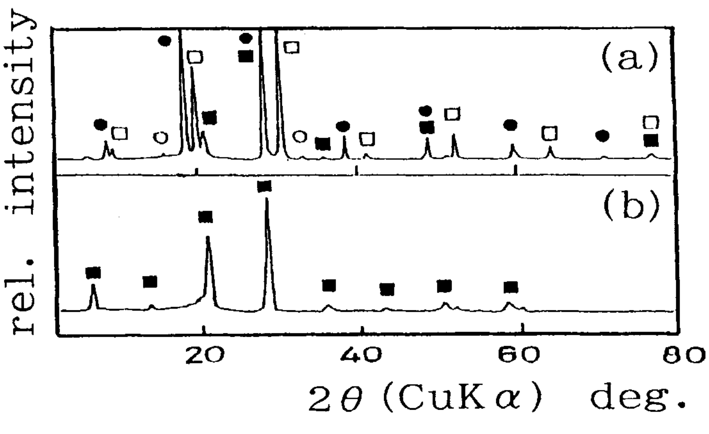

FIGURE 1 X-ray diffraction patterns (a) of K-Bz-GIC and (b) of K-(Bz)n-GIC, where ○, □, ● and ■ refer to reflections of KC$_8$, KC$_{24}$, K(Bz)$_{\sim2}$C$_{24}$ and K(Bz)$_{\sim1}$C$_{24}$, respectively.

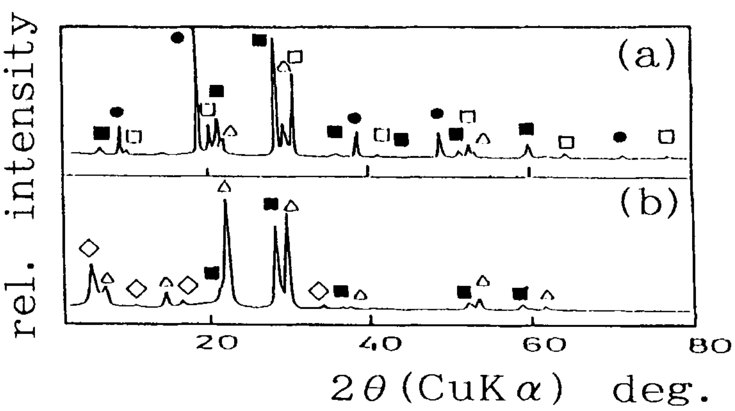

FIGURE 2 X-ray diffraction patterns of K-Bz-GIC immersed in water (a) for 1 minute and (b) for 1 week. The reflections labelled □, △, ◇, ● and ■ correspond to KC_{24}, KC_{36}, KC_{48}, $K(Bz)_{\sim 2}C_{24}$ and $K(Bz)_{\sim 1}C_{24}$, respectively.

potassium atoms with water molecules.

As for K-(Bz)n-GIC which was heat treated at 70℃ for a month, no decomposition was observed even after two-weeks immersion in water. Oligomerized benzene is considered to protect potassium atoms from water in a similar manner as reported before for cesium-ethylene-GIC[3,4].

The thermostability of K-(Bz)n-GIC can be evaluated by comparing XRD patterns shown in Fig.3. After the heat treatment at 150℃, the sample shows a similar XRD pattern to that of pristine K-(Bz)n-GIC, which means no decomposition was observed. At 200℃ K-(Bz)n-GIC decomposed partly, and at 200-400℃ it decomposed to graphite. Results of quantitative analyses shown in Table I also suggest that the decomposition took place at the temperature range of 200-400℃. As this temperature range is in agreement with the boiling points of biphenyl (254℃), *o*-terphenyl (332℃), *m*-terphenyl (363℃) and so on, liberation of oligomerized benzene from the interlayer of graphite is considered to initiate the thermal decomposition of K-(Bz)n-GIC.

We now turn to the reaction of K-(Bz)n-GIC. In the interlayer spacing of graphite oligomers of benzene are reported to be reduced to radical anions by transfer of electrons from the Fermi surface of the

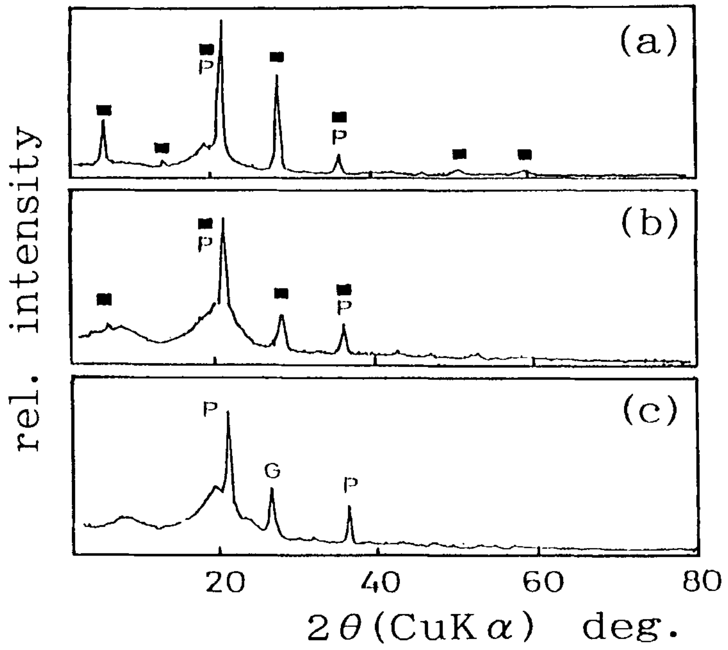

FIGURE 3 Thermostability of K-(Bz)n-GIC. HTT: (a) 150℃, (b) 200℃, (c) 400℃. (■: $K(Bz)_{-1}C_{24}$, P: polyethylene, G: graphite)

TABLE I Results of quantitative analyses; before and after the heat treatment of K-(Bz)n-GIC.

HTT (℃)	wt% C	wt% K
room temperature	86.9	8.7
150	87.3	7.6
200	86.9	6.7
300	89.4	3.2
400	93.0	0.7
1000	97.7	0.1

GICs[2], and hence they are able to react if appropriate molecules come into contact. Ammonia and chlorine gases were chosen for the reagent, because both gases can be inserted into the interlayer of graphite. The former produces ternary GICs with alkali metals[5] and the latter could be intercalated into graphite and forms chlorine-GIC when temperature is lower than -20℃[6].

After K-(Bz)n-GIC was exposed to NH_3 gas for one month, XRD measurements were carried out. In the diffractogram very weak 002 and 004 lines of graphite were solely detected. As the intensity of these lines was reduced to less than one thousandth of that of pristine HOPG, the periodic structure was supposed to be destroyed during the reaction. By elemental analysis nitrogen content in the product was determined. The nitrogen content was 2.0 wt% and did not vary even if the sample was treated under vacuum or washed in water. These experimental results might suggest that nitrogen molecules are inserted into K-(Bz)n-GIC and react in the interlayer with such chemical species as the radical anion of oligomerized benzene. A calculation shows the number of nitrogen atoms held in the product is approximately half of benzene rings in the starting K-(Bz)n-GIC. The measurement of IR spectra is in any event to be expected for the confirmation of the chemical bonding between nitrogen and benzene ring.

In case K-(Bz)n-GIC was reacted with Cl_2 in the same manner, the X-ray diffractogram of the product was quite similar to that shown above in the reaction with NH_3. The chlorine content was 3.2 wt%, which did not vary even if the sample was treated under vacuum or washed in water. As the product obtained by the reaction of KC_{24} with Cl_2 gas also gives similar features, Cl_2 gas is supposed to react with potassium in the interlayer of K-(Bz)n-GIC.

References

[1.] R. Setton, *Graphite Intercalation Compounds I, Structure and Dynamics* (Springer-Verlag, Berlin, 1990), p.305.

[2.] S.Matsuzaki, M.Taniguchi and M.Sano, *Synth. Metals*, **16**, 343 (1986).

[3.] H.Pilliere, Y.Takahashi, T.Yoneoka, T.Otosaka and N.Akuzawa, *Synth. metals*, **59**, 191 (1993).

[4.] Y.Takahashi, K.Oi, T.Terai and N.Akuzawa, *Carbon*, **29**, 283 (1991).

[5.] S.K.Hark, B.R.York, S.D.Mahanti and S.A.Solin, *Solid State Comm.*, **50**, 595 (1984).

[6.] G.Furdin, M.Lelaurain, E.McRae, J.F.Marcehe and A.Herold, *Carbon*, **17**, 329 (1979).