

## SYNTHESIS AND THERMAL DECOMPOSITION OF MAGNESIUM DICARBIDE\*

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*Dedicated to Academician Jiří Mestecký on the occasion of his 60th birthday.*

The conditions of formation of magnesium dicarbide from magnesium and acetylene were investigated; the optimum temperature, reaction period, and acetylene flow rate were sought so as to achieve high yields of dicarbide and minimize the free carbon deposit. The porosity of the magnesium dust was found to have a pronounced effect upon the yield; a considerable improvement was achieved by pressing the dust into pellets with controlled porosity. The powder X-ray diffraction patterns of  $MgC_2$  samples were studied. The intense reflection could be indexed for the bct symmetry ( $a = 392.9 \pm 0.6$  pm,  $c = 503.7 \pm 1.2$  pm), but as the intensity calculations for dicarbide models with different arrangements of the  $C_2^{2-}$  groups indicate, the symmetry of the  $MgC_2$  lattice will be lower than tetragonal. The thermal decomposition of the dicarbide leading to sesquicarbide was examined in dependence on time and temperature by hydrolyzing the samples and analyzing the gaseous products by GLC. Due to the thermal decomposition, traces of sesquicarbide appear even during the dicarbide synthesis. The decomposition process was approximated by kinetic equations. The Arrhenius equation constants, in the temperature region of 485–560°C, are  $A_A = 4.97 \cdot 10^{12} s^{-1}$ ,  $E_A = 257$  kJ mol<sup>-1</sup>.

Magnesium dicarbide can be synthesized, according to Novák<sup>1</sup>, by reacting magnesium with acetylene at temperatures of 440–520°C; however, if the temperature exceeds 490°C, the dicarbide starts to decompose giving sesquicarbide  $Mg_2C_3$  and carbon.

The thermal instability is the main reason why no preparations containing more than 70%  $MgC_2$  have as yet been prepared. Other effects contributing to this fact are the nonquantitative course of the reaction and the formation of pyrolytic carbon depositing on the sample grains. While the unreacted magnesium can be removed from the preparation by extraction<sup>2</sup>, pyrolytic carbon cannot be removed without disturbing the sample.

The objective of the present work was to synthesize samples with high contents

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of  $MgC_2$  by reacting magnesium with acetylene in conditions of low formation of carbon, respecting the thermal stability limit of the carbide. Since little information is available<sup>2</sup> concerning the thermal decomposition of the dicarbide, particularly at lower temperatures, we studied this effect in more detail and worked out an optimum procedure for the synthesis.

## EXPERIMENTAL

### Synthesis of Magnesium Dicarbide

Magnesium dicarbide was prepared by reacting magnesium dust with acetylene. Magnesium was of 99.96% purity and was contaminated by Fe (0.032%), Si (0.001%), Ni (0.0002%), Cu (0.0005%), Al (0.001%), Mn (0.005%), Cr (0.001%). The dust (grain size below 0.05 mm) was obtained by filing the metal under kerosene. Technical acetylene from a pressure cylinder was purified by washing in concentrated sulphuric acid and leading over solid potassium hydroxide. The magnesium dust was pressed into pellets 10.1 mm in diameter, 10.4 mm high, with a controlled porosity of 10–70%. The pellets were inserted in a corundum tubular furnace 25 mm in diameter. Steel and aluminium wool was interposed between the samples and the acetylene feed. The temperature was held at  $450 \pm 2^\circ C$  at the beginning of the reaction and at  $470 \pm 2^\circ C$  towards its end, the acetylene flow rate was  $3-4 \text{ l h}^{-1}$ , the reaction period was 2.5 h. Before the reaction the apparatus was flushed with hydrogen until a temperature of  $450^\circ C$  was reached; after the reaction the samples were allowed to cool down in the furnace in vacuum.

Preparations with high contents of dicarbide were obtained from magnesium pellets with a porosity of 50%. The samples after the reaction were freed from the carbon deposit by grinding the coating off in a dry-box, pulverized in a grinding mortar, and extracted in a Soxhlet apparatus with a 1 : 1 mixture of diethyl ether (previously dried with sodium and sodium hydride) and ethyl bromide (dried with calcium chloride). After 24 h extraction the preparation was dried in vacuum at  $67^\circ C$ .

### Thermal Decomposition of Magnesium Dicarbide

After homogenization in a dry box, the samples in graphite crucibles were placed in quartz glass test tubes, and after evacuation with a rotary oil vacuum pump, dipped into molten metal bath at the desired temperature, which was maintained constant with a precision of  $\pm 5^\circ C$ . After the preselected time the test tubes were cooled rapidly with water.

Making use of the fact that on hydrolysis, magnesium dicarbide gives acetylene, whereas magnesium sesquicarbide affords  $C_3H_4$  hydrocarbons<sup>3,4</sup>, the conversion of magnesium dicarbide was followed gas chromatographically. The product of the thermal treatment in the test tube was decomposed with distilled water. The hydrolysis proceeded slowly enough for no thermal breakdown of the hydrocarbons formed to take place. After the decomposition, the contents of acetylene and  $C_3H_4$  hydrocarbons were determined in the gas evolved. In the calculation of the degree of conversion, allowance was made for the sesquicarbide present in the starting sample, as detected gas chromatographically. The results were related to pure magnesium dicarbide; the number of moles of  $MgC_2$  that reacted from a mole of the initially present dicarbide was calculated as

$$n = 2(x_{MgC_2} - x_{C_2H_2}) / [x_{MgC_2}(2 - x_{C_2H_2})], \quad (1)$$

where  $x_{\text{MgC}_2}$  is the mole fraction of dicarbide in the starting mixture with sesquicarbide and  $x_{\text{C}_2\text{H}_2}$  is the mole fraction of acetylene in the mixture of  $\text{C}_2\text{H}_2$  and  $\text{C}_3\text{H}_4$  obtained from the hydrolysis.

#### Gas Chromatographic Analysis of the Hydrocarbons

The analyses were carried out on a Hewlett-Packard 5840 A instrument equipped with a 2 m column packed with Porapak Q. The temperature was held at 70°C, the flow rate of the carrier gas, helium, was 20 ml min<sup>-1</sup>. The molar specific factors for the thermal conductivity detector were determined by using pure standards of acetylene (Linde AG) and  $\text{C}_3\text{H}_4$  hydrocarbons obtained by hydrolysis of magnesium sesquicarbide.

#### Powder X-Ray Diffraction Patterns

The powder X-ray diffraction patterns were obtained on a Mikrometa II instrument fitted with a goniometer (Chirana, Prague), an MX 118 G-M tube (Mullard), and an NRX 501 evaluating unit (Chirana, Prague). Filtered  $\text{CuK}_\alpha$  radiation was used; voltage 30 kV, current 20 mA. The powder sample was protected with vaseline and paraffin oil against humidity. For an additional elimination of the effect of humidity, the scanning in the region of 15–50° was divided into three sections, a fresh sample being used for each of them. The measurements were repeated after a time for excluding reflections from the nonhydrolyzable impurities.

The theoretical diffraction patterns were calculated from the coordinates of the atoms in an asymmetric group in the elementary cell, and from the lattice parameters calculated from the diffractograms according to Burnham<sup>5</sup>. The Pulverix program<sup>6</sup> used for the calculation of the theoretical diffraction patterns involves an own library of coefficients of the scattering factors and values for dispersion corrections. The intensity of the diffracted radiation is calculated by the program based on the structure factor involving the anisotropy of the temperature factor, on the combined Lorentz-polarization factor, and the frequency factor.

#### Chemical Analysis

The content of  $\text{MgC}_2$  in the samples was determined by measuring the volume of gases evolved during hydrolysis. The composition of the gas mixture was established gas chromatographically. The analysis of the pellets included determination of the mass increment, chelatometric determination of magnesium, and gravimetric determination of free carbon.

### RESULTS AND DISCUSSION

The amount of magnesium dicarbide obtained from the reaction of magnesium dust with acetylene is governed, among others, by three principal factors: the reaction period, the temperature, and the flow rate of acetylene. These factors affect the reaction in various aspects. For suppressing the formation of free carbon, the acetylene flow should be slowed down and the reaction time shortened; and for suppressing the consecutive thermal decomposition, the reacting components should be held at a low temperature. On the other hand, for achieving a high degree of conversion of magnesium to dicarbide, the temperature should be increased and the reaction time prolonged. A too high flow rate of acetylene, however, has an adverse affect on the carbide yield. In tentative experiments the acetylene flow rate was lowered

gradually from  $15 \text{ l h}^{-1}$  down to  $1.5 \text{ l h}^{-1}$  and the temperature was decreased from  $490^\circ\text{C}$  to  $430^\circ\text{C}$ , but the reaction period had to be prolonged from 20 min to more than 2 h. The optimum carbide yields, with respect to the above factors, were reached at temperatures about  $450^\circ\text{C}$ , acetylene flow rate of  $3.5 \text{ l h}^{-1}$ , and reaction period of 2.5 h.

The carbide yield depends to a great extent also on the porosity of the magnesium pellet used (Table I). The dependence of the composition of the reacted pellet on its starting porosity is shown in Fig. 1, the theoretical composition of the pellet after

TABLE I

Composition of the samples of magnesium dicarbide in dependence on the porosity of the starting magnesium pellet

Porosity %	Mass increment after the reaction %	Content of $\text{MgC}_2^a$ %	Content of free carbon %	Content of free magnesium %
34.7	4.0	13.3	1.84	84.8
44.7	16.3	38.5	4.43	57.0
53.0	43.5	57.5	4.85	37.6
62.0	91.2	66.5	24.8	8.7
68.0	130.7	55.8	34.4	9.8

<sup>a</sup> Traces of  $\text{Mg}_2\text{C}_3$  are neglected.

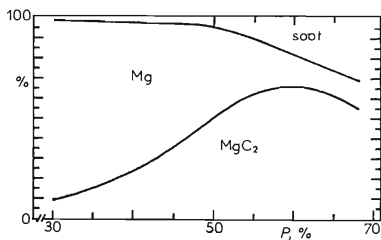


FIG. 1

Composition of the magnesium pellets after reaction with acetylene in dependence on their initial porosity

the extraction of the unreacted magnesium, in dependence on the porosity, is shown in Fig. 2. Although in the synthesis itself the dicarbide yield is highest for a porosity of 60%, lower porosities (45–50%) should be applied if the preparation is additionally enriched by extraction.

The dicarbide for the subsequent study was therefore prepared from pellets with a porosity of 50%; the product contained 56%  $\text{MgC}_2$ , 2.2%  $\text{Mg}_2\text{C}_3$ , 32.5% Mg metal, 5% free carbon, and impurities. After the surface carbon layer had been ground off and magnesium removed by extraction, the dicarbide content was as high as 83.8% and the free magnesium and free carbon contents were as low as 3% and 3.6%, respectively. The remaining part was probably magnesium oxide or hydroxide, formed despite the maximum effort made to eliminate humidity. This impurity, in a concentration of about 9%, did not manifest itself in the X-ray diffraction patterns. The  $\text{C}_2/\text{C}_3$  hydrocarbon ratio in the gaseous products can be assumed not to be affected by the impurity, as the ampoules were evacuated before the hydrolytic decomposition; therefore, the identity of the residual impurity was not examined in detail. The product enriched by extraction was grey-brown in colour and reacted with water giving rise to flame.

With the exception of some weak lines of unhydrolyzable impurities, the X-ray reflections could be indexed for a *bct*-lattice (*I4/mmm*,  $\text{CaC}_2$ -I type) with the condition that  $h + k + l = 2n$ . The diffraction patterns published<sup>2,7</sup> contain a high number of reflections that Irmann<sup>2</sup> indexed without allowing for the constraints. The lattice parameters were calculated by Irmann for an *fcc*-lattice; however, a number of reflections coincided with those of magnesium oxide, which in the work<sup>2</sup> complicated the structure considerations.

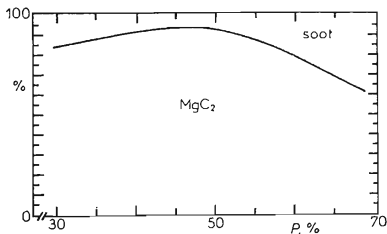


FIG. 2

Theoretical composition of the pellets after reaction with acetylene and extraction of magnesium, in dependence on their initial porosity

TABLE II

Comparison of the experimental powder X-ray diffraction data of  $\text{MgC}_2$  with the theoretical values calculated for the body centered tetragonal lattice ( $a = 392.9 + 0.6$  pm,  $c = 503.7 \pm 1.2$  pm), the  $I4/mmm$  space group and the atom positions in the asymmetric unit of the elementary cell for structures with a free rotation of the  $\text{C}_2^{2-}$  groups (positions: Mg 0; 0; 0, Cl 0; 0; 1/2, C2 0; 0; 1/2) and a rigid position of the  $\text{C}_2^{2-}$  groups (CaC<sub>2</sub>-I type; positions: Mg 0; 0; 0 C 0; 0; 0:3805)

<i>h k l</i>	$d_{\text{calc}}$ pm	$d_{\text{ob}}^a$ pm	$I_{\text{obs}}$	$I_{\text{calc}}$		$F(hkl)$	
				free rotation	CaC <sub>2</sub> -I type	free rotation	CaC <sub>2</sub> -I type
1 0 1	309.8			12.4	103.0	2.4	6.8
1 1 0	277.8	278.3	1 000	1 000.0	1 000.0	33.8	33.8
0 0 2	251.9	251.6	600	364.5	124.4	32.2	18.8
2 0 0	196.4	197.2	200	310.3	310.3	28.1	28.1
1 1 2	186.6	186.5	400	514.8	197.0	27.2	16.8
2 1 1	165.9	166.3	300	28.4	65.2	5.2	7.9
2 0 2	154.9	155.0	300	255.1	103.3	24.1	15.3
1 0 3	154.4			12.2	184.4	5.3	20.5
2 2 0	138.9			83.7	83.7	22.3	22.3
3 0 1	126.8	126.9	100	6.6	13.6	4.9	7.0
0 0 4	125.9			29.0	1.7	20.7	5.0
3 1 0	124.2			110.3	110.3	20.5	20.5
2 2 2	121.6			102.4	42.5	20.1	13.0
2 1 3	121.4	121.2	200	11.3	149.9	4.7	17.3
1 1 4	114.7			84.3	4.7	19.2	4.5
3 1 2	111.4			154.6	63.5	18.8	12.0

TABLE III

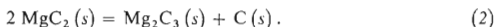
Calculated rate constants ( $k$ ), halfives ( $t_{0.5}$ ) and correlation coefficients ( $r$ ) approximating the magnesium dicarbide decomposition isotherms

Temperature °C	$k \cdot 10^6$ $s^{-1}$	$t_{0.5}$ min	$r$	Eq.
485	11.8	960	0.9968	(3)
500	16.5	720	0.9989	(3)
540	167	65	0.9992	(4)
560	396	22	0.9951	(4)
660	256 000 <sup>a</sup>	0.23	0.9961	(5)

<sup>a</sup> In  $s^{-0.39}$ .

The diffraction patterns obtained by us also did not agree, as far as the intensities are concerned, with the theoretical patterns calculated for dicarbide of the  $\text{CaC}_2$ -I type, with the carbon groups situated parallel to the  $z$ -axis. As the data of Table II indicate, a better fit is obtained if a structure is considered in which hypothetically the two carbon atoms of the  $\text{C}_2^{2-}$  group assume the same position, corresponding to the model of free rotation of the carbon group. However, with respect to the value of the ionic radius of magnesium, the carbon atoms are not free for rotation. This is also consistent with the observed symmetry, which (to a first approximation) is tetragonal rather than cubic. The carbon atom groups will be oriented in some prominent directions, analogously as in the  $\text{CaC}_2$ -III type<sup>8</sup> or in the low-temperature modification of  $\text{NaCN}$  (ref.<sup>9</sup>) of a monoclinic symmetry.

Fig. 3 shows the results of our experiments with the decomposition of magnesium dicarbide,



The reaction rate is seen to be highest at the beginning of the decomposition and to decrease as the dicarbide is diluted by the reaction products (Table III). The isotherms can be approximated satisfactorily by a 1st order kinetic equation, sought by the least squares method, only for low temperatures at which the decomposition of  $\text{MgC}_2$  proceeds relatively slowly ( $485^\circ\text{C}$ ,  $500^\circ\text{C}$ ). As the temperature is raised, the shape of the isotherms departs from the 1st order reaction kinetics, the reaction in the final stage slowing down more rapidly than as corresponds to the relation

$$\ln [1/(1 - n)] = kt \quad (3)$$

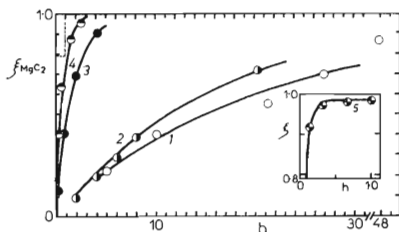


FIG. 3

Isotherms of decomposition of magnesium dicarbide. 1  $485^\circ\text{C}$ , 2  $500^\circ\text{C}$ , 3  $540^\circ\text{C}$ , 4  $560^\circ\text{C}$ , 5  $660^\circ\text{C}$

( $n$  is the degree of dicarbide conversion,  $k$  is the rate constant, and  $t$  is time). At 540 or 560°C the decomposition can be described better by the equation

$$\ln [1/(0.985 - n)] = kt. \quad (4)$$

At higher temperatures this effect becomes more pronounced and the rate constant calculated for the 1st order reaction drops appreciably as the conversion proceeds. An empirical relation was sought in the form

$$\ln [1/(0.985 - n)] = kt^z \quad (z < 1) \quad (5)$$

and the best fit was obtained with  $z = 0.39$ .

The temperature dependence of the rate constant of the  $\text{MgC}_2$  decomposition in the 485–560°C range was approximated by the Arrhenius equation. For a consistency, the rate constants for the 1st order reaction as corresponding to Eq. (3) were used also for temperatures 540 and 560°C. The frequency factor of the Arrhenius equation thus obtained is  $A = 4.97 \cdot 10^{12} \text{ s}^{-1}$ , the activation energy of the reaction is  $E = 257 \text{ kJ mol}^{-1}$ . A good fit was obtained, as documented by the fairly high correlation coefficient value (0.9935 for a rectification of the logarithmic dependence by the least squares method). The isotherms can be extrapolated to the 450°C temperature range, which is of importance for the carbide preparation, in order to estimate the extent to which the dicarbide will decompose to sesquicarbide during the synthesis. At 450 and 470°C, 1.2% and 3.7%  $\text{MgC}_2$ , respectively, should theoretically decompose in 2.5 h, and the hydrolysis products should afford mixtures of  $\text{C}_2\text{H}_2$  and  $\text{C}_3\text{H}_4$  in which the concentration of the latter should not exceed 0.6% and 1.9%, respectively. This is in accordance with the concentration found experimentally, viz 2.2%. If the extrapolation can be regarded as warranted, it can be inferred from the higher content of allylene and propadiene that the temperature applied approached the upper limit of the 450–470°C region.

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