

# Formation of Unsaturated C<sub>3</sub> Hydrocarbons by the Protolysis of Magnesium Sesquicarbide with Ammonium Halides

Sabrina Disch,<sup>†,‡,§</sup> Anthony K. Cheetham,<sup>‡</sup> and Uwe Ruschewitz<sup>\*,†</sup>

Institut für Anorganische Chemie, Universität zu Köln, Greinstr. 6, D-50939 Köln, Germany, Materials Research Laboratory, University of California, Santa Barbara, California 93106

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The protolysis of magnesium sesquicarbide,  $Mg_2C_3$ , with inorganic acids provides an interesting alternative to the more common hydrolysis of ionic carbides for obtaining their respective hydrocarbons. In particular, protolysis reactions with ammonium halides as precursors for hydrogen halides were investigated using in situ methods such as TGA/sDTA/MS and high-temperature XRPD. The protolysis reactions with NH<sub>4</sub>F and NH<sub>4</sub>Cl revealed two different reaction mechanisms yielding C<sub>3</sub>H<sub>4</sub> and the respective magnesium halides as expected products. In the case of NH<sub>4</sub>Cl, intermediate phases that have not been previously observed, specificly (NH<sub>4</sub>)<sub>2</sub>MgCl<sub>4</sub> (*I*4/*mmm*) and two modifications of NH<sub>4</sub>MgCl<sub>3</sub> (*P*6<sub>3</sub>/*mmc*), were structurally characterized.

#### Introduction

Magnesium sesquicarbide (Mg<sub>2</sub>C<sub>3</sub>) has been known for a long time. Its formation from magnesium and methane or *n*-pentane upon heating, as well as its decomposition to magnesium and amorphous carbon at temperatures higher than 700 °C, were first described in 1910.<sup>1</sup> A common property of ionic carbides is the release of hydrocarbons upon hydrolysis, leading to their classification into methanides, acetylides, and allylenides. As a typical allylenide, Mg<sub>2</sub>C<sub>3</sub> evolves a mixture of propadiene and propyne upon hydrolysis<sup>2,3</sup> (1), which suggested the presence of linear C<sub>3</sub> dumbbells within the solid, long before its crystal structure was finally determined in 1992.<sup>4</sup>

$$Mg_2C_3(s) \xrightarrow{H_2O} C_3H_4(g) + 2MgO(s)$$
 (1)

Because the synthesis and subsequent hydrolysis of  $Mg_2C_3$ yields a conversion of hydrocarbons to  $C_3$  derivatives containing reactive multiple bonds, this system might be interesting for use in catalytic cycles. Unfortunately, hy-

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drolysis of  $Mg_2C_3$  leads to  $Mg(OH)_2/MgO$  as a byproduct, making its recycling to magnesium metal energetically costly.

An alternative synthesis (2) of  $Mg_2C_3$  from MgO and methane around 1400 °C has therefore been developed,<sup>5</sup> but because of its high reaction temperature and the low thermal stability of  $Mg_2C_3$  this route requires a rapid quenching of the product, which makes it inconvenient and highly ineffective.

$$2MgO(s) + 3CH_4(g) \xrightarrow{1400 \circ C} Mg_2C_3(s) + 2H_2O(g) + 4H_2(g)$$
 (2)

In addition to this, patents have been published describing the direct conversion of released propadiene and propyne with a dehydrocyclization catalyst to form trimethylbenzene, which could constitute an even more interesting product of hydrolysis of  $Mg_2C_3$ .<sup>5,6</sup>

To create an alternative way of recycling the residue of the hydrolysis reaction, our particular aim was to achieve a solid residue that is less stable than MgO. In this work, we investigated the modification of the hydrolysis reaction into a protolysis reaction using inorganic acids instead of water. Binary magnesium salts were expected as byproducts, which can be converted to magnesium metal by electrolytic routes.

<sup>\*</sup> To whom correspondence should be addressed. Email: uwe. ruschewitz@uni-koeln.de.

<sup>&</sup>lt;sup>†</sup> Universität zu Köln.

<sup>&</sup>lt;sup>‡</sup> University of California.

<sup>§</sup> Present address: Institut f
ür Festkörperforschung, Forschungszentrum J
ülich, D-52425 J
ülich, Germany.

<sup>(1)</sup> Novák, J. Z. Phys. Chem. 1910, 73, 513.

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<sup>(6)</sup> Allison, J. D.; Tillman, R. M. Conoco Inc. U.S. Patent 4,899,004, 1990.

#### **Experimental Section**

All of the reagents were used as purchased: magnesium powder, NH<sub>4</sub>Cl (99%), and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (99%) from Fisher Scientific, NH<sub>4</sub>F (98%) from Acros, NH<sub>4</sub>Br (99%) from Alfa Aesar, and NH<sub>4</sub>NO<sub>3</sub> (98%) from Sigma Aldrich. Argon and methane gases were purchased in UHP quality from Air Liquide.

Magnesium sesquicarbide was prepared according to published methods.<sup>6</sup> Magnesium powder was placed in an inert atmosphere in the hot zone of a tube furnace. By heating the sample to 685 °C in a methane gas stream,  $Mg_2C_3$  was obtained in a high purity of 94%, on the basis of the crystalline fraction of the sample as refined from X-ray powder diffraction (XRPD) data. Although graphite reflections were observed in XRPD, this phase was neglected during refinement because of the strong preferred orientation effects, which would otherwise lead to a significant overestimation of the graphite content.<sup>7</sup>

Coupled TGA/sDTA/MS measurements were performed in a Mettler STARe Thermogravimetric Analyzer, TGA/sDTA 851e, coupled to a Balzers ThermoStar mass spectrometer. Roughly stoichiometric amounts of the reactants were ground to a homogeneous mixture inside an MBraun glove box and filled into 70  $\mu$ L alumina crucibles. As the TGA is not placed inside the glove box, the contact of the sample with air during loading could not be avoided but was kept as short as possible (<30 s). The sample was kept at a constant temperature for 2 min in advance of each measurement to purge the sample chamber with nitrogen gas. The measurements were carried out in a temperature range of 25–600 °C with a heating rate of 10 °C/min and nitrogen as purge gas (50 mL/min).

For ex situ investigations on the protolysis reaction with NH<sub>4</sub>F, samples of a stoichiometric mixture of Mg<sub>2</sub>C<sub>3</sub> and NH<sub>4</sub>F were filled in alumina boats, covered with alumina lids, and heated for 2 h to different temperatures between 100 and 300 °C in an inert atmosphere. XRPD data of the resulting samples were collected on a Huber G670 diffractometer using Cu K $\alpha_1$  radiation.

High-temperature synchrotron powder investigations on the protolysis reaction with NH<sub>4</sub>Cl were performed at the powder diffractometer of beamline B2 of the Hamburg synchrotron facility (HASYLAB) using the following setup:  $\lambda = 0.6875$  Å; position sensitive imaging plate detector system (OBI<sup>8</sup>); STOE capillary furnace. The quartz capillary (0.3 mm) containing the reacting sample was sealed with vacuum grease to maintain the inert atmosphere inside while avoiding a high pressure due to the gas evolution during the reaction. The measurements were performed at temperatures between 150 and 390 °C in steps of 10 °C while each measurement took about 18 min. All of the diffractograms were analyzed using the STOE software package *Win XPOW*.<sup>9</sup> The Rietveld refinements were performed using the *GSAS* software package.<sup>10</sup>

## **Results and Discussion**

Because inorganic acids are mostly hazardous, less accessible, or difficult to get in a constant gas flow, their respective ammonium salts were chosen as precursors. These



**Figure 1.** (a) Thermoanalytic data of the protolysis of Mg<sub>2</sub>C<sub>3</sub> with NH<sub>4</sub>F. TGA and sDTA data are presented as black and red lines, respectively. (b) Corresponding MS diagram, m/z values for C<sub>3</sub>H<sub>4</sub> (green, m/z = 38, 39, 40), water (blue, m/z = 18), and ammonia (orange and red, m/z = 16, 17) are shown.

are easier to handle and dose and therefore provide a better interaction between the reagents. As the protolysis reaction is expected to start upon decomposition of the ammonium salt, it could be realized in a relatively narrow temperature range, making it easily observable with in situ methods such as TGA/sDTA/MS measurements and temperature-dependent X-ray powder diffraction (XRPD).

**Protolysis with NH<sub>4</sub>F.** The protolysis of  $Mg_2C_3$  with NH<sub>4</sub>F as a precursor for HF is expected to yield MgF<sub>2</sub> as a solid residue besides NH<sub>3</sub> and the desired  $C_3H_4$  in the gas phase (3).

$$Mg_2C_3(s) + 4NH_4F(s) \xrightarrow{\Delta} C_3H_4(g) + 4NH_3(g) + 2MgF_2(s)$$
 (3)

After verifying MgF<sub>2</sub> as a solid product of this reaction (heating a mixture of  $Mg_2C_3$  and  $NH_4F$  at 350 °C), thermoanalytic methods were chosen to monitor the protolysis reaction in situ and verify its gaseous products. On the basis of TGA and sDTA measurements, the protolysis with  $NH_4F$  can be described as a three-step reaction (part a of Figure 1).

The TGA experiment shows a large weight loss occurring in three steps at 130, 200, and 270 °C due to the decomposition of the ammonium salt and the evolution of  $NH_3$  and  $C_3H_4$ . In the sDTA measurement, three distinct, endothermic signals can be observed simultaneously. To identify the gaseous products responsible for the weight loss, mass spectrometry measurements were carried out simultaneously with the TGA/sDTA experiments. As can be seen in part b

<sup>(7)</sup> See Supporting Information.

<sup>(8) (</sup>a) Knapp, M.; Joco, V.; Baehtz, C.; Brecht, H. H.; Berghaeuser, A.; Ehrenberg, H.; von Seggern, H.; Fuess, H. Nucl. Instrum. Methods Phys. Res., Sect. A 2004, 521, 565. (b) Knapp, M.; Baehtz, C.; Ehrenberg, H.; Fuess, H. J. Synchrotron Radiat. 2004, 11, 328.
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<sup>(9)</sup> *Win XPOW*, version 1.10 (03-Jun-2002); Stoe & Cie GmbH: Darmstadt, Germany.

<sup>(10)</sup> Larson, A. C.; von Dreele, R. B. Los Alamos Laboratory, Rep. No. LA-UR 1987, 86, 748; revised PC version of December 2006.



**Figure 2.** Ex situ XRPD on the protolysis reaction of Mg<sub>2</sub>C<sub>3</sub> with NH<sub>4</sub>F. XRPD data are presented for different annealing temperatures between 100 and 300 °C in steps of 20 °C. Observed reaction intermediates are (NH<sub>4</sub>)<sub>2</sub>MgF<sub>4</sub> (green) at 160 °C and NH<sub>4</sub>MgF<sub>3</sub> (red) at 220 °C, the finally obtained product is MgF<sub>2</sub> (blue). The additional reflection at 26.1°  $2\theta$  is due to graphite, which is contained in the initial Mg<sub>2</sub>C<sub>3</sub> sample.

of Figure 1, releases of  $C_3H_4$ , as well as NH<sub>3</sub>, are observed upon heating, corresponding to each signal in the sDTA measurement. At 200 °C, traces of water are also detected, which might have been absorbed by the NH<sub>4</sub>F. As the release of  $C_3H_4$  is not continuous but definitely corresponding to all of the decomposition processes, it is concluded that the protolysis as a three-step reaction involves the formation of two intermediates. Analogous to the formation of NH<sub>4</sub>HF<sub>2</sub> during the decomposition of NH<sub>4</sub>F, an intermediate such as (NH<sub>4</sub>)<sub>2</sub>MgF<sub>4</sub> may be suggested for the first step of protolysis.

Ex situ XRPD experiments were chosen to observe the processes in the solid phase during the protolysis reaction and to identify the intermediates. Therefore, samples of a mixture of  $Mg_2C_3$  and  $NH_4F$  were heated to different temperatures within the investigated temperature range, allowed to cool down, and examined by XRPD. The resulting diffractograms are presented in Figure 2. Beginning with the starting material still present at 100 °C, the first intermediate could be identified as  $(NH_4)_2MgF_4$  at 160 °C. Further reaction with residual  $Mg_2C_3$  led to  $NH_4MgF_3$  as the second intermediate at 220 °C. As the final solid product,  $MgF_2$  was obtained at temperatures above 280 °C.

Some more attention was given to the reaction temperature of the protolysis. Therefore, TGA and sDTA experiments were carried out with respect to the ratio of the reactants to show a possible influence of the concentration of the ammonium salt.<sup>7</sup> The reaction temperature was observed to decrease, whereas DTA measurements revealed the abovementioned endothermic signals to become less endothermic with decreasing amounts of ammonium salt. Because the measured sDTA signal is a combination of the exothermic signal due to protolysis and the endothermic signal due to decomposition of the ammonium salt, it is concluded that the decomposition of NH<sub>4</sub>F is driven to lower temperatures by the exothermic protolysis reaction.

**Protolysis with NH<sub>4</sub>Cl.** The protolysis reaction of  $Mg_2C_3$  with NH<sub>4</sub>Cl is expected to yield  $MgCl_2$  besides  $C_3H_4$  and



**Figure 3.** (a) Thermoanalytic data of the protolysis of Mg<sub>2</sub>C<sub>3</sub> with NH<sub>4</sub>Cl. TGA and sDTA data are presented as black and red lines, respectively. (b) Corresponding MS diagram, m/z values for C<sub>3</sub>H<sub>4</sub> (green, m/z = 38, 39, 40), water (blue, m/z = 18), and ammonia (red, m/z = 16, 17) are shown.

 $NH_3$  as gaseous products (4). As in the experiments with  $NH_4F$ , thermoanalytic measurements were carried out to monitor additional processes during the reaction (Figure 3).

$$Mg_{2}C_{3}(s) + 4NH_{4}Cl(s) \xrightarrow{\Delta} C_{3}H_{4}(g) + 4NH_{3}(g) + 2MgCl_{2}(s)$$
(4)

The TGA/sDTA experiments presented in part a of Figure 3 exhibit a single-step reaction of  $Mg_2C_3$  and NH<sub>4</sub>Cl in general. The sDTA measurement shows an endothermic signal at 190 °C, resulting from a structural phase transition of the NH<sub>4</sub>Cl from the CsCl to the rocksalt structure. The large endothermic signal at 290 °C corresponds to the large weight loss observed in the TGA, indicating the thermal decomposition of the ammonium salt and subsequent release of the gaseous products. At 320 °C, a small additional signal is observed in TGA and sDTA. Simultaneously recorded MS data (part b of Figure 3) verify the release of  $C_3H_4$  and  $NH_3$  corresponding to the main reaction signals at 290 °C. The mass spectrum also shows a smaller release of either ammonia or water, corresponding to the 320 °C signal in the TGA and sDTA measurements.

To clarify the presence of this additional effect at 320 °C and structurally identify solid intermediates during this reaction, in situ synchrotron powder diffraction measurements were carried out. These experiments revealed reaction intermediates similar to those found for the protolysis with NH<sub>4</sub>F. All of the intermediates observed have been assigned to their respective phases and are presented in Figure 4. After the structural phase transition of NH<sub>4</sub>Cl to its high-temper-



**Figure 4.** Quantitative phase analysis of in situ synchrotron diffraction data on the protolysis reaction of  $Mg_2C_3$  with  $NH_4Cl$ . The presented phases are  $Mg_2C_3$  (black),  $NH_4Cl$  (orange),  $NH_4Cl(HT)$  (red),  $(NH_4, Mg)Cl$  (purple),  $(NH_4)_2MgCl_4$  (blue),  $NH_4MgCl_3$  (green), and  $NH_4MgCl_3(HT)$  (olive).

Table 1. New Phases That Have Been Obtained as Intermediates in the Protolysis Reaction of  $Mg_2C_3$  with  $NH_4Cl$ 

new phase	$(NH_4)_2MgCl_4$	NH <sub>4</sub> MgCl <sub>3</sub>	NH <sub>4</sub> MgCl <sub>3</sub> (HT)
space group lattice T	$\begin{array}{l} I4/mmm \ (\text{No. 139}) \\ a = 5.03013(9) \ \text{\AA} \\ c = 16.2774(4) \ \text{\AA} \\ 340 \ ^{\circ}\text{C} \end{array}$	$\begin{array}{l} P6_{3}/mmc \mbox{ (No. 194)} \\ a = 7.1573(7) \mbox{ Å} \\ c = 11.951(1) \mbox{ Å} \\ 360 \mbox{ °C} \end{array}$	$\begin{array}{l} P6_{3}/mmc \ (\text{No. 194}) \\ a = 7.1570(3) \text{ Å} \\ c = 17.734(1) \text{ Å} \\ 390 \ ^{\circ}\text{C} \end{array}$
analogous phase	$(NH_4)_2MgF_4{}^{11}$	4H-RbMgCl <sub>3</sub> <sup>12</sup>	6H-RbMgCl <sub>3</sub> <sup>12</sup>
space group lattice temperature	I 4/mmm (No.139) a = 4.0567(1)  Å c = 13.8354(6)  Å RT	P 6 <sub>3</sub> /mmc (No.194) a = 7.10  Å c = 11.84  Å RT	P 6 <sub>3</sub> /mmc (No.194) a = 7.095(3)  Å c = 17.578(5)  Å RT

ature phase at 210 °C, a solid solution of small amounts of MgCl<sub>2</sub> in NH<sub>4</sub>Cl is observed. Its composition could be estimated to 0.85:0.15 (NH<sub>4</sub>Cl/MgCl<sub>2</sub>) by the application of Vegard's law.<sup>7</sup> (NH<sub>4</sub>)<sub>2</sub>MgCl<sub>4</sub> could be identified as one intermediate of the reaction between 270 and 350 °C, followed by NH<sub>4</sub>MgCl<sub>3</sub> at 350 °C and an additional modification of NH<sub>4</sub>MgCl<sub>3</sub> above 360 °C. Because the reaction was not finished when the in situ experiments were stopped at 390 °C, an additional ex situ experiment was carried out at 450 °C to verify MgCl<sub>2</sub> as the final product of this reaction.

The protolysis reaction with NH<sub>4</sub>Cl revealed three new phases that have not been reported previously and will therefore be discussed in greater detail (Table 1). (NH<sub>4</sub>)<sub>2</sub>MgCl<sub>4</sub> crystallizes in the tetragonal space group *I*4/*mmm* (No. 139), and its crystal structure is isotypic to that of (NH<sub>4</sub>)<sub>2</sub>MgF<sub>4</sub>.<sup>11</sup> It was found to be the only crystalline compound at T = 340 °C in the in situ measurements. NH<sub>4</sub>MgCl<sub>3</sub> crystallizes in the hexagonal space group *P*6<sub>3</sub>/*mmc* (No. 194) with its crystal structure isotypic to that of RbMgCl<sub>3</sub>.<sup>12</sup> Its high-temperature modification is isotypic to another modification

**Table 2.** Reaction Temperatures and Products of the Protolysis Reaction of  $Mg_2C_3$  with Various Ammonium Salts<sup>*a*</sup>

protolysis agent	T°C	gaseous products (MS)	solid residue
NH4F	130	C <sub>3</sub> H <sub>4</sub> , NH <sub>3</sub>	$\begin{array}{c} MgF_2 \\ MgCl_2 \\ MgBr_2 \\ Mg(NO_3)_2 {\scriptstyle \bullet} 6H_2O^a \\ (NH_4)_2 Mg_2(SO_4)_3 \end{array}$
NH4Cl	290	C <sub>3</sub> H <sub>4</sub> , NH <sub>3</sub>	
NH4Br	450	not measured	
NH4NO3	150	C <sub>3</sub> H <sub>4</sub> , H <sub>2</sub> O, N <sub>2</sub> O/CO <sub>2</sub>	
(NH4)2SO4	290	C <sub>3</sub> H <sub>4</sub> , NH <sub>3</sub> , SO <sub>2</sub> , CO <sub>2</sub>	

 $^a$  The crystal water contained in Mg(NO\_3)\_2 is a result of both handling the sample in air and the release of water as a decomposition product of NH\_4NO\_3.

of RbMgCl<sub>3</sub>, crystallizing in the same space group.<sup>12</sup> Because during ex situ experiments the latter modification turned out to be stable at room temperature as well, it may be concluded that for NH<sub>4</sub>MgCl<sub>3</sub>, similar to RbMgCl<sub>3</sub>, the thermodynamic stabilities of the two lattice types are not dramatically different.<sup>12</sup>

Although the synchrotron diffraction method revealed reaction intermediates and the final reaction product to be similar to those of the protolysis with NH<sub>4</sub>F, the reaction mechanisms, as far as what is observable by thermoanalytic methods, turned out to be different. Whereas for the protolysis with NH<sub>4</sub>F, three independent protolysis steps releasing C<sub>3</sub>H<sub>4</sub> could be identified by MS measurements, only a single reaction step involving the release of C<sub>3</sub>H<sub>4</sub> can be observed for the protolysis with NH<sub>4</sub>Cl. Therefore, the latter reaction can be understood as another representative for the ammonium chloride route to anhydrous metal chlorides as described by Meyer et al.<sup>13</sup> This route was described as a two-step procedure with an acid-base reaction (i.e., protolysis) and a complex formation first and a decomposition second.<sup>14</sup> The decomposition of (NH<sub>4</sub>)<sub>2</sub>MgCl<sub>4</sub> to NH<sub>4</sub>MgCl<sub>3</sub> and finally MgCl<sub>2</sub> might explain the release of NH<sub>3</sub> observed by the thermoanalytic methods as an additional effect. The temperature shift between thermoanalytic experiments and powder diffraction might be due to the different heating rates applied. However, for both protolysis reactions the evolution of C<sub>3</sub>H<sub>4</sub> as well as the respective magnesium halide as final product could be verified.

**Further Protolysis Agents.** In addition to the protolysis reactions mentioned above, more ammonium salts have been investigated using in situ methods, to find other suitable protolysis agents. A summary of all of the applied ammonium salts and the resulting products is presented in Table 2.

As a further ammonium halide,  $NH_4Br$  was reacted with  $Mg_2C_3$  and verified to yield  $MgBr_2$  as the solid product. This protolysis reaction occurs at significantly higher temperatures than the protolysis with  $NH_4F$  or  $NH_4Cl$ .

Ammonium nitrate, NH<sub>4</sub>NO<sub>3</sub>, and ammonium sulfate,  $(NH_4)_2SO_4$ , have been studied as precursors for the oxidizing inorganic acids HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. TGA/sDTA/MS experiments verified the protolysis reaction by the detection of C<sub>3</sub>H<sub>4</sub> as a gaseous product. However, in both cases signals

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#### Formation of Unsaturated C<sub>3</sub> Hydrocarbons

for m/z = 44 were detected by mass spectrometry. Whereas this signal can be interpreted as the evolution of either N<sub>2</sub>O (typical decomposition product of NH<sub>4</sub>NO<sub>3</sub>) or CO<sub>2</sub> in the case of the reaction with NH<sub>4</sub>NO<sub>3</sub>, it is clear evidence of the formation of CO<sub>2</sub> in the case of the reaction with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, because the evolution of CO<sub>2</sub> can only be understood as a result of the oxidation of the C<sub>3</sub> unit in Mg<sub>2</sub>C<sub>3</sub>. For this reason, oxidizing inorganic acids are not applicable for the protolysis of Mg<sub>2</sub>C<sub>3</sub>.

## Conclusion

In this work, we have shown that the protolysis of  $Mg_2C_3$ with ammonium halides is possible, provides an interesting alternative to the hydrolysis, and follows two different reaction mechanisms for NH<sub>4</sub>F and NH<sub>4</sub>Cl. The protolysis with NH<sub>4</sub>F has been identified as a three-step reaction with (NH<sub>4</sub>)<sub>2</sub>MgF<sub>4</sub> and NH<sub>4</sub>MgF<sub>3</sub> as intermediates and MgF<sub>2</sub> as the final solid product. At each reaction step,  $C_3H_4$  is released. The protolysis with NH<sub>4</sub>Cl has been explained as a single-step reaction leading to (NH<sub>4</sub>)<sub>2</sub>MgCl<sub>4</sub> as a solid product, which decomposes at higher temperatures to NH<sub>4</sub>MgCl<sub>3</sub> and finally MgCl<sub>2</sub>. The crystal structures of (NH<sub>4</sub>)<sub>2</sub>MgCl<sub>4</sub> and two modifications of NH<sub>4</sub>MgCl<sub>3</sub> have been determined and refined for the first time.

The protolysis reaction is certainly an interesting alternative to the more common hydrolysis of saltlike carbides to obtain hydrocarbons. With every ammonium halide used as a protolysis agent,  $C_3H_4$  and the respective magnesium halide were obtained as products. Because the electrolysis of  $MgCl_2$  to magnesium metal is a commonly used process in industry, the protolysis with  $NH_4Cl/HCl$  provides an interesting approach to close the cycle for the preparation of  $C_3H_4$  from methane via  $Mg_2C_3$  and  $MgCl_2$ .

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**Supporting Information.** XRPD data of  $Mg_2C_3$ , TGA, and sDTA data of the protolysis of  $Mg_2C_3$  with NH<sub>4</sub>F, Rietveld refinement of the in situ synchrotron powder diffraction data of the protolysis with NH<sub>4</sub>Cl, and TGA/ sDTA/MS data of the protolysis with NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. This material is available free of charge via the Internet at http://pubs.acs.org.

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