

## Formation of boron carbide under the action of low-voltage nonstationary electrical discharges on trialkyl orthoborates

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Application of a low-voltage nonstationary electric arc to trialkyl orthoborates at low medium temperatures ( $\leq 130^\circ\text{C}$ ) leads to boron carbide and carbon as the main products.

Boron carbide is an extremely hard inert substance widely used as an abrasive, and boron carbide enriched in the  $^{10}\text{B}$  isotope is a neutron absorber in nuclear reactors.<sup>1</sup> Numerous works on the synthesis of boron carbide were carried out in recent years.<sup>2,3</sup> All the methods can be divided into the following basic groups: carbothermic,<sup>4–7</sup> magnesium-thermic<sup>8</sup> or calcium-thermic<sup>9</sup> reduction, synthesis from the elements,<sup>10,11</sup> gas-phase synthesis,<sup>12–14</sup> synthesis from polymeric precursors,<sup>15–18</sup> liquid-phase reactions,<sup>19,20</sup> ion beam synthesis,<sup>21,22</sup> and vapour-liquid-solid growth.<sup>23–25</sup> Elemental boron, boric acid or boric anhydride, sodium tetraborate, boron halides and boron hydrides are used as the sources of boron atoms. Petroleum coke, graphite, activated carbon, light hydrocarbons, polyvinyl alcohol, ethylene glycol, citric acid and carbohydrates are the sources of carbon. Each of the methods has its advantages and disadvantages. The main disadvantage of the majority of methods is the need of using high temperatures (to  $2000^\circ\text{C}$ ) and sophisticated equipment.

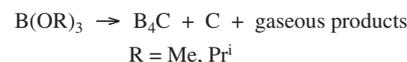
The application of electrical discharges makes it possible to change process conditions and to combine high arc temperatures, which are necessary for activating the reactions, with low temperatures in the reaction medium.<sup>26</sup> Nonstationary electrical discharges were used to develop methods for the synthesis of acetylene from hydrocarbon raw materials.<sup>27</sup>

Herein, we studied the action of nonstationary electrical discharges on trimethyl and triisopropyl orthoborates at a temperature of  $40\text{--}130^\circ\text{C}$ . The reaction was carried out in a glass reactor with two graphite electrodes at an ac voltage of  $60\text{--}80\text{ V}$  and a frequency of  $50\text{ Hz}$  (Figure 1).<sup>†</sup> A graphite ball served as a contact maker in the electrical circuit. As a result of short circuit, heat was released to cause the local evaporation of the esters; gaseous products were generated to reject the ball and to break



Figure 1 Reactor for electrocracking in nonstationary discharges.

contacts. An electrical arc discharge with a temperature of several thousand degrees, which initiated chemical processes, appeared between the contacts in the gas phase. In this case, the temperature in the reactor was not higher than the boiling point of the corresponding ester. Solid degradation products formed a black suspension in the initial esters. Using X-ray diffraction analysis and solid-state NMR spectroscopy,<sup>‡</sup> we found that boron carbide and carbon were formed under these conditions upon the decomposition of trimethyl or triisopropyl borate:



According to elemental analysis data, the concentration of free carbon in the resulting solid samples was about 70%; the

<sup>†</sup> Commercial trimethyl borate and triisopropyl borate were used as purchased.

The glass reactor with a diameter of 40 mm was equipped with two glass tubes at the bottom; graphite electrodes with a diameter of 10 mm were arranged in these tubes, and the distance between the electrodes was 1–2 mm. The graphite ball diameter was 6–8 mm. A water-cooled condenser was arranged at the top of the apparatus. The reactor was filled with argon, and 45 ml of trialkyl borate was placed in. Alternating current was supplied to the graphite electrodes through a variac (see Figure 1).

Upon supplying a voltage across the electrodes, the periodic process of closing and breaking the contacts with a graphite ball accompanied by the formation of electric arc came into play. The process was conducted at  $60\text{--}80\text{ V}$  for 1.5–2 h until the beginning of the wearout of the graphite ball. The pyrolysis products were separated by decantation; the resulting sediment was washed with methanol, filtered off through a dense metallic filter and dried in air.

<sup>‡</sup> Elemental analysis was performed on a Perkin–Elmer Series II 2400 analyzer. X-ray diffraction analysis was performed on a DRON-2 diffractometer in the range of  $2\theta = 10\text{--}45^\circ$  using  $\text{CuK}\alpha$  radiation. The crystallite size was calculated using the Debye–Scherrer formula and the strongest reflections at  $2\theta = 37.8^\circ$  for boron carbide and  $2\theta = 26.4^\circ$  for graphite.

The  $^{11}\text{B}$  solid state NMR experiments (128.39 MHz; pulse program, onepulse) were performed on a wide-bore Bruker AVANCE III 400 spectrometer using a double-resonance 2.5-mm MAS probe. Samples were spun at 8.0 kHz at room temperature for all experiments. The spectra widths were about 700 ppm; the acquisition times were 0.046 s (8192 points were collected), and the relaxation delays were 1 s. The spectra were acquired with 600 scans.  $^{11}\text{B}$  chemical shifts were referenced to the adamantane signal at 38.48 ppm on the TMS scale.

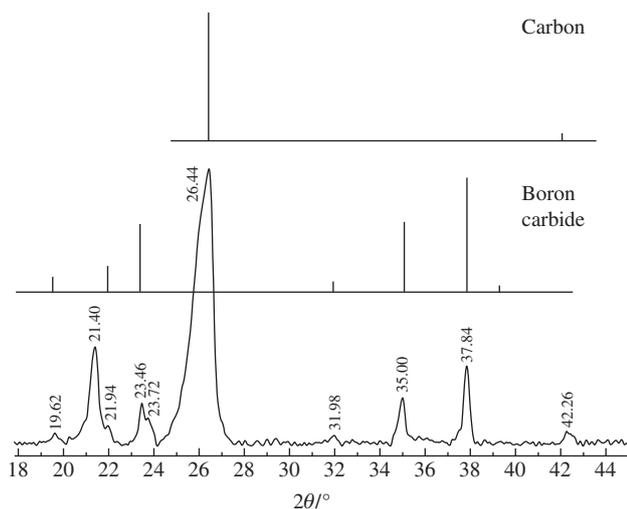


Figure 2 X-ray diffraction pattern of a boron carbide sample.

residual substance was a mixture of the crystalline and amorphous phases of boron carbide.

The X-ray diffraction patterns of the solid powders thus obtained exhibited an intense peak at  $2\theta = 26.4^\circ$  due to the presence of graphite (Figure 2). Reflections at  $2\theta = 19.6, 21.9, 23.5, 32.0, 35.0$  and  $37.8^\circ$  correspond to the hexagonal phase of boron carbide with large particle size of  $\sim 300\text{--}350 \text{ \AA}$ . The particle size of graphite was  $\sim 70\text{--}80 \text{ \AA}$ , whereas the standard samples of the electrode material contained graphite with a particle size of  $\sim 300 \text{ \AA}$ . As compared with ordinary graphite, the concentration of crystalline graphite in the test sample was not higher than 10%, and the concentration of crystalline boron carbide was 2.5–3.0%; the residue was a mixture of amorphous carbon and amorphous boron carbide.

The solid-state  $^{11}\text{B}$  NMR spectra contained one broad signal (a maximum at  $-5.8$  ppm; width at half height, 11.6 kHz) with a big shoulder at the low-field side (Figure 3). Thus, we concluded that at least two chemically nonequivalent boron atoms were present in the sample, which correspond to the two or more strongly overlapping wide signals. The experimental results are consistent with published data on the  $^{11}\text{B}$  NMR spectra of boron carbide.<sup>28</sup>

The main advantage of the developed method of producing boron carbide as compared to the previously described known methods is the possibility of performing the high reaction temperature chemical process in a conventional low medium temperature

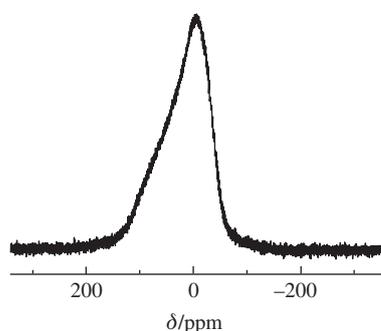


Figure 3 Solid-state  $^{11}\text{B}$  NMR spectrum of boron carbide.

laboratory unit under standard conditions from readily available starting materials. The disadvantage is a relatively high free carbon content in the reaction material.

In conclusion, we developed a new low-temperature method for the liquid-phase synthesis of boron carbide from trimethyl or triisopropyl borates at a medium temperature of  $40\text{--}130^\circ\text{C}$  in a nonstationary low-voltage electric arc at a voltage of  $60\text{--}80 \text{ V}$ .

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