Inorg. Chem. **2009**, *48*, 2333−2338

Inorganic Chemistry
Article

Mechanochemical Synthesis of Alkaline Earth Carbides and Intercalation Compounds

Sandra M. Hick, Carolin Griebel, and Richard G. Blair*

Department of Chemistry, University of Central Florida, 4000 Central Florida Boulevard, Chemistry Building (CH) 117, Orlando, Florida 32816-2366

Received November 21, 2008

High-energy ball milling has been successfully employed to produce alkaline earth carbides from the elements. In particular, CaC_2 yields of up to 98% can be realized in as little as 12 h. Similarly, the carbides of Mg (39% yield), Sr (87% yield), and Ba (82% yield) have been prepared. An intermediate in the synthesis of CaC_2 is the newly discovered gold-colored Ca-graphite intercalation compound CaC_6. Sr and Ba also go through initial intercalation phases (SrC_6 and BaC_6) before ultimately producing the carbides. The magnesium product consisted of Mg_2C_3 with no MgC_2 observed. The addition of sulfur to CaC_2 forming reactions did not adversely affect the overall synthesis; this suggests that this method may be utilized to sequester sulfur from high-sulfur coal. The preparation of these compounds by high-energy ball milling represents a novel method for producing pure carbides, as well as a convenient route to isotopically enriched ethyne.

Introduction

Alkaline earth carbides are generally of the form MC_2 or M_2C_3. Currently, calcium carbide is the only commercially available alkaline earth metal carbide. Calcium carbide (CaC_2) is an industrial source of acetylene. It is prepared from CaO by carbothermic reduction (eq 1);[1] this technical grade material is typically 80% pure and is contaminated with both CaO and carbon. Approximately 13% of the acetylene consumed in the United States is prepared from CaC_2.[2]

$$CaO + 3C \rightarrow CaC_2 + CO \qquad \text{(in an electric arc)} \quad (1)$$

Oxide-free CaC_2 could be a potential allyne source for organic and organometallic syntheses. Additionally, an efficient, small-scale method for producing reactive carbides would provide a convenient route to isotopically (C-11 and C-13) enriched allynes. Pure, uncontaminated CaC_2 can be synthesized on the laboratory scale from the elements or from calcium cyanamide. The synthesis from calcium cyanamide (eqs 2 and 3) requires high temperature pyrolysis while the synthesis from the elements requires repeated remelting at 2100 °C.[3]

$$CaCO_3 + 2HCN \rightarrow CaCN_2 + CO + H_2 + CO_2 \qquad (850\ ^\circ C) \quad (2)$$

$$CaCN_2 + C \rightarrow CaC_2 + N_2 \qquad (1400\ ^\circ C) \quad (3)$$

This method is not suitable for the commercial scale because of the need to sustain a high-temperature and an oxygen-free atmosphere for prolonged periods, as well as the use of hydrogen cyanide gas. Additionally, the syntheses from CaO and $CaCN_2$ results in carbon loss to CO and CO_2. This is not desirable in the preparation of C-11 and C-13 sources.

The preparation of MgC_2 and Mg_2C_3 is slightly less energy intensive than an electric arc synthesis, but both materials require prolonged heating in a tube furnace under flowing gas. The synthesis of MgC_2 requires acetylene gas to be passed over hot magnesium powder at 450 °C.[4]

$$Mg + C_2H_4 \rightarrow MgC_2 + 2H_2 \qquad (450\ ^\circ C) \quad (4)$$

Mg_2C_3 can be prepared by heating hot magnesium powder in the presence of pentane.

---

* To whom correspondence should be addressed. E-mail: rblair@mail.ucf.edu.

(1) Greenwood, N. N.; Earnshaw, A. Carbides. In *Chemistry of the Elements*; Butterworth-Heinemann Ltd: Woburn, MA, 1984; pp 319−320.

(2) Kirschner, M. *ICIS Chem. Bus.* **2005**, *267* (3), 31.

(3) Brauer, G. Calcium Carbide. In *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Riley, R. F. , Ed.; Academic Press: New York, 1963; Vol. 1, pp 943−946.

(4) Brauer, G. Magnesium Carbides. In *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Riley, R. F. , Ed.; Academic Press: New York, 1963; Vol. 1, pp 920−921.

10.1021/ic8022437 CCC: $40.75

$$5Mg + 3C_5H_{12} \rightarrow 5Mg_2C_3 + 18H_2 \qquad (700\ °C) \quad (5)$$

The product of both syntheses needs to be purified; the yield of MgC_2 is 70% pure and Mg_2C_3 is up to 85% pure. While these preparations could be carried out on an industrial scale, both require flowing hydrogen and subsequently hydrocarbon gases at elevated temperature for prolonged periods of time.

High-energy ball milling is a process that has seen interest in the production of structural materials such as alloys and ceramics (carbides, borides, and silicides).[5−8] In this process, a small ball is placed in a sealed vial and the vial is vigorously shaken (on the order of 1200 shakes per minute). This type of processing supplies the activation energy to initiate the formation of the desired compounds. Although the mechanochemical synthesis of transition and p-block metal carbides is well documented,[9] there are no reports on the mechanochemical synthesis of alkaline earth carbides. The high reactivity of these metals suggests that it should also be possible to form their carbides using the same techniques used to prepare compounds such as TiC.[10]

The reaction of alkaline earth metals with carbon can result in layered phases as well as carbides. To date, first-stage compounds (consisting of alternating layers of metal and graphitic carbon) have been observed for all metals except magnesium.[11] Recently,[12] the first stage compound CaC_6 was prepared by soaking highly oriented pyrolytic graphite (HOPG) in a Li−Ca melt for 3−10 days. We have observed this phase in as little as 1 h by using high-energy ball milling. A similar procedure has been used to produce Li-intercalation phases by planetary ball milling.[13,14]

Experimental Section

Reagents. Metals were used as obtained: magnesium turnings (Alfa Aesar, Puratronic, 99.98%), dendritic calcium (Alfa-Aesar, 99.98%), calcium granules redistilled (Alfa-Aesar, 99.5%), calcium ingot (Alfa-Aesar, 99%), strontium (Alfa-Aesar, 99%), and barium (Alfa-Aesar, 99.2%). Carbon was supplied by Asbury Carbons (Asbury, NJ, www.asbury.com); the following grades were utilized: graphite grade 3775 (98%−99%), graphite grade 146 (95% carbon), graphite grade 3806 (98%−99%), graphite grade 3243 (99%), graphite grade TC301 (99.9%), graphite grade TC306 (99.9%), and carbon black grade 5991R (99+%). Sulfur (Alfa Aesar, Puratronic, 99.999%) was added to a graphite (grade 3243) sample to simulate high-sulfur coal. All materials were stored and manipulated in an inert atmosphere glovebox.

Milling. All milling experiments were carried out in SPEX Certiprep mixer/mills. Milling was performed in 8000 M and 8000D mixer/mills. Milling vials were constructed of 440C stainless steel and had an approximate volume of 65 mL. Viton o-rings were used to maintain an airtight seal during milling. High kinetic energy milling was performed with three, 0.5″ stainless steel balls weighing approximately 8 g each. Each ball has a volume of 0.34 mL resulting in a free volume of 64 mL.

Synthesis. Stoichiometric mixtures of the elements (Mg, Ca, Sr, Ba, and C) were measured into milling vials in an inert atmosphere glovebox. The metals were cut into 4 mm or smaller pieces, and the reactions were measured for a total reactant mass of 2−6 g. Kinetic studies of the magnesium and calcium systems were performed with 2 g loads resulting in a free volume of approximately 63 mL. Reactants were milled in 30−60 min increments with 30 min of cooling between each increment to reduce wear on the mill's motor.

Gravimetric Analysis. The extent of reaction was monitored gravimetrically. Conversion of carbon to alkaline earth carbide was determined by hydrolyzing approximately 0.1 g of the reacted material in 1 M HNO_3. Any carbides present were decomposed to ethyne or propadiene and propyne. Any unreacted alkaline earth metals were converted to soluble salts and washed away. The mass loss of carbon was determined by filtration through a 47 mm diameter Whatman Nuclepore track etched polycarbonate membrane filter with a pore size of 0.220 μm. The residue was dried in an 80 °C oven for 12 h and then weighed.

Iron Content Analysis. Iron content of the starting materials and milled products was analyzed by monitoring the absorbance at 478 nm of the $Fe(SCN)_6^{3-}$ complex with an Agilent model 8453 UV−vis spectrophometer. Typically, 0.1 g samples were digested by stirring in hot 0.8 M HNO_3 for 1 h. Quantitation was achieved by utilizing a standard curve prepared from solutions containing 1−9 ppm Fe^{3+}.

Gas Chromatography with Mass Sensitive Detection. GC-MS analysis was performed on an Agilent 6850 GC with an Agilent 19091-433E HP-5MS column (5% phenyl methyl siloxane, 30 m × 250 μm × 0.25 μm nom.) coupled with a 5975C VL mass selective detector. Approximately 0.1 g of prepared carbide was crimp sealed in a 5 mL serum vial. The sample was hydrolyzed by the addition of 10 μL of water. Ten microliters of the gas formed were extracted and injected onto the column.

X-ray Diffraction. Powder X-ray diffraction (XRD) was taken using a Rigaku Multiflex theta-theta powder X-ray diffractometer with a copper source (Cu K_α λ =1.5418). Spectra were collected from 5 to 80 degrees two theta using 0.03 degree steps and 1 s dwell time. Because these samples are air-reactive, they were sealed into polyimide tubes for the analysis.

Infrared Spectroscopy. Infrared spectroscopy was performed using a Jasco 420 FTIR equipped with a 10 cm path length gas cell. Approximately 0.1 g of prepared carbide was placed in a Schlenk flask inside the glovebox; then, attached to a Schlenk line along with the gas cell. Vacuum was pulled on both flask and cell. Approximately 1 mL of water was introduced into the flask, and the resulting gas was allowed to fill the system. This resulted in a gas cell containing gaseous hydrolysis products.

Superconductivity. Superconductivity measurements were performed using a Quantum Design MPMS 5XL (Magnetic Properties Measurement System).

Results

Magnesium. There are two forms of magnesium carbide; until now, neither had been synthesized from the elements.

---

(5) Anselmi-Tamburini, U.; Maglia, F.; Doppiu, S.; Monagheddu, M.; Cocco, G.; Munir, Z. A. *J. Mater. Res.* **2004**, *19* (5), 1558–1566.

(6) Deidda, C.; Delogu, F.; Cocco, G. *J. Mater. Sci.* **2004**, *39* (16−17), 5315–5318.

(7) Deidda, C.; Delogu, F.; Maglia, F.; Anselmi-Tamburini, U.; Cocco, G. *Mater. Sci. Eng., A* **2004**, *A375−A377*, 800–803.

(8) Delogu, F.; Deidda, C.; Mulas, G.; Schiffini, L.; Cocco, G. *J. Mater. Sci.* **2004**, *39* (16−17), 5121–5124.

(9) Matteazzi, P.; Le Caer, G. *J. Am. Ceram. Soc.* **1991**, *74* (6), 1382–90.

(10) Maglia, F.; Anselmi-Tamburini, U.; Deidda, C.; Delogu, F.; Cocco, G.; Munir, Z. A. *J. Mater. Sci.* **2004**, *39* (16−17), 5227–5230.

(11) Udod, I. *Synth. Met.* **1997**, *88*, 127–131.

(12) Emery, N.; Herold, C.; Lagrange, P. *J. Solid State Chem.* **2005**, *178* (9), 2947–2952.

(13) Janot, R.; Conard, J.; Guerard, D. *Carbon* **2001**, *39* (12), 1931–1934.

(14) Wang, C. S.; Wu, G. T.; Li, W. Z. *J. Power Sources* **1998**, *76* (1), 1–10.

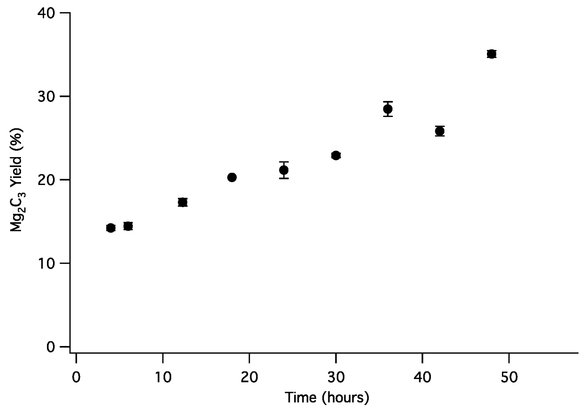

Figure 1. Percent yield of Mg_2C_3 during extended milling. The net reaction was $2Mg + 3C \rightarrow Mg_2C_3$.

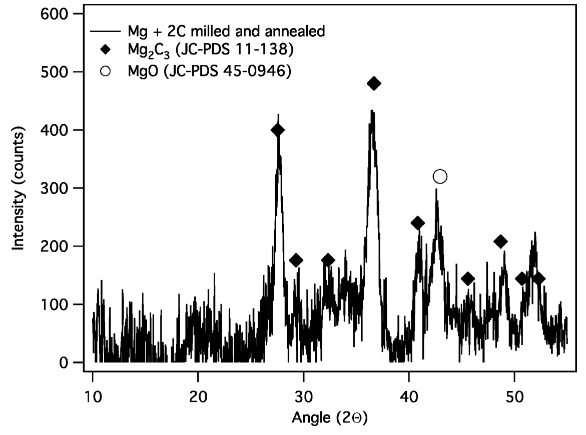

Figure 2. Powder XRD of the reaction of Mg + 2C milled 85 h and annealed 12 h at 490 °C. Before annealing the material produced was amorphous with no discernible reflections. After annealing the Mg_2C_3 and MgO were detectable.

MgC_2 decomposes to Mg_2C_3 above 500 °C; Mg_2C_3 decomposes to the elements above 700 °C. Hydrolysis of MgC_2 produces acetylene while hydrolysis of Mg_2C_3 produces a mixture of propyne and propadiene. Hydrolysis of products prepared from Mg:C ratios of 1:2 and 2:3 indicated the presence of propadiene and propyne (confirmed by FT-IR and mass spectrometry). No ethyne was detected. Attempts at synthesizing MgC_2 by mechanochemical methods have been unsuccessful so far.

Milling for extended periods produced a carbide content of 35%, as determined by gravimetric analysis (Figure 1).

After extended milling, the product was amorphous by powder XRD. Annealing at 490 °C for 12 h allowed the observation of crystalline Mg_2C_3 (Figure 2), but there is no increase in carbide content as measured by gravimetric analysis.

Calcium. It is possible to synthesize CaC_2 directly from the elements using high-energy ball milling (Figure 3). It should be noted that the CaC_2 phase produced (PDF 16-0178) is a cubic high-temperature phase (CaC_2−IV). Annealing for 12 h at a temperature near half the melting point of CaC_2 (1000 °C) resulted in conversion to more crystalline monoclinic CaC_2−III (Figure 4).

During the preparation of CaC_2, the gold-colored intercalation phase (CaC_6) was observed after 30 min of milling. Powder XRD analysis of this material showed one weak peak at 19.6° corresponding to the 001 line of CaC_6 (Figure 8).[12] CaC_6 is a superconducting phase with a T_c of 11.5 K.[15] Our material exhibited a T_c of 5 K (Figure 5).

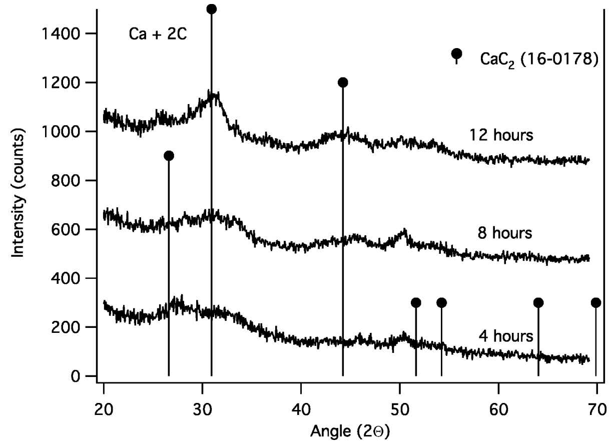

Figure 3. Powder diffraction patterns of the reaction $Ca + 2C \rightarrow CaC_2$. The carbon source was graphite and the calcium was dendritic calcium. The reaction mixture quickly becomes amorphous and poorly crystalline CaC_2 can be detected after 12 h of milling.

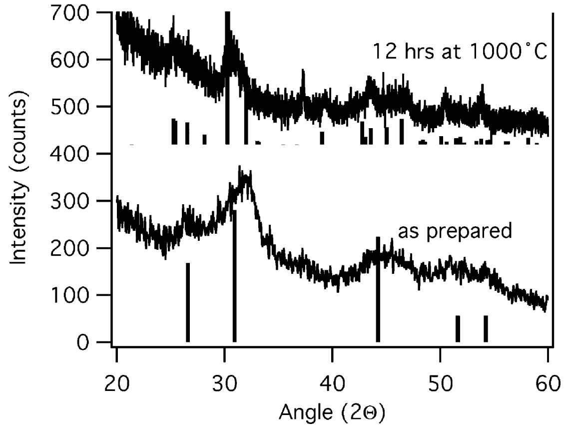

Figure 4. Powder diffraction patterns of the reaction $Ca + 2C \rightarrow CaC_2$ milled for 12 h before and after annealing at 1000 °C. The poorly crystalline cubic CaC_2−IV phase (JC-PDS 16-0178) initially formed is converted to monoclinic CaC_2−III (JC-PDS 73-1575). The peak at 37.2° 2θ is due to CaO.

The reaction progress of CaC_2 formation was followed gravimetrically by hydrolyzing the reaction mixture and measuring the amount of carbon remaining. Any carbon loss will be due to the formation of acetylene gas. It was found that carbide formation from calcium and graphite proceeds as a first order reaction in carbon. Three reaction regimes were observed (Figure 6): an initial slow rate ($0.137\ h^{-1}$), followed by a fast rate ($0.650\ h^{-1}$), and a final slow rate ($0.151\ h^{-1}$) similar to the initial rate.

Three purities of calcium were utilized: dendritic (99.98%), redistilled (99.5%), and ingot (99%). Dendritic calcium and redistilled calcium gave similar yields after 12 h of milling (>80%). It took 24 h of milling ingot calcium to approach yields close to the dendritic and redistilled forms. The formation of CaC_6 was not observed using ingot calcium.

The effect of the carbon source on yield of CaC_2 was tested using various grades of carbon (Figure 7). Yield of CaC_2

---

(15) Emery, N.; Herold, C.; d'Astuto, M.; Garcia, V.; Bellin, C.; Mareche, J. F.; Lagrange, P.; Loupias, G. *Superconductivity of Bulk CaC6. Physical Review Letters* **2005**, *95* (8), 087003/1−087003/4.

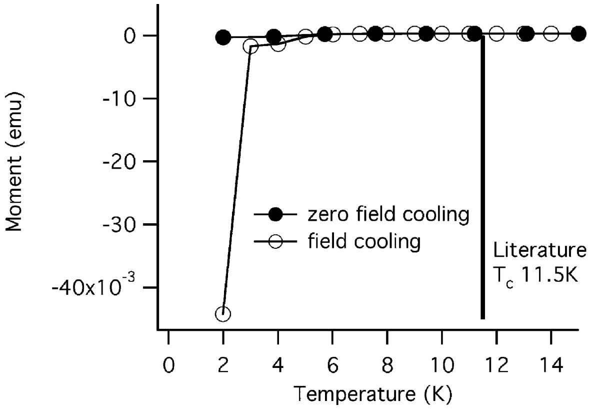

Figure 5. Onset of superconductivity observed in CaC_6 prepared mechanochemically from Ca + 6C. A T_c of 5 K was observed.

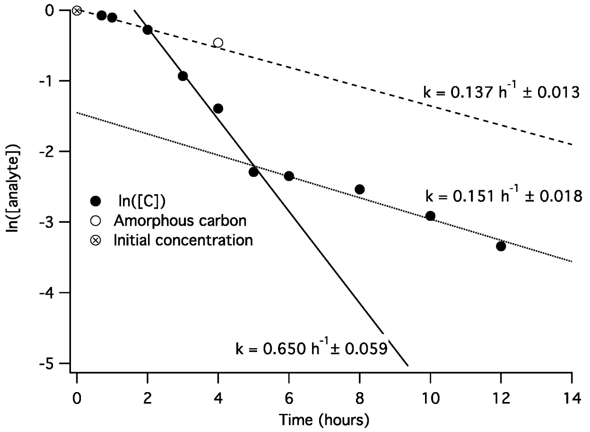

Figure 6. Kinetic plot of the synthesis of CaC_2 prepared by the high-energy ball milling of calcium and carbon. The concentration of carbon is expressed in (moles C)/(liters of free volume).

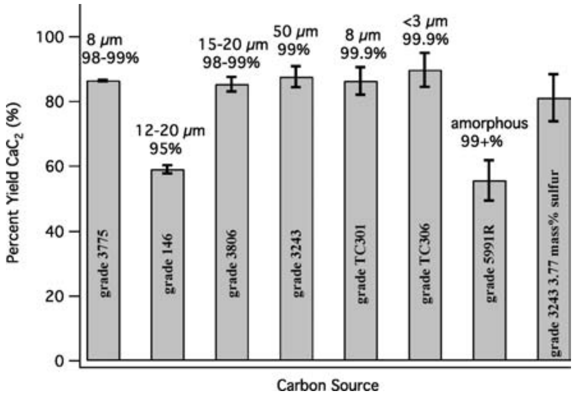

Figure 7. Good yields were obtained after milling for 12 h. Various carbon sources were tested. It was found that the more crystalline materials gave the best yield. The addition of sulfur (to emulate high-sulfur coal) did not affect the carbide synthesis appreciably.

from each source was determined after 12 h of milling. High purity graphite samples (grades 3775, 3806, 3243, TC301, and TC306) have yields of greater than 80%. Reduced yield was seen from samples of graphite with a purity of less than 98% (grade 146) and a poorly crystalline sample (grade 5991R).

To simulate high-sulfur coal, 3.77 mass percent of sulfur was added to a graphite (grade 3243) sample. The addition of sulfur had very little impact on the yield of CaC_2 suggesting that this method may offer a route to sequestering sulfur in coal. Powder XRD analysis of the sulfur-spiked product indicated the presence of poorly crystalline CaS. Acidification during hydrolysis resulted in the production of H_2S, as well as C_2H_2.

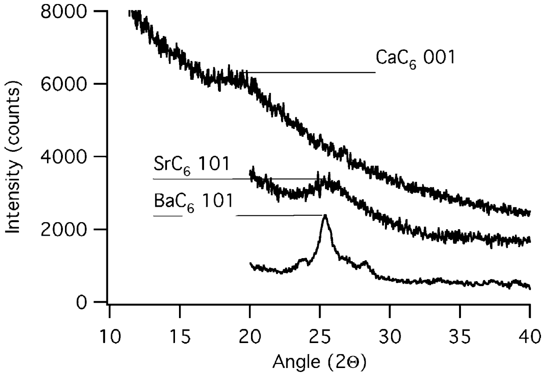

Figure 8. Intercalation phases observed in the formation of the MC_2 carbides.

Strontium and Barium. Both strontium and barium readily formed carbides with the observation of an intercalation phase during the synthesis. Powder diffraction patterns show the presence of the intercalation phases (Figure 8). Additionally, a gold-colored solid was observed in both reaction mixtures after 2−4 h of milling.

After 12 h of milling, SrC_2 was produced with a yield of 87%. After 16 h of milling, BaC_2 was produced with a yield of 82%.

Discussion

A scalable process for producing carbides of Ca and Mg utilizing less energy than that required for an arc-furnace would be industrially relevant.

In addition to the preparation of CaC_2 for the synthesis of acetylene:

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + HC{\equiv}CH \qquad (6)$$

Magnesium carbide (Mg_2C_3) can be hydrolyzed to form propadiene and propyne:

$$Mg_2C_3 + 2H_2O \rightarrow Mg(OH)_2 + H_2C{=}C{=}CH_2 + H_3C{-}C{\equiv}CH \qquad (7)$$

It has been shown that this mixture (of propyne and propadiene) can be catalytically converted to arenes by passing over an ion-exchanged Y zeolite.[16]

Magnesium. As shown in Figure 1, extended milling of magnesium and carbon does not greatly increase the yield of Mg_2C_3. There are several factors that may be contributing to this poor yield. Mg_2C_3 has a narrow temperature range in which formation is favored (500−700 °C). The localized high pressure and temperature events occurring during milling may result in decomposition, as well as formation, of the carbide. This could be alleviated by controlling the milling regime so that local conditions do not favor decomposition. Magnesium ingot and turnings requires a significant amount of time to homogenize the material in the vial (without

---

(16) Ruschewitz, U. *Coord. Chem. Rev.* **2003**, *244* (1−2), 115–136.

homogeneous mixing of the reactants, complete reaction will not occur) this may mean that increased yields could be realized with finely divided magnesium or extended milling times. With increased milling time the risk of oxygen contamination increases. The main source of this contamination is the failure of seals in the milling vials. This could be addressed by milling in an inert environment or through redesign of the milling containers for more robust seals. Finally, the slow rate of formation can also be attributed to the lack of a magnesium-graphite intercalation phase. In calcium, this intercalation phase results in a rapid conversion to CaC_6 to CaC_2 (see Figure 6); no such pathway is available for Mg_2C_3 synthesis.

Calcium. The diffraction pattern (Figure 3) of the synthesized CaC_2 is of a cubic high-temperature phase of the material; this may be due to the fact that high-energy ball milling results in nanosized materials. It is known that macroscopically disfavored modifications are favored in the nanoscale.[17] Additionally, the high temperature cubic phase of CaC_2 differs from the low temperature tetragonal phase in that the orientation of the C_2 units are disordered.[18] The energetic process of milling could easily result in this disordering.

The observation of the gold-colored intercalation compound (CaC_6) after 30 min of milling suggests that CaC_6 is an intermediate in the formation of calcium carbide (CaC_2). Once the intercalation phase is formed, the energy supplied by the impact of the ball is enough to induce the formation of CaC_2. This is analogous to observations in the lithium−carbon system.[19] The depression of T_c exhibited by the synthesized CaC_6 may be due to disordering induced by mechanical processing.

If the intercalation phase is part of this mechanism, then the reaction sequence for CaC_2 formation may be governed by the reactions outlined in eqs 8−11. The formation of the intercalation compound and carbide are considered irreversible processes in this analysis. This is borne out by the fact that CaC_2 is stable in an electric arc and that CaC_6 can be produced in high yields under relatively mild conditions.[12]

The set of reactions occurring may be the following:

$$\mathrm{Ca} + 6\mathrm{C}_{\mathrm{graphite}} \rightarrow \mathrm{CaC}_6 \qquad k_1 \tag{8}$$

$$\mathrm{CaC}_6 \rightarrow \mathrm{CaC}_2 + 4\mathrm{C}_{\mathrm{amorphous}} \qquad k_2 \tag{9}$$

$$\mathrm{Ca} + 2\mathrm{C}_{\mathrm{amorphous}} \rightarrow \mathrm{CaC}_2 \qquad k_3 \tag{10}$$

$$\mathrm{C}_{\mathrm{graphite}} \rightarrow \mathrm{C}_{\mathrm{amorphous}} \qquad k_4 \tag{11}$$

The fact that CaC_6 formation was observed initially suggests that the increased rate observed between 2 and 6 h of milling is from reaction 9. Reaction 10 proceeds at a slower rate. A similar mechanism may be used to explain why magnesium carbide forming reactions are so slow—magnesium is not known to form an intercalation phase.

This proposed mechanism (eqs 8−11) does not conflict with the proposed mechanism for calcium carbide formation from CaO.[20]

$$\mathrm{CaO}_{(s)} + \mathrm{C}_{(s)} \rightarrow \mathrm{Ca}_{(g)} + \mathrm{CO}_{(g)} \tag{12}$$

$$\mathrm{Ca}_{(g)} + 2\mathrm{C}_{(s)} \rightarrow \mathrm{CaC}_{2(s)} \tag{13}$$

The validity of the proposed mechanism (eqs 8−11) was tested by utilizing amorphous carbon as a carbon source. Synthesis performed with amorphous carbon gave a reduced carbide yield that falls on the interpolated rate from the initial slow formation of CaC_2 (see Figure 6). This provides strong evidence that the increased rate observed is due to reaction 9. In fact, the production of CaC_2 must be considered when attempting to synthesize the intercalation phase mechanochemically. Too much milling will result in the formation of the carbide instead of the intercalation phase.

The increase in milling time to achieve similar yields using ingot calcium can be attributed to impurities which hamper the formation of the CaC_6 intercalate. The largest impurities in the ingot calcium were aluminum and magnesium. Both of these metals can adversely affect the formation of the intercalation phase by producing a less malleable metal. This is illustrated in Figure 8. The most malleable metal (barium) produced the most crystalline intercalation phase.

Sulfur Content. Sulfur spiked carbon was used as a model for high sulfur coal. As can be seen in Figure 7 the purity level and crystallinity of the carbon source greatly affect the yield. By choosing carbon with a high CaC_2 yield the effect of sulfur on the reaction could be more accurately judged. The synthesis of calcium carbide from grade 3243 carbon gave a yield of 87.7 ± 1.9%. If all of the sulfur in the spiked sample is converted to CaS then adding 3.77 mass % sulfur should diminish the yield to 92.5% of the original yield. This gives an expected yield of 81.1%. An experimental yield of 81.2 ± 1.7% was found in a reaction spiked with 3.77% sulfur, suggesting that the sulfur present in the reaction is indeed being converted to CaS.

Media Wear. A major factor in the costs associated with mechanical processing is wear on the milling media and vessel. To reduce this wear vials and balls composed of 440C stainless steel were chosen. With a hardness of Rockwell C-65 this steel is one of the hardest commercially available stainless steels. The starting carbon (grade TC306) was found to possess an iron content of 321 ± 9 ppm. Redistilled calcium granules had an iron content of 13 ppm (from the certificate of analysis). The CaC_2 synthesized from this carbon by milling with calcium for 12 h possessed an iron content of 370 ± 11 ppm. From the iron content of the starting materials the product should have a content of 128 ppm. The difference can be attributed to iron picked up from media wear. This corresponds to about 0.5 mg of iron contamination per 2 g synthesis. Contamination could be further reduced by switching to aluminum oxide or tungsten carbide vials and balls.

---

(17) Bandaranayake, R. J.; Wen, G. W.; Lin, J. Y.; Jiang, H. X.; Sorensen, C. M. *Appl. Phys. Lett.* **1995**, *67* (6), 831–833.

(18) Knapp, M.; Ruschewitz, U. *Chemistry (Weinheim, Ger.)* **2001**, *7* (4), 874–80.

(19) Avdeev, V. V.; Savchenkova, A. P.; Monyakina, L. A.; Nikol'skaya, I. V.; Khvostov, A. V. *J. Phys. Chem. Solids* **1996**, *57* (6−8), 947–949.

(20) Kameyama, N.; Ota, Y.; Inoue, Y., III *Kogyo Kagaku Zasshi* **1941**, 44.

Conclusion

High-energy ball milling is an efficient route to oxide-free alkaline earth carbides (CaC_2, Mg_2C_3, SrC_2, and BaC_2) and intercalation compounds (CaC_6, SrC_6, and BaC_6). This method also offers an efficient route to isotopically enriched alkynes which can be utilized as precursors for more complex compounds.[21] Carbides that proceed through an initial intercalation phase (calcium, strontium, and barium) can be synthesized in high yield. Also, presented is the first successful synthesis of Mg_2C_3 from the elements.

Acknowledgment. The authors would like to thank Asbury Carbons, Inc (Asbury, NJ, www.asbury.com) for their generous donation of carbon sources and Jonathan Levine of the Kaner group at the University of California, Los Angeles, for his assistance with SQUID magnetometry measurements.

IC8022437

---

(21) Nazih, R.; Blauser, J. P.; Mock, B. H.; DeGrado, T. R. *Appl. Radiat. Isot.* **2005**, *63* (3), 305–309.