Carbonization of Trichloroethanes with Anhydrous Potassium Hydroxide

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ABSTRACT: Chemical dehydrochlorination of 1,1,1- and 1,1,2-trichloroethanes with anhydrous potassium hydroxide (KOH) in the presence of a poly(ethylene glycol) oligomer as phase transfer catalyst leads to polymeric carbons with partly carbynoid structures. The FTIR spectra show a strong band at 2130 cm^{-1} and FT-Raman exhibits a strong line at around 1900 cm^{-1}, either of which is interpreted as the C≡C—C stretching mode of the linear carbon chain with alternating carbon–carbon triple and single bonds (polyyne). Carbons prepared by this technique are amorphous nanoparticles with diameters in the 30–50 range nm. After iodine doping they have dc conductivities of 10^{-3} S cm^{-1}. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 185–189, 2000
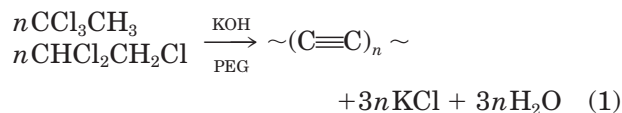
Key words: trichloroethane; poly(ethylene glycol); potassium hydroxide; dehydrochlorination; polyyne

INTRODUCTION

Synthesis of carbyne attracted a great deal attention in the past few years,[1] which is mainly due to the fact that we still know much less about this material than the other carbon polymorphs such as graphite, fullerenes, and diamond.[2] Several routes to carbyne synthesis were reported. They include oxidative dehydropolymerization of acetylene, condensation of carbon vapor or liquid carbon, phase transition of diamond or graphite, and shock compression of glassy carbon.[3] Another synthetic strategy to carbynes consists of an extensive reductive dehalogenation of perhalogenated compounds and polymers. This reaction proceeds electrochemically[4] or chemically at room temperature by action of some anion radicals, alkali metals, and alkali metal amalgams.[5] Carbynes also can be prepared from several polymeric precursors such as poly(vinylidene ha-

lides)[6] and chlorinated polyacetylene[7] by dehydrochlorination, which accelerates in the presence of phase transfer catalysts. However, dehydrochlorination of low molecular weight carbon halides into carbynes was only reported in a short communication.[8]

Poly(ethylene glycol)s [HO(CH$_2$CH$_2$O)$_n$H, PEGs] with a repeat number n greater than 3 are extraordinary phase transfer catalysts for dehydrochlorination of low molecular weight carbon halides[9] and halogenated polymers.[10] Their catalytic activity and thermal stability are much higher than those of widely used ammonium or phosphonium halides.[9] In this article we report that 1,1,1- and 1,1,2-trichloroethanes can be carbonized by anhydrous potassium hydroxide (KOH) particles in the presence of the catalyst PEG with average molar mass of 400 g mol^{-1}. The reaction can be simply represented by eq. (1):

$$\begin{array}{c} n\,\text{CCl}_3\text{CH}_3 \\ n\,\text{CHCl}_2\text{CH}_2\text{Cl} \end{array} \xrightarrow[\text{PEG}]{\text{KOH}} \sim(\text{C}\!\equiv\!\text{C})_n\sim$$

$$+\,3n\,\text{KCl} + 3n\,\text{H}_2\text{O} \quad (1)$$

EXPERIMENTAL

Chemicals

Fine 1,1,1- and 1,1,2-trichloroethanes (Shanghai 1st Chem. Co.) were used after distillations. The anhydrous KOH was dried under a vacuum at 100°C for 24 h and ground in a dry box into particles with maximum diameters of less than 2 mm. Analytical grade pure methanol and tetrahydrofuran (THF) were used as received. The PEG with an average molar mass of 400 g mol^{-1} was also dried under a vacuum at 100°C for 24 h before use.

Carbonization of Carbon Halides

In a typical reaction 0.3 mol of trichloroethane was mixed with 5 mL of PEG, and then the mixture was dropped into 2.7 mol KOH powder within 2 h under a dry nitrogen atmosphere and mechanical stirring. The temperature in the reaction system was kept in the 20–30°C range by a water bath. Black carbon powders formed on the surfaces of the KOH particles simultaneously. After finishing the dropping the reaction was continued at room temperature for another 3 h. Then the system was cooled in an ice bath to close to 0°C; 200 mL of cold water was added to dissolve the excess KOH, and KCl formed in the reaction process. Fifty milliliters of THF was poured over the aqueous solution surface and stirred. As a result, carbon particles were transferred into the organic phase because of their low density or their hydrophobicity. The organic phase was separated and collected. The water phase was repeatedly extracted by THF until no carbon was present in this medium. All the THF phases were collected and carbons were separated by centrifugation. The rough products were washed with a large amount of water and successively with methanol 5 times each. Finally they were dried under a vacuum at room temperature for at least 48 h. Carbon yields were calculated to be 40–44% by weighing the carbon particles.

Doping Carbon Samples

The doping of carbons was carried out by immersing the carbon particles in iodine saturated carbon tetrachloride solution for 2 h and then taking them out of the solution and washing 3 times with clean solvent. Finally they were dried under a vacuum at 60°C for 24 h.
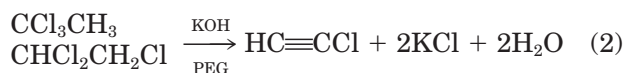
Characterization Techniques

IR and Raman spectra were recorded on a Nicolet 170SX FTIR spectrometer in KBr pellets and an RFS-100 FT-Raman spectrometer (Bruker), respectively. The Raman spectra were taken with an excitation of 1064-nm laser light and accumulated for 1000 scans. Elemental analysis was performed by a Perkin–Elmer 240C elemental analyzer. The X-ray photoelectron spectroscopy (XPS) spectra were recorded using a photon electron spectrometer model VGS 5000. Curve fitting of the C1s spectrum was accomplished using the nonlinear least squares procedure.[11] Quantification of the surface concentrations of the elements was accomplished by correcting the photoelectron peak areas for photoionization cross sections.[12] Transmission electron microscopy measurements were taken by using an XD-3A X-ray diffraction analyzer. The electrical conductivities of the iodine doped carbon samples were measured by the conventional four probe dc technique.

RESULTS AND DISCUSSION

System Selection

As shown by eq. (1), carbonization of one molecule of trichloroethane produces three molecules of water. Thus, removing water from the system supports the formation of carbon. On the contrary, the reaction can be hindered by adding a large amount of water. Indeed, if anhydrous KOH was replaced by a 60% (by weight) aqueous KOH solution no carbon product was formed. Only a colorless gas was bubbled out from the solution, which was mainly due to the formation of chloroacetylene as suggested by Kimura and Regen:[9]

$$\begin{matrix} CCl_3CH_3 \\ CHCl_2CH_2Cl \end{matrix} \xrightarrow[\text{PEG}]{\text{KOH}} HC{\equiv}CCl + 2KCl + 2H_2O \quad (2)$$

On the other hand, in the system with a large amount of excess anhydrous KOH, water can be absorbed by the base and carbon is the final product.

The PEG oligomer also takes a very important role in this reaction. In the system without PEG the conversion of the reaction was found to be lower than 5% for 4 h. This was mainly because the inorganic base has no solubility in the carbon halides. However, as a certain amount of PEG
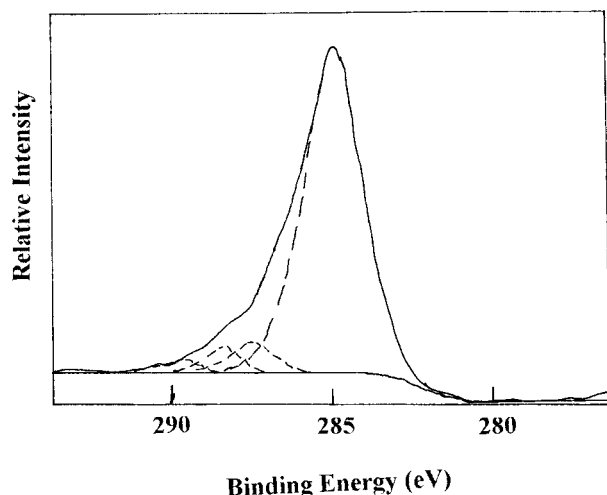
Figure 1   C1s core-level spectrum of the carbon made from 1,1,1- or 1,1,2-trichloroethane.

was added, the reaction started immediately and dramatically. PEG acts as a solubility promoter for the base. Furthermore, it can coordinate the cation, K^+, and increase the activity of KOH. Thus, PEG is an extraordinary phase transfer catalyst for the reaction.

Structure Characterization

The XPS spectrum (Fig. 1) of the C1s electron of the carbon product made from 1,1,1- or 1,1,2-trichloroethane shows one strong C1s line at about 284.6 eV, which can be assigned to elemental carbon.[13] Several weak shoulder bands of carbonyl carbon ($—C{=}O$) and hydrochlorocarbons ($—CHCl—$ and $—CCl_2—CH_2—$) are found at 287.3, 288.4, and 289.5 eV, respectively.[14] The observed overall stoichiometry for the particles is $C_{6.21}Cl_{0.02}O_{1.00}$. The very low content of chlorine indicates an extensive dechlorination of the halides. Elemental analysis also showed the products have 75.70–75.85% carbon, 4.49–5.03% hydrogen, and 19.12–19.80% oxygen and chlorine. These results demonstrate that the products are mainly elemental carbons with complicated surface oxides.

   The FTIR spectrum of the carbon made from 1,1,1- or 1,1,2-trichloroethane is illustrated in Figure 2. The absorption bands typical of C—Cl in trichloroethanes at 520, 610–630, 700, and 780 cm^{-1} disappeared,[15] indicating an extensive dehydrochlorination. New absorption bands appeared at 1600 and 2130 cm^{-1}. They are typical of

valence vibrations of carbon–carbon double and triple bonds, respectively.[16] The band in the region of 1700 cm^{-1} may be attributed to cumulative double bonds or $C{=}O$ groups resulting from the incorporation of oxygen from the air during sample purification and characterization processes.[7] Absorption bands typical of valence vibrations of CH_2 are found in the region of 2800–2990 cm^{-1}. No band was found in the wavenumber greater than 3050 cm^{-1}, indicating no substitution side reaction is present in carbonization.

   The 1064 nm excited FT-Raman spectrum of the carbon product made from 1,1,1- or 1,1,2-trichloroethane is shown in Figure 3. The broad band centered at about 1900 cm^{-1} is attributed to conjugated carbon–carbon triple bonds.[4] The much weaker band centered at about 1600 cm^{-1} is of the in-plane C—C stretching model of E_{2g} in graphite and the band centered at 1400 cm^{-1} is a disorder-induced Raman band for small graphite crystallites.[17] The intensity ratio of the 1900 cm^{-1} ($I_{C{\equiv}C}$) band and that of 1600 cm^{-1} (Ig-c) is calculated to be about 4 ± 0.5. No other solid carbon material exists that shows such an intense Raman signal of triple-bonded carbon. Thus, carbonization of trichloroethanes by anhydrous KOH powder can produce a carbyne analogue with high concentrations of conjugated carbon bonds.
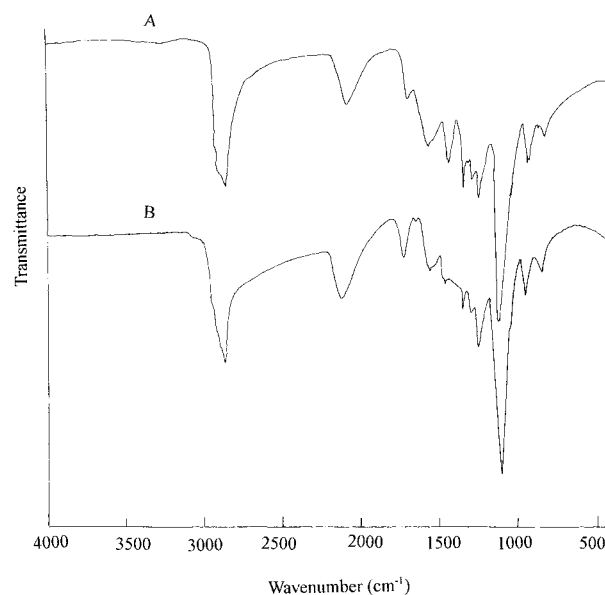

Figure 2   The FTIR spectrum of the carbon made from (A) 1,1,1- or (B) 1,1,2-trichloroethane.
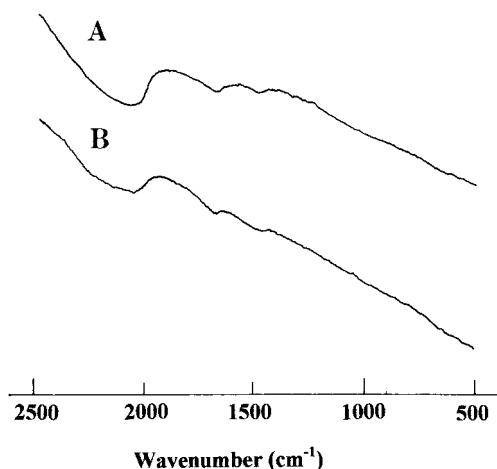
Figure 3 The FT-Raman spectrum of the carbon made from (A) 1,1,1- or (B) 1,1,2-trichloroethane.

Figure 5 An X-ray diffraction pattern of the carbon made from (A) 1,1,1- or (B) 1,1,2-trichloroethane.

Morphology and Properties

The transmission electron micrograph of the carbon made from 1,1,1- or 1,1,2-trichloroethane indicates the particle diameters are in the range of 30–50 nm as shown by Figure 4. Powder X-ray analysis showed a broad peak at 2θ at around 21°, indicating the products to be amorphous with a little polycrystalline graphite (Fig. 5). The conductivities of the carbyne pellet samples prepared under a pressure of 3.2×10^7 N m^{-2} were measured to be on the order of 10^{-7} S cm^{-1}, which is close to those of the carbynes synthesized chemically or electrochemically. After iodine doping their conductivities increased up to the order of 10^{-3} S cm^{-1}.
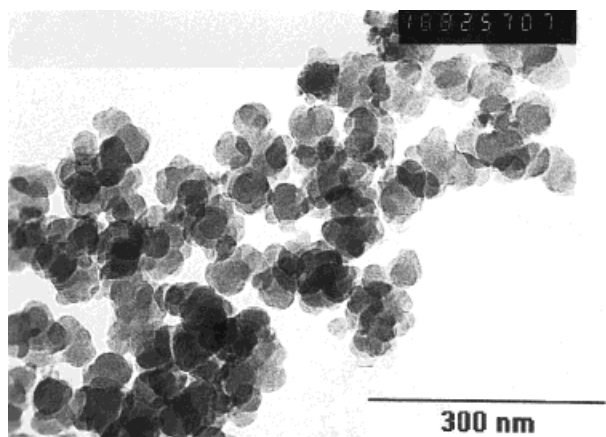
CONCLUSIONS

The 1,1,1- and 1,1,2-trichloroethanes can be dehydrochlorinated into carbyne analogues with a little graphite structure. The carbynes prepared by this technique were amorphous nanoparticles. They have high concentrations of carbon–carbon triple bonds with long conjugated sequences. PEG with a number average molar mass of 400 g mol^{-1} is an extraordinary phase transfer catalyst and accelerates the reaction dramatically.

Figure 4 A transmission electron micrograph of the carbon made from 1,1,1-trichloroethane.

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