

HYDROLYSIS OF MAGNESIUM SESQUICARBIDE Mg_2C_3 *

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Received June 26th, 1979

Samples of magnesium carbide containing 88.9% Mg_2C_3 were prepared by choosing suitable conditions (temperature $685 \pm 5^\circ C$, magnesium dust particles below 0.05 mm, n-pentane flow rate with reduced pressure 10 l/h, reaction period 1.25 h). In their hydrolysis products, propadiene was found gas chromatographically to be present in quantities about 6% vol. at room temperature; its concentration does not change with time, but it rises with increasing temperature. At temperatures above $200^\circ C$, the hydrocarbons formed start to decompose as a result of their reaction with water vapour; if the temperature exceeds $400^\circ C$, the reaction leads instantaneously to an equilibrium mixture of CH_4 , C_2H_4 , C_3H_6 , and carbon oxide. During reaction with water at higher temperatures and pressures, reforming reactions proceed to a greater extent. Samples containing more than 60% Mg_2C_3 cannot be hydrolyzed with liquid water without hazard of thermal decomposition of the hydrocarbons, analogous to the reaction with water vapour at higher temperatures. The actual temperature of the reacting carbide surface can be estimated, up to approximately $300^\circ C$, from the content of propadiene in the hydrolysis products. In accordance with the results of the hydrolysis experiments, the carbide structure is assumed to involve linear $C=C=C^{4-}$ groupings.

The gaseous product of hydrolysis of magnesium sesquicarbide is generally assumed to consist of a single compound — propine¹⁻⁴. When the hydrolysis is conducted in conditions favourable for isomerization of propine (temperature exceeding $150^\circ C$, presence of carbon black as a catalyst), propadiene can be traced in the gas too⁵⁻⁷. Propadiene is present also in products of hydrolysis of magnesium sesquicarbide prepared by conversion of calcium carbide with magnesium chloride⁸; its formation at room temperature is explained in terms of an extraordinary catalytic ability of finely dispersed carbon, created during the sesquicarbide preparation, in view of the fact that in the hydrolysis products of Mg_2C_3 prepared by procedures other than the conversion of calcium carbide, propadiene has not been detected.

As part of our study of the relation between the carbide structure and the composition of its hydrolysis products, we concerned ourselves with the problem of formation of propine and propadiene during hydrolysis of magnesium sesquicarbide. The aim of the work was to examine the effect of factors favouring isomeriza-

* Part XI in the series Studies on Hydrolyzable Carbides; Part X: J. Radioanal. Chem. 21, 407 (1974).

tion of C_3H_4 hydrocarbons and other gas phase reactions on the composition of the magnesium sesquicarbide hydrolysis products. Samples prepared from magnesium and n-pentane were used, whereby the effect of finely dispersed carbon was eliminated. The objective of the study was thus primarily the dependence of the composition of the gaseous products on the second important factor – the temperature, affected during the hydrolysis mainly by the reactivity of the carbide sample used and thus also by the way of the hydrolytic decomposition.

EXPERIMENTAL

Preparation of Magnesium Sesquicarbide

Magnesium sesquicarbide was prepared by reaction of magnesium metal (99.96% Mg, 0.032% Fe, 0.001% Si, 0.0002% Ni, 0.0005% Cu, 0.001% Al, 0.005% Mn, 0.001% Cr) with n-pentane (99.9%, Carlo Erba). From a series of tests, the following procedure emerged as affording the substance in highest yields: Magnesium dust with grain size below 0.05 mm was obtained by filing a metal block in dried kerosene, sucking off under argon, and washing with dried n-heptane. A portion was rammed in a sintered corundum boat and inserted into a furnace made of the same material, inner diameter 25 mm. From the direction of the n-pentane inlet, the boat was surrounded with steel and aluminium wool. After heating the magnesium to $682 \pm 2^\circ C$ under purified hydrogen, n-pentane was fed at reduced pressure using the flow rate 10 l/h. After 1.25 hour's reaction period, when the boat temperature rose to $688 \pm 2^\circ C$, the pentane inlet was discontinued and the furnace was allowed to cool down. The samples were analyzed; the carbide-type carbon was determined based on the volume of the gas formed by the hydrolysis, taking into account the results of the gas chromatographic analysis of the mixtures; magnesium was determined chelometrically, free carbon gravimetrically, and the content of bonded oxygen was calculated as the weight difference.

Hydrolysis of Magnesium Sesquicarbide with Water Vapour

Decomposition at temperatures $-30^\circ C$ to $+30^\circ C$. Samples of Mg_2C_3 were decomposed with water vapour in a prior evacuated glass vessel containing two capsules, with the carbide and with water. In order to slow the hydrolysis down, the carbide was covered with finely ground barite. The temperature in the thermostat was held constant with the precision of $\pm 0.1^\circ C$ during the decomposition. After the decomposition, samples for gas chromatographic analysis were taken at a constant temperature. Tests carried out with pure propadiene confirmed that the concentration of propadiene in the closed vessels or in the syringe did not change within the period necessary for the sample transfer to the analysis.

Decomposition at temperatures 100–160°C. The samples were hydrolyzed with water vapour with the pressure of approximately 10 kPa in a quartz tube with two heating zones: the first, held at a constant temperature near $100^\circ C$, served for the water evaporation, the second, heated to the desired temperature, accommodated the carbide. After the working temperature was attained, water was delivered from one side of the furnace and gas samples for analysis were taken from the sample side.

Hydrolysis of Magnesium Sesquicarbide with Liquid Water

Hydrolysis at ambient and sub-ambient temperatures. The samples were hydrolyzed in eva-

cuated ampoules by applying two procedures: *a*) controlled, adding excess water to a small amount of the carbide, *b*) uncontrolled, adding water to excess carbide. In both cases, less reactive samples with low contents of the sesquicarbide were used, obtained by thermal decomposition of magnesium dicarbide⁹.

High-percentage samples were decomposed at low temperatures. Water was delivered into an evacuated test tube containing the carbide and cooled below the water freezing point, and controlled course of the hydrolysis was achieved by controlling the rate of melting of the ice formed.

Other carbide samples in evacuated test tubes were cooled down to -100°C and excess 29.8% aqueous solution of calcium chloride was added. After the decomposition at -56°C , lasting 240 hours, several drops of bromine were added to two samples at the same temperature, for cyclopropene, which could form on the hydrolysis, to convert to the more stable dibromocyclopropane. In the remaining samples, the composition of the gas liberated was determined gas chromatographically after heating up to room temperature. The bromo derivatives formed on addition of bromine to the C_3H_4 hydrocarbons at low temperature were extracted into tetrachloromethane and their infrared spectrum was scanned in the region $600\text{--}4000\text{ cm}^{-1}$ and compared with that of the bromo derivatives obtained by bromine addition to C_3H_4 hydrocarbons at room temperature, where cyclopropene could not be present.

Hydrolysis at elevated temperature and pressure. Samples of Mg_2C_3 in a sealed ampoule were placed in a steel autoclave fitted with a jacket thermocouple, which contained a known excess quantity of water and several steel balls for crushing the ampoule after attaining the desired temperature. After cooling, a gas sample was taken for gas chromatographic analysis.

Infrared Spectroscopic Analysis of the Gaseous Hydrolysis Products

The increase in the concentration of the hydrocarbon products during the hydrolysis of Mg_2C_3 with water vapour was monitored *in situ* in an infrared spectrometric cell using a Perkin-Elmer 325 spectrophotometer. The magnesium sesquicarbide samples were placed in a boat 10 cm long together with another boat filled with water. After evacuation, the spectrum was measured in the region of $1900\text{--}2200\text{ cm}^{-1}$; the measurement was repeated in preselected time intervals, until the hydrocarbons ceased to evolve.

Gas Chromatographic Analysis

The analyses were carried out on a Chrom IV apparatus equipped with a flame ionization detector, using a combined column (Carlo Erba) 6 m long, inner diameter 4 mm, packed with 4 m of dimethylsulfolane and 2 m of polypropylene glycol on Chromosorb. The column temperature was 36°C , carrier gas (nitrogen) flow rate 6.5 ml/min. The column made it possible to determine hydrocarbons from methane to C_4 . The content of the hydrocarbons was expressed in mol per cent values by using the internal normalization method.

RESULTS AND DISCUSSION

The preparation procedure used led to samples richer in Mg_2C_3 than as hitherto reported in literature. The best sample contained 88.9% Mg_2C_3 , 1.6% Mg, 2.0% MgO , and 7.5% free carbon, was light grey colour, and reacted violently with water with the appearance of flame. The higher yield was favoured by the temperature lowering from the 700°C used by Irmann⁴ and Novák² down to 685°C ; in this man-

ner, the rate of the thermal decomposition of the carbide formed is reduced appreciably, while the rate of its formation lowers to a substantially lesser extent. The application of magnesium dust of smaller particle size allows the reaction period to be shortened to 1/3 as compared with the works of Novák² and Irmann⁴. Furthermore, the carbide yield depends on the efficiency of freeing the reaction atmosphere from oxygen and nitrogen traces, on the purity of the magnesium dust, and on the porosity of the sample in the boat (affecting the degree of contamination by pyrolytic carbon).

Propadiene has been identified in addition to propine in all hydrolysis products of magnesium sesquicarbide. After washing the acetylene type hydrocarbons with ammoniacal solution of AgNO_3 , the remaining gas exhibited a single chromatographic peak with the retention time 8.5 min. Mass spectrometric analysis with correction for the presence of argon evidenced that the substance was propadiene. Its presence was confirmed also by the infrared spectrum of the gas mixture. The maxima of the absorption bands of propine and propadiene were identified by means of the spectra of the pure substances^{5,10}. The region of $1900\text{--}2200\text{ cm}^{-1}$ was chosen for monitoring the evolution of the two hydrocarbons during the hydrolysis, since it embraces the peaks of propine (2150 cm^{-1}) and of propadiene (1967 cm^{-1}) of comparable intensity, suitable for the evaluation of the changes in the concentration of the two compounds. As found from the peak intensity ratios by using standards, the propine-to-propadiene ratio does not change during the decomposition of Mg_2C_3 with water vapour. The mixture of a given composition is formed immediately on the reacting surface of the carbide, and at constant temperature no consecutive isomerization, polymerization, or hydrogenation reactions in the gas mixture occur, such as observed, *e.g.*, during hydrolysis of rare earth element carbides.

While the composition of the gaseous hydrocarbon mixture forming during the hydrolysis of Mg_2C_3 with water vapour does not change with time, it depends considerably on the hydrolytic decomposition temperature, as can be seen from Table I. In addition to the expected C_3H_4 hydrocarbons, the gases contain traces of methane, ethine, propane, and propene. The presence of the two latter compounds can be explained by hydrogenation of C_3H_4 by hydrogen formed on the reaction of the magnesium metal with water. Methane and ethine obviously do not form at temperatures below 200°C by thermal decomposition of higher hydrocarbons, because they are always present in the gas mixtures resulting from the decomposition of magnesium sesquicarbide prepared by any procedure, even if the hydrolysis is a slow controlled one. Characteristic of the hydrocarbon gas composition is the increasing concentration of propadiene with increasing temperature of the hydrolytic decomposition, and at temperatures above 200°C , the starting decomposition to methane and ethene. In view of the proportion of hydrocarbons in the gas mixture, the hydrocarbons can be assumed to react to an appreciable extent with the water vapour to give CO and CO_2 , rarefying the hydrocarbon gas. A rather intense thermal decomposition of the hydrocarbons formed occurs during the decomposition of mag-

nesium sesquicarbide with water under pressure, as follows from Table II. Only a very small amount of condensed products forms, in contrast to the analogous reaction of calcium carbide affording in the same conditions more than 50% liquid and solid hydrocarbons¹¹.

Comparing the experimental results with the calculations of the theoretical equilibrium composition of the system $C_3H_4 + H_2O \rightarrow C_3H_4, H_2O, C_2H_2, CH_4, CO, CO_2, C_3H_6, H_2$ (Table III) based on the minimization of the total reaction Gibbs energy¹², we find that the real gaseous mixture at temperatures 100–400°C

TABLE I

Average Composition of Gaseous Hydrocarbon Products of Slow Hydrolytic Decomposition of Magnesium Sesquicarbide with Water Vapour at Atmospheric Pressure (in mol.%)

Product	Temperature, °C						
	20 ^a	100 ^b	200 ^c	300 ^c	400 ^d	500 ^d	600 ^c
Methane	0.1	0.12	0.1	14	71.4	70	92
Ethane, ethene	—	—	—	2.5	16.7	21.8	8
Ethine	0.03	0.04	—	—	—	—	—
Propane	0.02	0.05	0.07	0.1	2.6	3.4	—
Propene	0.11	0.18	0.20	0.3	9.3	4.7	—
Propine	93.6	85.6	83.1	67.7	—	—	—
Propadiene	6.17	14.1	16.5	15.5	—	—	—

Reaction period (min): ^a 30, ^b 5, ^c 10, ^d 20.

TABLE II

Composition of Gaseous Hydrocarbon Products of Magnesium Sesquicarbide Hydrolysis at Elevated Temperature and Pressure

Conditions A and B, respectively: temperature (°C) 200 and 300, total pressure after decomposition (MPa) 4.5 and 8.8, partial water pressure after decomposition (MPa) 1.55 and 8.0.

Experiment	Gas content, mol.%						
	CH ₄	C ₂ H ₄₋₆	C ₃ H ₈	C ₃ H ₆	C ₂ H ₂	propadiene	propine
A	77	4.7	0.8	1.8	0.2	3.46	12.12
B	58	5.6	1.8	14.5	4.2	3.64	11.93

does not attain the equilibrium in the given time (Fig. 1). Only at temperatures exceeding 400°C the kinetic hindrance to the reactions no more operates and the compositions of the gas mixture correspond to the thermodynamic equilibrium composition.

In order to find which factors govern the equilibrium between propadiene and propine during hydrolysis of Mg_2C_3 , we calculated the propine-to-propadiene molar

TABLE III

Calculated Equilibrium Composition of the System $C_3H_4(g) + H_2O(g) = C_3H_4, H_2O, C_2H_2, CH_4, C_2H_4, CO, CO_2, C_3H_8, H_2$ at 101.3 kPa

Compound	Content, mol.% for the temperature, °C			
	26·85	126·85	326·85	526·85
C_3H_4	—	—	—	—
H_2O	—	—	—	—
C_2H_2	—	—	—	—
CH_4	30·2	34·68	42·6	42·2
C_2H_4	—	0·06	1·66	8·11
CO	0·3	15·66	42·52	41·5
CO_2	29·8	19·0	0·06	—
C_3H_8	49·8	30·6	13·16	8·82
H_2	—	—	—	—

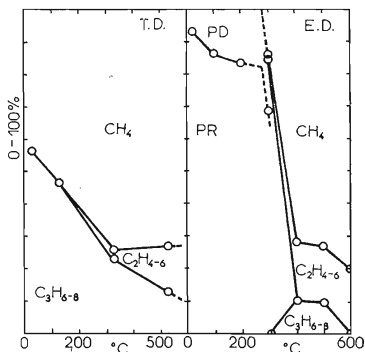


FIG. 1

Theoretical Equilibrium Values and Experimental Data of the Composition of the Hydrocarbon Gases Evolved during Hydrolysis of Magnesium Sesquicarbide at Higher Temperatures

ratios for all gas mixtures obtained, and compared the calculated K value with the values of the equilibrium constant of isomerization of propadiene to propine, calculated from thermodynamic data¹², and with the values obtained experimentally by Cordes¹³ (Table IV). The K value for hydrolysis with water vapour at higher temperatures agrees well with the experimental equilibrium constant. At temperatures below 100°C, for which the equilibrium data are not available, the K values follow the initial trend. At temperatures below 0°C, however, the propadiene concentrations increase above the expected values.

During a slow decomposition with water at room temperature (Table IV), the propine-to-propadiene ratio is approximately 15, a value found also for hydrolysis with water vapour at 20°C. The scatter of the values measured is obviously due to the different reactivity of the carbide preparations effecting different heating during the hydrolysis. In the gas mixtures formed during the uncontrolled hydrolysis of the sesquicarbide (Table V), where the reaction mixture heated considerably, the propine-to-propadiene ratio is rather variable; however, under the assumption that the equilibrium between the two hydrocarbons established, the ratio corresponds to reaction surface temperature lower than 100°C. The gas evolved on the decomposition of Mg_2C_3 with calcium chloride solution (Table V), which proceeded at temperatures between 0°C and -56°C, contained propadiene in a higher concentration - in a case even higher than as corresponds to the equilibrium composition at 150°C. Gas mixtures with propadiene contents exceeding the equilibrium values emerged also during decomposition under pressure.

TABLE IV

Comparison of the Theoretical and Experimental Propine-to-Propadiene Ratios (K) for Hydrolysis with Water Vapour at Different Temperatures

Temperature, °C	K_{aver}	Number of measurements	Mean error %	Reaction period	K_{exp}^a	K_{cal}^b
-30	11.0	13	±27.5	2 months	—	—
0	17.3	17	±17.5	1 month	—	—
15	17.4	11	±19.0	14 days	—	—
20	15.2	12	±22.5	14 days	—	24.5
30	12.0	12	±31.5	7 days	—	—
100	6.08	4	± 7	5 min	6.14	14.30
200	5.06	4	± 1	2 min	5.06	9.00
300	4.39	4	± 5	2 min	4.34	6.87

^a Ref.¹³, ^b our calculations.

In the crystal lattice of Mg_2C_3 the presence of linear C_3^{4-} anions is assumed³, which is consistent with the failure of our attempts to isolate cyclopropene from the mixture after hydrolysis at low temperatures. Proceeding, analogously as Cordes¹⁴, from considerations of the isoelectronic structures of the C_3^{4-} , CN_2^- , and N_3^- groupings¹⁵, and taking into account our present knowledge of the structure of calcium and strontium cyanamides^{16,17}, we arrive at the conclusion that in the linear C_3 groupings in the carbide lattice, the electrons should be distributed symmetrically and thus the $\text{C}=\text{C}$ internuclear distances should be identical. Consequently, the reaction of water with the $\text{C}=\text{C}=\text{C}^{4-}$ groups should primarily afford propadiene, which consecutively, as a less stable compound, should isomerize to propene in equilibrium concentration. Possibly, during low-temperature hydrolysis the isomerization could be slowed down and discontinued by rapid separation of the gaseous phase from the carbide surface covered with water, whereby a gaseous product with higher propadiene concentration would be obtained.

Since the composition of the hydrolysis products of magnesium sesquicarbide depends substantially on temperature, it depends consequently — owing to the high reactivity of the carbide with water — on the way in which the hydrolysis is conducted, on the concentration of Mg_2C_3 , as well as on the size of the sample grains. Carbide samples containing less than 60% Mg_2C_3 (besides MgO , C , etc.) can be hydrolyzed

TABLE V
The Propene-to-Propadiene Ratio for Decomposition with Water under Various Conditions

Decomposition procedure	K_{aver}	Number of measurements	Mean error %	Time of sampling after the reaction start
With CaCl_2 solution at -56°C	8	6	± 12	10 days
With water delivered at temperature below 0°C	7	6	± 15	3 h
Slow decomposition of low-percentage preparation with excess water at $20-40^\circ\text{C}$	15	18	± 22.5	2 h
Decomposition of 30—50% carbide in excess, uncontrolled process, $20-150^\circ\text{C}$	11.5	10	± 33.6	5 min
Under pressure at 200°C	3.50	2	± 5	6 h
Under pressure at 300°C	3.28	2	± 5	6 h

both with water vapour and with water without thermal decomposition of the hydrocarbons formed. The reaction procedure reflects in the propyne-to-propadiene ratio, which can serve as a measure of the temperature in the point of contact of the reacting carbide with water. Samples containing more than approximately 60% Mg_2C_3 can only be hydrolyzed by a "controlled" procedure using low pressure water vapour; reaction with liquid water at room temperature leads to such a heating of the surface that the hydrocarbons ignite, or — in vacuum — the sample heats up enormously, and the composition of the hydrocarbon products is highly variable and corresponds roughly to the results obtained from hydrolysis with water vapour at high temperatures, as given in Table I.

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Translated by P. Adámek.