

## THERMAL DECOMPOSITION OF MAGNESIUM SESQUICARBIDE\*

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The structure of  $Mg_2C_3$  and the course of its decomposition were studied. The powder X-ray diffraction patterns were analyzed to obtain the lattice parameters for hexagonal  $Mg_2C_3$ ,  $a = 743.4 \pm 0.5$  pm,  $c = 1056.4 \pm 1.6$  pm. Thermal decomposition data were obtained for temperatures 670–740°C and pressure 130 Pa; they could be fitted satisfactorily by kinetic equations for various processes, including the 1st order decomposition reaction, and so the controlling phenomenon of the reaction cannot be deduced based on the kinetic data. The 1st order rate constants and reaction halflives were evaluated for various temperatures and approximated by the Arrhenius equation to calculate the parameters  $A_A = 1.97 \cdot 10^{14} s^{-1}$ ,  $E_A = 333$  kJ mol<sup>-1</sup>. The conditions of synthesis of  $Mg_2C_3$  are discussed from the point of view of the choice of a suitable hydrocarbon for the reaction with magnesium. The thermal stability of the sesquicarbide increases with increasing pressure; it could be formed from dicarbide and sustained even at a temperature of 1450°C by applying a pressure as high as 6 GPa.

The formation of magnesium sesquicarbide,  $Mg_2C_3$ , from magnesium and hydrocarbons is interpreted<sup>1</sup> as a reaction of radicals with magnesium vapours. The maximum obtainable yield of the sesquicarbide depends on the hydrocarbon used. The optimum temperatures are also different for different hydrocarbons<sup>2</sup>; for instance, for n-pentane or n-octane the optimum temperature is 700°C, for methane, 760°C. At these temperatures, however, the sesquicarbide starts to decompose to the elements<sup>2</sup>, and so the carbide yield is governed by the ratio of the carbide formation rate to the thermal decomposition rate.

In the present work the thermal decomposition of magnesium sesquicarbide has been studied in detail, particularly with respect to the reaction kinetics. Attention has been also paid to the behaviour of the substance at high pressures and temperatures.

### EXPERIMENTAL

Magnesium sesquicarbide was prepared as described previously<sup>3</sup> and identified by powder X-ray diffractometry on a Mikrometa II apparatus equipped with a goniometer (Chirana, Prague)

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and a G-M tube as the detecting element. The lattice parameters were obtained by statistical processing<sup>4</sup>. The elemental analysis of the carbide was performed as described in ref.<sup>3</sup>.

Homogenized  $Mg_2C_3$  samples were placed in annealed graphite crucibles, sealed in quartz test tubes in vacuum of 130 Pa, and submerged in molten metal batch at 670, 710, or 740°C; the temperature was held constant with a precision of  $\pm 5^\circ C$ . After a preselected time the decomposition was discontinued by cooling the test tubes with water. The degree of conversion of sesquicarbide was found from the free carbon increment, determined gravimetrically after the sample decomposition with dilute (1 : 1) nitric acid *p.a.*

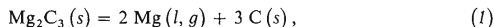
The thermal stability of  $Mg_2C_3$  at high pressures and temperatures was examined on pellets of magnesium dicarbide from which the sesquicarbide was formed on heating<sup>2</sup>. The preparation of the pellets has been published previously<sup>5</sup>. The pellets, whose volume was about  $1\text{ cm}^3$ , were held at a temperature of 1450°C and a pressure of 6 GPa for 5 and 20 min in a press designed for the synthesis of artificial diamonds (BELT System). A blank experiment was carried out under identical conditions. The content of carbides in the pellets was determined by gas chromatographic analysis of the products of carbide hydrolysis<sup>5</sup>; the content of magnesium was determined chelatometrically, that of free carbon, gravimetrically.

## RESULTS AND DISCUSSION

The magnesium sesquicarbide samples used contained 82%  $Mg_2C_3$ , 3% Mg, 10% MgO, and 5% free carbon.

The diffraction patterns of our preparation (Table I) were slightly different from those obtained by Irmann<sup>6</sup>. No reflections were observed for  $d = 141.8$ , 127.6, 124.2, and 107.4 pm, while a marked line, indexed as 314, was found for  $d = 148.2$  pm. The lines indexed by Irmann as 402 and 314 were assigned by us as 400 and 402 + 206 (doublet), respectively. The line intensity treatment by the two-dimensional Patterson synthesis failed to lead to usable results due to the low number of observed diffraction lines. The projection in the  $xy$  plane appears to be the planar tightest arrangement of the circular projections of the  $C_3$  groups (3 projections at a cell edge), the Mg atom projections being situated between them in the free triangular space. The arrangement in the  $z$ -axis direction, however, could not be elucidated satisfactorily. The absence of prominent lines with nonzero  $l$  and the broad diffuse maximum in the region of  $7-11^\circ$  ( $1\theta$ ) led us to assume a partly disordered structure or the occurrence of a systematic preferential orientation of grains in the powder samples.

The isotherms of decomposition of magnesium sesquicarbide,



are shown in Fig. 1. The data are fitted by the 1st order reaction kinetics curves calculated by the least squares method. The calculated rate constants, reaction halfives, and correlation coefficients for the rectification of the experimental data by the logairthmized rate equation are given in Table II. However, equally good data fits could be achieved with equations for a solid phase reaction under the autocata-

lytic effect of the products formed or for diffusion-controlled topochemical reactions; thus the controlling phenomenon of the sesquicarbide decomposition could not be determined based on the kinetic data.

The 1st order reaction constants for different temperatures were approximated by the Arrhenius equation with the frequency factor value  $A_A = 1.97 \cdot 10^{14} \text{ s}^{-1}$  and the activation energy  $E_A = 333 \text{ kJ mol}^{-1}$ .

TABLE I

Powder X-ray diffraction data for  $\text{Mg}_2\text{C}_3$  ( $\text{CuK}_\alpha$  radiation)

$h k l^a$	$d_{\text{obs}}$ pm	$d_{\text{calc}}$ pm	$I_{\text{obs}}^b$ rel. units
2 0 0	321.8	321.9	100
1 1 2	304.2	304.0	$20.3 \pm 4$
2 0 2	274.8	274.9	$19.7 \pm 3$
2 1 0}	243.7	243.4	$89.0 \pm 7$
1 0 4}		244.3	
2 1 2	221.3	221.0	$69.5 \pm 8$
0 0 5}	211.0	211.3	20 (MgO?)
3 0 1}		210.3	
3 0 2	198.0	198.8	$14.6 \pm 3$
2 2 0	186.5	185.9	$43.3 \pm 3$
3 1 0	178.8	178.6	$20.7 \pm 4$
3 2 2	174.5	175.3	$20.1 \pm 4$
3 0 4	165.8	166.6	$6.5 \pm 1.6$
4 0 0	160.8	161.0	$11.2 \pm 2$
4 0 2}	154.4	154.0	$34.0 \pm 6$
2 0 6}		154.5	
3 1 4	148.2	147.9	$31.4 \pm 2$
3 1 5	136.6	136.4	$7.0 \pm 1$
5 0 0	128.3	128.8	$10.0 \pm 1$
2 1 7		128.3	
4 2 0	121.5	121.7	14 (MgO?)
4 2 2	118.7	118.6	$10.4 \pm 0.4$
3 2 6}	113.0	113.2	$5.7 \pm 1$
5 1 2}		113.0	
4 2 4	110.2	110.5	$2.9 \pm 0.7$
5 1 5	101.7	101.4	$8.1 \pm 0.6$
4 2 6	100.2	100.1	$6.7 \pm 1$

$$a = 743.4 \pm 0.5 \text{ pm}, \quad c = 1056.4 \pm 1.6 \text{ pm}, \quad c/a = 1.421$$

<sup>a</sup> Assignment based on the Hull-Davey curves for the hexagonal system and the  $c/a$  ratio, ref.<sup>6</sup>;  
<sup>b</sup> the standard deviations were calculated based on the results obtained with 10 samples.

The ratio of the gas pressure above the carbide to the magnesium vapour pressure, at a given temperature, also affects the reaction rate to an extent. The magnesium vapour pressure at 700°C is 135 Pa, so that at lower pressures the reaction will be somewhat accelerated.

In fact, higher carbide yields are obtainable than as follows from our kinetic measurements. If the synthesis of the carbide is conducted only in a mild vacuum (n-pentane) or even under a slight overpressure (methane), the thermal decompositions of the sesquicarbide formed will not be supported by exhaust of magnesium vapours. As long as the starting magnesium is present, some concentration of its vapours is desirable in view of the presumed radical mechanism of the sesquicarbide formation reaction.

TABLE II

Rate constants  $k$ , reaction half-lives  $t_{0.5}$ , and correlation coefficients  $r$  for an approximation of the isotherms of decomposition of  $Mg_2C_3$  by the 1st order reaction kinetic equation

Temperature °C	$k \cdot 10^6$ $s^{-1}$	$t_{0.5}$ s	$r$
670	67	8 200	0.985
710	450	1 744	0.991
740	1 220	652	0.968

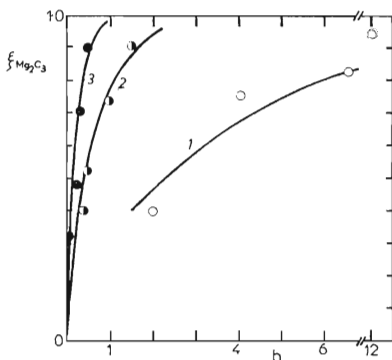


FIG. 1  
Isotherms of decomposition of magnesium sesquicarbide. 1 670°C, 2 710°C, 3 740°C

The carbide yield depends upon how easily the hydrocarbon employed is thermally cleaved to radicals; this accounts for the different optimum reaction temperatures for the various hydrocarbons. Methane requires a relatively higher temperature<sup>2</sup>; on the other hand, the reaction can be conducted at atmospheric pressure, whereupon the rate of the thermal decomposition of sesquicarbide is lowered. Higher saturated hydrocarbons are cleaved more readily so that a lower temperature can be used,

TABLE III

Calculated volume changes accompanying the decomposition of carbides of magnesium, for the component phases stable at atmospheric pressure and the temperature applied and for the formation of carbon in the graphite or diamond modification (the density of carbides at room temperature was taken from ref.<sup>6</sup>, for the temperature of 1 100°C the density of magnesium, graphite, and diamond was calculated from the thermal expansion data<sup>7,8</sup>, the volume expansion of magnesium carbides was estimated based on that of calcium carbide<sup>9</sup>)

Reaction	Volume change, %, at the temperature			
	1 100°C		20°C	
	graphite	diamond	graphite	diamond
$2 \text{MgC}_2 = \text{Mg}_2\text{C}_3 + \text{C}$	- 9.8	-13.6	- 8.9	-12.9
$\text{Mg}_2\text{C}_3 = 2 \text{Mg} + 3 \text{C}$	+15.1	+ 1.0	+16.9	+ 1.6

TABLE IV

Contents of carbides of magnesium and some other components in a pellet after annealing at a pressure of 6 GPa

Temperature °C	Reaction period min	Content, %					
		initial		after the pressure treatment			
		MgC <sub>2</sub>	C <sub>free</sub>	MgC <sub>2</sub>	Mg <sub>2</sub> C <sub>3</sub>	C <sub>free</sub>	Mg <sub>Bfree</sub> <sup>a</sup>
25	15	58.4	7.2	58	—	7.4	32.5
1 450	5 <sup>b</sup>	53.7	6.3	0	15	79.9	5.4
1 450	20 <sup>b</sup>	58.6	8.7	0	0.2	90	10

<sup>a</sup> Part of magnesium distilled off during the heating; <sup>b</sup> time for which the system was held at 1 450°C; the time of heating from 700 to 1 450°C and the time of cooling down from 1 450°C to 700°C was 15 min.

but as the pressure given by the vapour pressure above the liquid hydrocarbon is lowered too, the thermal decomposition of sesquicarbide is accelerated. Pentane appears to suit best as a compromise between the requirement of an easy cleavage and that of a sufficiently high gas vapour pressure.

The volume changes in the reactions (Table III) indicate that the decomposition of sesquicarbide to the elements should not be favoured by pressure, whereas its formation by the decomposition of dicarbide should. Theoretically, all dicarbide could be transformed into sesquicarbide and the latter sustained by heating at high pressures. We tested this hypothesis by experiments using pellets containing magnesium dicarbide and magnesium (Table IV); thus the danger of hydrolysis by atmospheric humidity was also reduced. The experiments carried out at 1450°C bear out the above assumption; by heating at high pressures, sesquicarbide was prepared from dicarbide at temperatures at which the two carbides would decompose immediately if normal pressures were applied<sup>1</sup>. No formation of carbon in the diamond form was observed although the volume changes were such as favour this reaction.

Our experiments indicate that at temperatures above 670°C,  $Mg_2C_3$  is unstable, and in conditions in which it is formed on the reaction of magnesium with n-pentane the sesquicarbide can decompose, particularly at reduced pressures when the carbide dissociation is favoured by the evaporation of magnesium. For the yield of sesquicarbide to be as high as possible, the hydrocarbon of choice should be easily cleaved to radicals and its vapour pressure should be high enough for its good transport to the sample. From this point of view, n-pentane<sup>2</sup> appeared to suit best. Isobutane can be expected to suit as well. We performed some tentative experiments in which magnesium from a heated tantalum boat was evaporated into isobutane atmosphere. The obtained light-brown deposit on the vessel walls was extremely reactive with humidity. The results will be published in a forthcoming paper.

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