HYDROCARBONS FROM CARBIDES

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The past few years have witnessed the development of an enormous chemical industry based upon the hydrolysis of calcium carbide (74). Acetylene resulting from this reaction may be easily hydrated to acetaldehyde, which, in turn, can be oxidized to acetic acid or reduced to ethyl alcohol. A single Canadian plant using this process has an annual capacity of 50,000 tons of glacial acetic acid (6). Plastics (4), solvents, even a chemically resistant product with physical properties similar to those of rubber are successfully manufactured (6). Table 1 gives some idea of the magnitude of the domestic carbide chemicals industry (1, 67).

The development of a synthetic organic chemicals industry based on the carbide of calcium lends interest to a study of some of the other carbides, several of which yield pure acetylene or its reduction products, while others give such diverse hydrocarbons as allylene, methane, and decane. Indeed, the fact that solid and liquid hydrocarbons result from the action of water on meteorites has in the past led many geologists to believe that petroleum was formed by the action of water on the core of the earth (7, 46). Although this theory of petroleum formation is no longer generally accepted, it is very likely that the first organic compounds of primitive times had their origin in this manner (31).

CLASSIFICATION OF THE CARBIDES

The carbides may be divided into two main classes: (1) those which readily react with water or dilute acids, and (2) those which do not. Generally speaking, the carbides of the metals and metalloids whose oxides are acidic are not decomposable to hydrocarbons. In this class belong the carbides of boron (34), phosphorus (32), arsenic (32), vanadium (42), tungsten (34), tantalum (34), chromium (34), molybdenum (34), silicon (34), titanium (55), and zirconium (34). The carbides of metals whose oxides are basic are readily hydrolyzed: thus, the carbides of sodium, calcium, cerium, magnesium, and aluminum readily react with water, while the carbides of copper, silver, iron, and manganese react with dilute acids (34). On the basis of chemical and crystallographic structure, the carbides decomposable by water or mineral acids may be further subdivided into three groups (52).

Group I. The crystal lattice is such that the carbon atoms are separated from each other by metal atoms. This group comprises the carbides of nickel, iron, cobalt, and manganese having the formula M_3C, and the carbides of beryllium and aluminum, Be_2C and Al_4C_3, respectively. The products formed on treatment with water or dilute acids result from the action of nascent hydrogen on each separate carbon atom. Methylene ($CH_2=$) radicals are the primary product, and these, by hydrogenation and/or polymerization, are converted to methane and other hydrocarbons. Acetylene is not formed by the decomposition of these carbides.

TABLE 1

*Carbide chemicals manufactured in the United States**

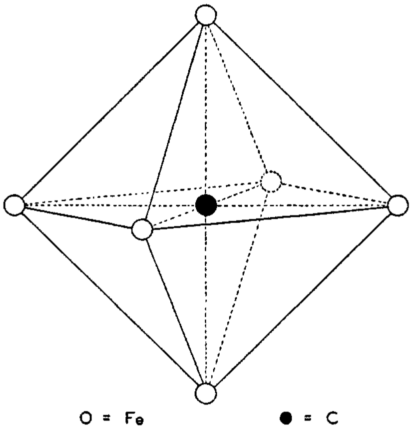
CARBIDE CHEMICALS	1933	1931	1929	1927
Calcium carbide:				
Tons	101,488	128,263		201,955
Value	$6,059,205	$8,024,029		$9,397,556
Acetylene:				
Thousands of cu. ft.	734,089	742,898	969,534	682,481
Value	$11,038,959	$12,911,727	$16,553,763	$16,196,388
Glacial acetic acid:†				
Lbs	36,359,413			
Value	$2,223,965			

* Includes only chemicals manufactured for sale as such.

† By far the greater part, but not all, of the glacial acetic acid was manufactured by the calcium carbide process.

Two representative examples of group I are illustrated in figure 1. X-ray analysis of the iron carbide crystal has shown that each carbon atom is completely enclosed by an octahedron of iron atoms. Since each carbon atom is so completely surrounded by iron atoms, there is ample opportunity for reduction of the carbon by nascent hydrogen. Similarly, in the beryllium carbide crystal each carbon atom is enclosed by a cube of beryllium atoms. It is therefore not surprising that pure methane is formed by the hydrolysis of beryllium carbide. (However, as we shall see later, the high polarization potential of the evolved hydrogen may also favor the formation of methane.)

Group II. Carbides which give acetylene on hydrolysis comprise this group. The formation of acetylene is believed to be due to actual $C \equiv C$ linkages in the crystal lattices of these carbides. Included in this group are the carbides of the alkali, alkaline earth, and rare earth metals. Figure 2 illustrates a well-known member of Group II, tetragonal calcium carbide. Six calcium atoms define the unit cell, a prism whose length is 6.37 A.U., and whose cross section (100 plane) is a square of edge 5.48 A.U. The carbon atoms are joined together in groups of two, forming



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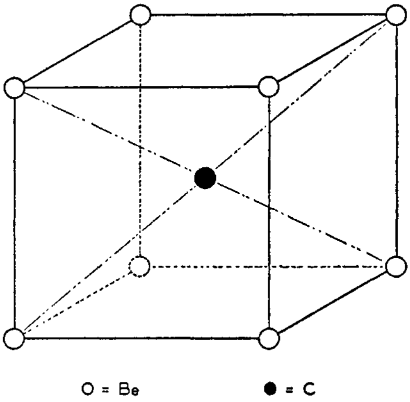

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FIG. 1A. Relation of carbon to iron in iron carbide (Fe_3C) crystal (34)
FIG. 1B. Relation of carbon to beryllium in beryllium carbide (Be_3C) crystal (58)

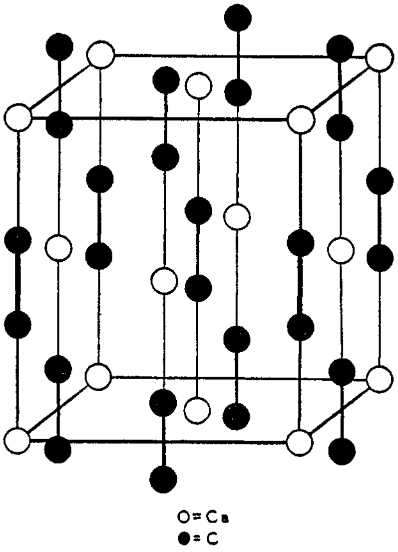

FIG. 2. Model of calcium carbide crystal

ions whose length is 4.2 A.U. and whose diameter is 3.3 A.U. When the carbide is hydrolyzed, this acetylenic linkage is preserved intact (57).

Thorium and the carbides of the rare earth metals give not only acetylene but also other unsaturated and saturated hydrocarbons. The irregular behavior of these carbides may be attributed to the conversion of the metal, upon decomposition of the carbide, from the bivalent to the trivalent or quadrivalent form, resulting in the formation of more hydrogen than that required for acetylene. That acetylene may be reduced in aqueous solution by nascent hydrogen has been shown by Traube and Passarge (60).

Group III. Carbides which yield allylene ($CH_3C{\equiv}CH$) on hydrolysis comprise this group, of which magnesium carbide is the only known member. Although its crystal structure is not known, its hydrolysis to pure allylene would indicate the presence of $C{-}C{\equiv}C$ linkages in the lattice.

TABLE 2

Hydrolysis of cementite to free carbon

Molar concentration of sulfuric acid	2.5	2.5	2.5	0.017	0.017	0.017
Molar concentration of ferrous sulfate	0.0	0.60	1.39	0.0	0.60	0.96
Per cent of total carbon liberated	15	36	73	18	55	73
Molar concentration of benzenesulfonic acid	1.5	1.5	1.5	0.25	0.25	0.25
Molar concentration of ferrous benzenesulfonate	0.0	0.18	0.63	0.0	0.18	0.63
Per cent of total carbon liberated	33	60	87	34	60	87
Molar concentration of acetic acid	1.5	1.5	0.5	0.5		
Molar concentration of ferrous acetate	0.0	0.385	0.0	0.385		
Per cent of total carbon liberated	41	70	68	99		

EFFECTS OF CONDITIONS OF HYDROLYSIS ON PRODUCTS OBTAINED

Free carbon is invariably one of the hydrolysis products of pure cementite, Fe_3C (50). The data given in table 2 have been calculated from the results of Schenck and Stenkhoff (50), and were obtained by dissolving 0.200-g. samples of pure cementite in 600 ml. of solutions containing varying concentrations of acids and their corresponding ferrous salts. In each experiment the temperature was held constant at 60°C. The percentage of the combined carbon which was liberated by the action of each dissolving solution is given in table 2.

The results in table 2 show rather conclusively that the amount of carbon liberated as free carbon increases with both the pH and the ferrous-ion concentration. It has been suggested (50) that the increase in pH lowers the reaction rate, and consequently decreases the polarization or "overvoltage" (27) of the hydrogen on the carbide. This would cause the hydrogen to be less effective as a reducing agent, and more free carbon would be obtained. Similarly, increase in the ferrous-iron concentration would lessen the tendency of iron to go into solution, resulting also in a decrease in polarization. Nevertheless, an exact correlation between reaction rate and completeness of reduction is still lacking. For example, Moissan (36) found that when manganese carbide (Mn_3C) was hydrolyzed, the use of hydrochloric acid in place of water favored the formation of hydrocarbons of lower hydrogen-to-carbon ratio, and Schmidt and Oswald (53), in more recent experiments with nickel carbide, Ni_3C, were unable to obtain reproducible results.

The temperature of reaction exerts an influence on the hydrolysis of cerium carbide, a greater proportion of the acetylene being reduced to ethylene and methane at room temperature than at 0°C. (36). Temperature also has a marked effect on the hydrolysis of calcium carbide. By passing steam at atmospheric pressure and 500° to 700°C. over calcium carbide, Plauson and Tischenko (43) were able to obtain up to 60 per cent yields of benzene. At the same temperature, but under reduced pressure, a mixture of aluminum and calcium carbides yielded pentinene, whereas polymerized products such as terpenes were obtained at higher pressures (43). Although neither of the pure carbides gives ethylene, the hydrolysis of a mixture of aluminum and calcium carbides at room temperature yields a small amount of the gas (47).

Apparently, contact agents may exert an influence on the hydrolysis products of carbides. Lebeau and Damiens (29) found that the presence of graphite in uranium carbide, UC_2, caused the hydrolysis to proceed more slowly. The evolved gases contained less hydrogen and more hydrocarbons than that produced from carbides containing no graphite (29).

Other peculiar examples are the manganese carbides (Mn_3C and Mn_5C_2), which are formed by passage of excess of methane over manganese oxides at 800° to 1000°C. In this synthesis, the formation of carbides decomposable by water is favored by the presence of barium oxide and aluminum oxide. The formation of carbides whose hydrolysis requires a strong mineral acid is favored by nickelous oxide, chromic oxide, and ferric oxide. Compounds that exert little or no influence are potassium carbonate, calcium oxide, titanium dioxide, cupric oxide, vanadium trioxide, and cerium dioxide (15).

DECOMPOSITION OF CARBIDES WITH ORGANIC COMPOUNDS

At 150° to 300°C., and under 12 to 40 atmospheres pressure, calcium carbide readily reacts with alcohols, phenols, or halogen derivatives of hydrocarbons, to form acetylenic compounds (9). Two examples of this type of reaction are:

$$2C_2H_5OH + CaC_2 \rightarrow Ca(OH)_2 + C_2H_5C{\equiv}CC_2H_5$$

$$2C_6H_5Cl + CaC_2 \rightarrow CaCl_2 + C_6H_5C{\equiv}CC_6H_5$$

Methyl alcohol, propyl alcohol, phenol, and many other compounds may be used as starting materials. When alcohol is used, part of the calcium carbide reacts to form calcium ethoxide and acetylene (36). Corson, who investigated this process, did not state the yields (9).

Calcium carbide also reacts with ketones, acetylenic alcohols being formed (26). For example, 3-methyl-3-hydroxy-1-butine may be obtained in 70 per cent yield by reacting acetone at a temperature of 0°C. with calcium carbide and potassium hydroxide in ether solution. When the reaction is carried out at a slightly higher temperature, a 74 per cent yield of 2,5-dimethyl-2,5-dihydroxy-3-hexine results. The probable reactions given by Kazarian (26) are as follows:

$$CaC_2 + KOH \rightarrow K{-}C{\equiv}C{-}CaOH \tag{1}$$

$$K{-}C{\equiv}C{-}CaOH + CH_3COCH_3 \rightarrow KOC(CH_3)_2C{\equiv}C{-}CaOH \tag{2}$$

$$\begin{aligned}KOC(CH_3)_2C{\equiv}C{-}CaOH + 2H_2O \rightarrow Ca(OH)_2 + KOH +\\ HOCH(CH_3)C{\equiv}CH\end{aligned} \tag{3}$$

$$\begin{aligned}K{-}C{\equiv}C{-}Ca(OH) + 2CH_3COCH_3 \rightarrow\\ (CH_3)_2KOC{-}C{\equiv}C{-}C(CH_3)_2CaOH\end{aligned} \tag{4}$$

$$\begin{aligned}(CH_3)_2KOC{-}C{\equiv}C{-}C(CH_3)_2CaOH + 2H_2O \rightarrow\\ (CH_3)_2HOC{-}C{\equiv}C{-}C(CH_3)_2OH + KOH + Ca(OH)_2\end{aligned} \tag{5}$$

CHEMISTRY OF THE METALLIC CARBIDES

Alkali metal carbides

Acetylene possesses marked acid properties, one hydrogen atom being replaceable under ordinary conditions (10, 35, 68). In the presence of an inert solvent, the alkali metals readily react to give the corresponding monobasic acetylide. Moissan first prepared the compounds $NaHC_2$, KHC_2, and $2LiHC_2 \cdot 3NH_3$ by passing acetylene into a solution of the alkali metal in liquid ammonia (35), a typical reaction being

$$2Na + 3C_2H_2 \rightarrow 2NaHC_2 + C_2H_4$$

No hydrogen is evolved, but a small amount of the acetylene is reduced to ethane (10). Similar results are obtained when boiling xylene is used as the solvent (13). Contrary to many statements in the literature (8), a liquid ammonia solution of $NaHC_2$ will not react further with sodium (56, 68). The alkali metal acetylides are soluble in liquid ammonia, and the solutions are good electrolytic conductors (56).

On heating sodium acetylide to 180°C., acetylene is evolved, and a white powder of *sodium carbide*, Na_2C_2, remains (35, 68). When prepared in this way, nitrogen compounds are always present in varying quantities (68), owing, presumably, to ammonolysis (10, 56). Sodium carbide decomposes at 600°C., yielding sodium and carbon (19). However, Hackspill and Schwartz were able to prepare traces of the carbide by heating sodium and carbon under pressure at 980°C. (20).

Metallic *potassium, rubidium,* and *cesium* differ from sodium in that they readily combine with carbon at temperatures below 70°C., to form compounds of the type MC_8. In the case of potassium, a dark copper-red carbide of the formula KC_4 and a blue-black carbide of the formula KC_{16} are known. The existence of these compounds has been definitely proven by a study of the partial pressure of potassium resulting from their dissociation (16). Furthermore, the "heat of solution" of 1 mole of graphite in an excess of potassium has been determined as 1500 cal. On hydrolysis of the carbides, Fredenhagen and Cadenback (16) were unable to obtain hydrocarbons, pure hydrogen being evolved. Under certain conditions, the potassium content of the potassium carbides did not readily go into solution in water, being held very tenaciously by adsorption or chemical combination.

Of the alkali metals, *lithium* alone readily combines with carbon to form a carbide with acetylenic linkages. The electrothermal reduction of lithium carbonate with carbon yields lithium carbide, Li_2C_2 (36). It is interesting to note that the heat required to form 1 mole of lithium carbide by carbon reduction of the oxide is 101.7 Cal. (21), in comparison with the value of 108.0 Cal. for calcium carbide (33).

Alkaline earth metal carbides

In addition to the usual lime–carbon process, of which Mantell (33) has given a good description, *calcium carbide* may be prepared by carbon reduction of calcium silicates (73), calcium phosphate (54), or calcium sulfate (71). Although calcium carbide has always been the principal industrial source of acetylene (33), its predominant position in this field may eventually be threatened by processes based on the pyrolysis of hydrocarbons (12, 65).

Monobasic calcium acetylide, like the corresponding alkali metal compounds, is precipitated when acetylene is passed into a liquid ammonia solution of the metal. This compound is transformed to calcium carbide on gentle heating (69).

Barium carbide may be prepared at 1150°C. in 60 per cent yield by reduction of the oxide with carbon in a stream of methane. The formation of barium hydride (BaH_2) is believed to prevent a higher yield (14). The carbide may also be prepared by reduction of the carbonate with aluminum (30), and by reduction of the oxide, hydrate, or carbonate with coal in a blast furnace (24, 59, 77).

Carbides of aluminum, beryllium, magnesium, and ammonium

The principal difficulties in the preparation of *aluminum carbide*, Al_4C_3, are due to its volatility (61, 64, 75). At the boiling point, 2270°C., the vapor consists of approximately equal volumes of aluminum and aluminum carbide (48). Slow heating favors the formation of the yellow, crystalline carbide (45, 63). When carbon is heated with porcelain at as low a temperature as 1400°C., a film of aluminum carbide can be detected by x-ray analysis (28). Water reacts with aluminum carbide twenty-three times faster than does deuterium oxide, pure methane and tetradeuteromethane being formed (66).

When *beryllium* oxide is reduced with carbon, the carbide, Be_2C, is formed. Each carbon atom is enclosed by a cube of beryllium atom (figure 1 b); the distance between carbon atoms is 3.06 A.U. and between beryllium and carbon atoms is 1.87 A.U. (58). This compound yields methane on hydrolysis (58). At high temperatures, beryllium has more affinity for copper than for carbon (37).

By reaction of *magnesium* with acetylene in liquid ammonia, the acetylide, $Mg_2C_2 \cdot C_2H_5 \cdot 5NH_3$ has been prepared. Analogous to hydrated magnesium chloride, the compound must be heated under reduced pressure if the monobasic or dibasic acetylides are to be prepared in the pure condition. At atmospheric pressure, as much as 92 per cent of the compound is ammonolyzed to magnesium amide, $Mg(NH_2)_2$ (10). The magnesium acetylides are also readily prepared by treating Grignard reagents with acetylene (18). The electrothermic reduction of magnesium oxide with carbon gives very low yields of the carbide MgC_2, metallic magnesium being the principal product (62).

One of the most remarkable of all carbides is formed when dibasic magnesium acetylide is heated above 500°C., the allylide Mg_2C_3 being produced (39). At 650°C., the conversion of the acetylide to magnesium, carbon, and magnesium allylide is complete. Unfortunately, magnesium allylide begins to decompose at 600°C., and the yield by this method is only 30 per cent. The hydrolysis of this compound yields pure allylene, which Novak thoroughly characterized by several methods which included analysis of the silver salt and α-iodo derivative ($CH_3C{\equiv}CI$) (38). Since allylene does not react with ammoniacal cuprous chloride, quantitative separation of the hydrocarbon gases was obtained by absorption of the acetylene in this reagent, followed by absorption of the allylene with ammoniacal silver nitrate (39).

By passing hydrocarbon gases over magnesium at 690° to 760°C., the maximum yields of magnesium allylide which Novak obtained were as follows: methane, 50 per cent; pentane, 74 per cent; octane, 58 per cent; benzene, 70 per cent; toluene, 2 per cent; xylene, 7 per cent. Furthermore, the optimum temperature for each hydrocarbon was determined. As Novak pointed out twenty-five years ago, allylene prepared by this method should provide a comparatively inexpensive raw material for the preparation of such compounds as propionaldehyde (39).

The non-existence of appreciable quantities of ammonium acetylides in liquid ammonia solutions of acetylene has been inferred from the high electrical resistance of the solution (10). However, this solution readily attacks magnesium (10) and the alkaline and alkaline earth metals (10, 35, 68).

Iron, nickel, cobalt, and manganese carbides

Iron forms the carbides Fe_3C (23), Fe_2C (3, 17, 22), and probably also FeC and FeC_2 (70). The solubility of carbon in iron is as follows (34):

Temperature (°C.)	1220°	1522°	1823°	2122°	2169°	2220°	2271°	2420°
Per cent carbon...	4.58	5.46	6.59	7.51	8.21	9.6	8.97	8.09

When the solutions were very rapidly cooled, nearly all of the carbon was obtained in combined form (34). By heating iron above 2600°C. Vittorf (70) found that as much as 30 per cent of carbon dissolved. In his experiments with synthetic diamonds, Moissan found that very little carbon separated out when boiling, saturated iron–carbon solutions were rapidly cooled (36).

Cementite, Fe_3C, is the most common iron carbide. It has a white silver color. Since it reacts with acids more slowly than iron, a separation from iron may be rather easily effected (34, 36). This carbide is stable above 700°C., but slowly decomposes at 500°C. (50). The heat of formation is $-12{,}300$ cal., the compound being endothermic (76). By the action of carbon monoxide on iron at 400°C., cementite is formed; between 230° and 400°C., the product is a mixture of cementite and Fe_2C; below 230°C., the product is pure Fe_2C (3).

Cementite is the only carbide of iron whose hydrolysis has been investigated. Under favorable conditions, 40 per cent of the carbon content may form a mixture of solid and liquid hydrocarbons (34) that are but slightly soluble in ether, and which consist of a large number of compounds of the paraffin and olefin series (35). More or less free carbon is always obtained (50).

Nickel carbide, Ni_3C, is best prepared by passing carbon monoxide over heated nickel (2). Very little, if any, free carbon results on hydrolysis (2, 53). This was explained by Schmidt (52) on the basis of the nickel carbide crystal lattice. Each carbon atom is surrounded by a hexagonal prism of six nickel atoms (25) which hydrogenate the carbon atom before it gets a chance to form free carbon (52). The hydrolysis of nickel carbide with 3 *N* hydrochloric acid yields 67 per cent of the carbon as gaseous hydrocarbons, and 33 per cent as liquid hydrocarbons (2). Dilute nitric acid gives nitro compounds (2).

In slightly acid solutions, nickel chloride reacts with calcium carbide to form an acetylide (11).

TABLE 3

Composition of the gaseous mixture resulting from the hydrolysis of carbides

CARBIDE	C_2H_2	C_2H_4	CH_4	H_2
	per cent	*per cent*	*per cent*	*per cent*
ThC_2	75.8	3.8	20.9	
CeC_2	47.6	5.8	29.4	17.1
UC_2	0.17–0.72	5.16–6.17	78.05–80.6	13.52–15.01

The order of stability of the carbides of the iron group is cobalt, iron, and nickel (5, 49).

By means of x-ray analysis, Jacobson and Westgren (25) have proven the existence of *manganese carbides* of the compositions Mn_4C, Mn_3C, and Mn_7C. Fischer and Baugert (15) obtained in addition Mn_6C_2. When Mn_3C, the carbide obtained by the electrothermal reduction of MnO_2, is hydrolyzed, the gases evolved consist of 2.5 per cent of unsaturated hydrocarbons, 45 per cent of saturated hydrocarbons, and 52.5 per cent of hydrogen (36). The carbide Mn_3C is ferromagnetic, has a hardness between 1 and 2 on the Mohr scale (72), and readily decomposes water (15).

Miscellaneous carbides

By reduction of thorium dioxide with carbon, *thorium carbide* is obtained as large, yellow, transparent crystals melting at 2500°C. (44). Table 3 gives the volume composition of the gaseous mixture resulting from its hydrolysis (36).

The rare earth carbides are isomorphous with those of the calcium group (78). *Cerium carbide* readily reacts with water (29), evolving a gas whose composition (36) is given in table 3.

Uranium forms the carbide UC_2 (51), which water slowly decomposes at room temperature (34). On hydrolysis, one-third of the carbon is evolved in the gas mixture whose composition is given in table 3 (36). The rest of the carbon, about two-thirds of the total quantity, forms liquid and solid hydrocarbons (36). Uranium carbide gives a larger quantity of liquid and solid hydrocarbons than any other carbide.

Durand found that calcium carbide reacted with aqueous solutions of several metallic salts to form acetylenic carbides. Among the carbides he claimed to have prepared in this manner were Cu_2C_2, CuC_2, AgC_2, Hg_2C_2, HgC_2, and PbC_2 (11). Each of these carbides is soluble in mineral acids (34). The precipitation of the explosive silver carbide has long been the basis of an analytical method for acetylene determination (40, 41).

Carbides of zinc, cadmium, antimony, and bismuth are unknown.

UNSOLVED PROBLEMS

1. Apparently the only information available concerning magnesium allylide is Novak's work (38, 39), which was done twenty-five years ago. His low yields when toluene and xylene were used to prepare the carbide are difficult to explain. Moreover, the accuracy of the analytical methods which he used is in doubt as a result of recent work (40, 41). Confirmation of his results and further investigation of this interesting carbide are needed.
2. The hydrolysis of mixtures of carbides is a subject of considerable theoretical interest.
3. No analyses have yet been made of the hydrolysis products of iron carbides other than Fe_3C, or of manganese carbides other than Mn_3C.
4. Very little work has been done on the effects of temperature, pH, salt concentrations, and contact agents on the hydrolysis products of the carbides of uranium, manganese, iron, nickel, and cobalt.
5. The decomposition of carbides with reactants other than water under higher temperatures and pressures offers a possible synthesis of many new compounds.

The hydrolysis of carbides is an interesting subject that should be worthy of further investigation. From both an industrial and a purely scientific standpoint, this field should amply reward the research worker.

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