studies to correlate the velocity constants with any of the other physical properties of sulfuric acid, such as ionization, activity or acidity and the present series in Table I is no exception. Hall and Spengeman[13] have recently measured the acidity function H_0 of sulfuric acid dissolved in acetic acid. According to Hammett $H_0 + \log k$ is a constant when the velocity depends on the acidity of the solution. The velocity constant for the disappearance of hydrogen cyanide, however, is not in close agreement with this. For a 2 molal solution $H_0 + \log k$ is -5.10 for a 4 molal solution -5.38 and for a 6 molal solution -5.62.

It is worth noting that the rate of disappearance of hydrogen cyanide keeps on increasing as the amount of water decreases—in fact the fastest rate appears in the presence of anhydrous acetic acid containing acetic anhydride. This is just the reverse of what happened with hydrochloric acid. Russell and Cameron[14] found a great increase in acidity for sulfuric acid dissolved in glacial acetic acid when acetic anhydride is added to such a solution. So, in spite of the fact that the rates of hydrolysis do not strictly follow Hammett's acidity function, the acidity of the solution does influence these rates.

We are continuing the investigation, especially the study of the hydrolysis of organic nitriles in organic solvents and the hydrolysis of substituted amides and of amides of acids other than carboxylic.

Summary

A study has been made of the hydrolysis of hydrogen cyanide in various concentrations of acetic acid, glacial acetic acid, and acetic acid containing as much as 33% of acetic anhydride using hydrochloric acid and sulfuric acid as catalysts.

It has been shown that the rates of hydrolysis increase rapidly as the concentration of water in the solvent decreases. For sulfuric acid the rate is most rapid in glacial acetic acid containing acetic anhydride. For hydrochloric acid glacial acetic, without the addition of acetic anhydride, is the best solvent. Hydrochloric acid is a very much better catalyst than sulfuric acid and hydrolyzes hydrogen cyanide several million times faster in acetic acid than it does in water. This rate is very sensitive to small changes in concentration of hydrochloric acid.

For hydrochloric acid the rate varies as the square of the mean ion activity or as the activity of the molecule of the acid. It has not been possible to correlate the rates of hydrolysis where sulfuric acid is the catalyst with any physical property of its solutions.

HARTFORD, CONNECTICUT RECEIVED APRIL 26, 1943

[13] Hall and Spengeman, THIS JOURNAL, **62**, 2487 (1940).

[14] Russell and Cameron, *ibid.*, **60**, 1345 (1938).

The Crystal Structure of Magnesium Carbide

BY M. A. BREDIG[1]

In connection with a study of the formation of calcium and magnesium metal and of their carbides by reduction of the oxides with carbon in a vacuum, the crystal structures of some of the carbides MeC_2 such as MgC_2, CaC_2, SrC_2 and BaC_2 were discussed.[2a,b] A very satisfactory powder X-ray diagram of magnesium acetylide was produced,[2a] careful consideration of which showed that this carbide was not isotypic with the tetragonal forms of the other three carbides. Its structure appeared to be of lower symmetry, and could therefore not be determined by means of powder X-ray patterns, the only ones available, since single crystals could not be prepared.

In contradiction to this finding, W. H. C. Rueggeberg[3] recently has proposed the values 4.86 and 5.67 Å. for the constants a_0 and c_0 of a tetragonal lattice of magnesium carbide, analogous to tetragonal calcium carbide (I). The experimental evidence consists of the—rather unsatisfactory—agreement of the measured spacings of four weak, or very weak, X-ray lines with spacings, calculated from those lattice constants. The deviations of the experimental figures from the calculated values range from 1.6 to 4.3%, that is more than 2 to 5 times the experimental error which is expected even if no particular care is applied in preparing and measuring the X-ray pattern.

[1] Address: Vanadium Corporation of America, New York, N. Y.

[2a] H. H. Franck, M. A. Bredig and Kin-Hsing Kou, *Z. anorg. allgem. Chem.*, **232**, 75 (1937).

[2b] M. A. Bredig, *J. Phys. Chem.*, **46**, 801 (1942).

[3] W. H. C. Rueggeberg, THIS JOURNAL, **65**, 602 (1943).

TABLE I

POWDER X-RAY DIAGRAMS OF MAGNESIUM ACETYLIDE

	Rueggeberg			Franck, Bredig and Kou	
Indices	$d_{\text{calcd.}}$, Å.	$d_{\text{exp.}}$, Å.	Intens.	$d_{\text{exp.}}$, Å.	Intens.
111	2.94	..	..	3.10 ± 0.03	v. w.
002	2.88	..	..	2.79 ± .03	v. s.
200	2.43	2.48	w	2.51 ± .02	v. s.
?	..	..	..	2.44 ± .02	v. w.
?	..	..	..	2.11 ± .02	m
?	..	..	..	1.97 ± .01	m
202	1.86	1.83	w	1.86 ± .01	s
220	1.72	..	..	1.76 ± .01	w
113	1.68	..	..	1.66 ± .01	m
311	1.49	1.51	w	1.55 ± .01	m
222	1.47				
?	..	..	..	1.49 ± .01	w
?	..	..	..	1.44 ± .01	w
?	..	..	..	1.39 ± .01	w
?	..	..	..	1.34 ± .01	w
204	1.24	1.27	v. w.	1.27 ± .01	w
400	1.22				

It can be shown that the proposition of a structure analogous to tetragonal calcium carbide (I) is not in agreement with the experimental facts. In the table, the spacings, measured with an experimental error of approximately ±0.5%, of magnesium acetylide, prepared from magnesium metal and acetylene at 500° (ref. 2a, Fig. 5, p. 80, and Table 14, p. 110) are compared with the spacings, obtained by Rueggeberg for a magnesium acetylide prepared from ethylmagnesium bromide and acetylene at room temperature, and also with spacings calculated from Rueggeberg's lattice constants. Contrary to the belief of Rueggeberg, none of the lines observed in the high-temperature product can be attributed to an impurity such as graphite. The only foreign substance present in an amount considered detectable by X-ray diffraction was approximately 50% carbon which, however, when separated by hydrochloric acid did not produce any X-ray lines of crystalline graphite. This is naturally further borne out by the absence, in the X-ray diagram of the magnesium acetylide, of the strongest line of graphite, with *d* 3.38. Besides, the accuracy of the measurements precludes absolutely the possibility that the lines *d* 1.66 and 1.97 are the lines with *d* 1.69 and 2.02, of graphite. The extremely low intensity of the line with *d* 2.44, corresponding to the strongest line in the pattern of magnesium metal, as well as the chemical analysis, indicated that magnesium, present in considerable amounts in the original reaction product, has been reduced by leaching with ethyl iodide to not more than traces.

No indices can be assigned to the lines with *d* 2.11 and 1.97 of medium intensity, by assuming the face-centered tetragonal lattice. Furthermore, no agreement exists for most of the other lines (*d* 3.10, 2.79, 2.51, 1.76 and 1.27) between spacings calculated from tetragonal lattice constants, and those measured by the writer, or even those measured by Rueggeberg. The X-ray evidence submitted by the latter does not indicate, either, that besides the magnesium acetylide, prepared from the metal and acetylene at 500°, a possible second crystal modification, forming from ethylmagnesium bromide and acetylene at room temperature, which would be isotypic with tetragonal calcium carbide (I), might exist and have been observed by Rueggeberg. The agreement between the four lines of the latter's sample, obtained from ethylmagnesium bromide and acetylene at room temperature, and the strongest lines of the other sample prepared from magnesium metal at 500°—though not too satisfactory—seems to suggest the identity of the structure of both samples, although it is not clear why the strongest line, with *d* 2.79, was not recorded by Rueggeberg.

In view of the existence of Mg_2C_3, having a higher metal:carbon ratio than MgC_2, the question of the isotypy of MgC_2, suggested previously by the writer,[2a] with CaC_2 III rather than with CaC_2 I, is also interesting in connection with the very peculiar sensitivity of these two calcium carbide modifications to just such conditions that may influence the calcium:carbon ratio.[2a,b] This problem may also be of interest to the organic chemist, concerned with the polymerization of acetylene, because of the possible slight variations in the nature of the products of hydrolysis from calcium carbide of varying calcium:carbon ratio.[2b] Much further experimental study will be required to clarify these relations.

Summary

It is shown that it is not possible to ascribe a face-centered tetragonal crystal lattice such as that of calcium carbide I to magnesium acetylide. There are some indications that MgC_2 may instead be isotypic with the metastable crystal form III of calcium carbide.

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