A General Mechanism for the Formation of Volatile Hydrides by Hydrolysis Reactions[1]

BY DALLAS T. HURD

Introduction

One of the very general reactions in inorganic chemistry is the preparation of volatile hydrides by the hydrolysis of binary compounds between metals and non-metals. For illustration we may cite the synthesis of monosilane by the hydrolysis of magnesium silicide in dilute acid, the formation of phosphine by the hydrolysis of calcium phosphide in water, or the preparation of hydrogen fluoride by the acid hydrolysis of calcium fluoride. That these reactions are examples of a general reaction can be seen when it is considered that volatile covalent hydrides of nearly one-fifth of the chemical elements have been prepared by similar reactions.

The ability of an element to form volatile hydrides apparently is a function of its electronegativity and it has been pointed out by T. H. Liu[2] that the electronegativity of these elements forming volatile covalent hydrides exceeds 1.6 on Pauling's electronegativity scale.[3] If the electronegativity of an element is below 1.0 it is expected to have a salt-like electrovalent hydride. If the electronegativity lies between 1.0 and 1.6 the hydride will be non-existent, indefinite, or unstable. The elements that qualify as volatile hydride forming thus are boron and the members of the A subgroups of the the fourth, fifth, sixth, and seventh groups of the Periodic Classification of the elements[4] (Fig. 1).

interpretation of experimental results in terms of a general reaction mechanism. For example, certain binary compounds will react readily with water to form the hydrides of their non-metal components, e. g., calcium carbide, whereas other compounds may require acids for their hydrolysis, e. g., ferrous sulfide, while a few, such as certain metallic nitrides, may be reactive toward alkaline hydrolysis. Some reactions analogous to hydrolysis can be effected in liquid ammonia or other non-aqueous media to form volatile hydrides. Again, different compounds of the same non-metal may yield different hydrides of that non-metal and in some cases the hydride products are found to be complex mixtures. This is particularly true of metallic carbides. Furthermore a great many of the binary metal–non-metal compounds are inert, or decomposed only with difficulty in strong reagents, and will not yield their non-metal components in the form of hydrides.

Considerable information may be found in the chemical literature regarding those compounds which produce volatile hydrides upon hydrolysis, particularly the compounds of the more familiar elements such as carbon and nitrogen, etc. Much less is known about the chemical behavior of the corresponding compounds of those elements which form hydrides with more difficulty such as tin, lead and bismuth. However, in a consideration of the general subject of volatile hydride formation

H																	He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	A
K 0.8	Ca 1.0	Sc 1.3	Ti 1.6	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge 1.7	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.3	Zr 1.6	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn 1.7	Sb 1.8	Te 2.1	I 2.4	Xe
Cs 0.7	Ba 0.9	R.E.	Hf	Ta	W·	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	85	Rn
87	Ra	Ac	Th	Pa	U												

Fig. 1.—The elements forming volatile hydrides. Electronegativity values for certain elements are indicated.

Evidence of Generality

In trying to extend broadly the generality of hydride producing hydrolysis reactions we encounter many confusions which obscure the general nature of the reaction and make difficult the

(1) Presented before the Symposium on Hydrides, Division of Physical and Inorganic Chemistry, American Chemical Society, 110th meeting, Chicago, Illinois, Sept. 10, 1946.

(2) T. H. Liu, J. Chinese Chem. Soc., 9, 119–124 (1942).

(3) L. Pauling, "Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940.

(4) Within any given group there is a progressive decrease in hydride stability with increase in atomic weight and electropositivity.

several points of consistency have been marked from a survey of the literature.

I.—Those compounds most readily forming volatile hydrides upon hydrolysis are in general those in which the metallic components are strongly electropositive elements. The alkali metal carbides, silicides, nitrides, etc., react vigorously with water to form hydrides. This reactivity to water is shown to a lesser degree by the compounds of the group 2A and alkaline earth metals. With less electropositive metals the presence of acids usually is necessary for hydrolysis, often these compounds are inert and do not yield hydrides.

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H                                                                          He
Li   Be                                      B   C   N   O   F   Ne
Na   Mg                                       Al  Si  P   S   Cl  A
K    Ca   Sc  Ti  V   Cr  Mn  Fe  Co  Ni  Cu  Zn  Ga  Ge  As  Se  Br  Kr
Rb   Sr   Y   Zr  Cb  Mo  Ma  Ru  Rh  Pd  Ag  Cd  In  Sn  Sb  Te  I   Xe
Cs   Ba   R.E. Hf Ta  W   Re  Os  Ir  Pt  Au  Hg  Tl  Pb  Bi  Po  85  Rn
87   Ra   Ac  Th  Pa  U
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Stannides E = 1.7

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H                                                                          He
Li   Be                                      B   C   N   O   F   Ne
Na   Mg                                       Al  Si  P   S   Cl  A
K    Ca   Sc  Ti  V   Cr  Mn  Fe  Co  Ni  Cu  Zn  Ga  Ge  As  Se  Br  Kr
Rb   Sr   Y   Zr  Cb  Mo  Ma  Ru  Rh  Pd  Ag  Cd  In  Sn  Sb  Te  I   Xe
Cs   Ba   R.E. Hf Ta  W   Re  Os  Ir  Pt  Au  Hg  Tl  Pb  Bi  Po  85  Rn
87   Ra   Ac  Th  Pa  U
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Silicides E = 1.8

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H                                                                          He
Li   Be                                      B   C   N   O   F   Ne
Na   Mg                                       Al  Si  P   S   Cl  A
K    Ca   Sc  Ti  V   Cr  Mn  Fe  Co  Ni  Cu  Zn  Ga  Ge  As  Se  Br  Kr
Rb   Sr   Y   Zr  Cb  Mo  Ma  Ru  Rh  Pd  Ag  Cd  In  Sn  Sb  Te  I   Xe
Cs   Ba   R.E. Hf Ta  W   Re  Os  Ir  Pt  Au  Hg  Tl  Pb  Bi  Po  85  Rn
87   Ra   Ac  Th  Pa  U
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Borides E = 2.0

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H                                                                          He
Li   Be                                      B   C   N   O   F   Ne
Na   Mg                                       Al  Si  P   S   Cl  A
K    Ca   Sc  Ti  V   Cr  Mn  Fe  Co  Ni  Cu  Zn  Ga  Ge  As  Se  Br  Kr
Rb   Sr   Y   Zr  Cb  Mo  Ma  Ru  Rh  Pd  Ag  Cd  In  Sn  Sb  Te  I   Xe
Cs   Ba   R.E. Hf Ta  W   Re  Os  Ir  Pt  Au  Hg  Tl  Pb  Bi  Po  85  Rn
87   Ra   Ac  Th  Pa  U
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Phosphides E = 2.1

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H                                                                          He
Li   Be                                      B   C   N   O   F   Ne
Na   Mg                                       Al  Si  P   S   Cl  A
K    Ca   Sc  Ti  V   Cr  Mn  Fe  Co  Ni  Cu  Zn  Ga  Ge  As  Se  Br  Kr
Rb   Sr   Y   Zr  Cb  Mo  Ma  Ru  Rh  Pd  Ag  Cd  In  Sn  Sb  Te  I   Xe
Cs   Ba   R.E. Hf  Ta  W   Re  Os  Ir  Pt  Au  Hg  Tl  Pb  Bi  Po  85  Rn
87   Ra   Ac  Th  Pa  U
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Carbides E = 2.5

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H                                                                          He
Li   Be                                      B   C   N   O   F   Ne
Na   Mg                                       Al  Si  P   S   Cl  A
K    Ca   Sc  Ti  V   Cr  Mn  Fe  Co  Ni  Cu  Zn  Ga  Ge  As  Se  Br  Kr
Rb   Sr   Y   Zr  Cb  Mo  Ma  Ru  Rh  Pd  Ag  Cd  In  Sn  Sb  Te  I   Xe
Cs   Ba   R.E. Hf Ta  W   Re  Os  Ir  Pt  Au  Hg  Tl  Pb  Bi  Po  85  Rn
87   Ra   Ac  Th  Pa  U
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Nitrides E = 3.0

Fig. 2.—Hydride forming compounds of a few representative elements as reported in the literature. (Dotted line indicates compounds of questionable existence.)

II.—With an increasing electronegativity of the non-metal component element there is a general increase in the number of its binary compounds with metals that will produce volatile hydrides upon hydrolysis (Fig. 2). With weakly electronegative elements such as boron and silicon only those compounds with strongly electropositive metals are hydrolyzable to form hydrides. With more electronegative elements such as carbon and phosphorus, compounds with less electropositive metals are found to be reactive. Strongly electronegative elements such as oxygen, fluorine and nitrogen readily are obtained as hydrides even from their compounds with very weakly electropositive metals. Thus for example, while very few metallic borides may be hydrolyzed to form boranes (electronegativity of boron = 2.0) virtually all fluorides will yield hydrogen fluoride upon hydrolysis (electronegativity of fluorine = 4.0). Similarly a greater number of reactive metallic carbides (electronegativity of carbon = 2.5) than reactive metal silicides (electronegativity

of silicon = 1.8) are known. Comparisons equally illuminating may be made with the compounds of other hydride forming elements (see Fig. 2). Although insufficient data as yet are available for any close evaluation it does appear as a general observation that a certain minimum difference must exist between the electronegativities of the metal and non-metal components for hydride formation to occur on hydrolysis of their binary compound. This implies in turn a certain degree at least of ionicity in the compounds. Such a value probably should be stated as a function of the ratio of the electronegativities of the metal and non-metal rather than a simple difference. From the limited data available it appears that a compound will form volatile hydrides upon hydrolysis if the ratio E_{nm}/E_m is greater than about 1.5, and will be inert or will not yield hydrides if this ratio is less than about 1.4. In any case predictions of chemical behavior based on such a function of electronegativities must consider the possibility of obscure borderline cases as well as clearly defined examples. It is hoped that more experimental data will allow a more precise evaluation of the function if such is possible.

III.—The compounds that form volatile hydrides are of definite composition and, more important, have formulas corresponding to normal chemical valencies of their component elements. On the other hand the interstitial metallic compounds, which often may be of indefinite composition, generally do not yield hydrides upon decomposition in solution. Although many apparent contradictions to this statement may be found, particularly among the carbides, it may be shown that even in these cases the compounds have formulas entirely consistent with the normal free valencies of the complex ions present, i. e., the valence of the non-metal is that which would be expected if the non-metal atoms were present as complex negative ions. Examples of this will be shown later.

IV.—Hydrolysis reactions resulting in hydride formation apparently involve the reaction of protons rather than elemental hydrogen and, except in a few rare cases, an electrolytic reduction mechanism is not likely.

The first part of this statement seems more or less obvious considering the conditions usually employed for hydrolysis reactions and the composition of the product gases. Although in some cases compounds of the less electronegative nonmetals may evolve considerable hydrogen along with the hydride product, many more compounds yield products containing little or no hydrogen. The presence of hydrogen may be explained by the instability of the hydrides rather than assuming it as a primary reaction product.

Attempts to prepare hydrides by electrolysis of various electrolytes using electrodes of magnesium silicide or boride, as well as by the solution of mixtures of magnesium and silicon powders in acids

have yielded no observable amounts of hydride. The great difficulty in preparing magnesium boride sufficiently active to yield boranes upon solution also infers that the primary reaction is not a reduction of the boron by hydrogen atoms but one more closely connected with the structure of the boride.

Couple reactions involving acid solution of simple mixtures of finely divided metal and non-metal to produce hydrides are effective only in those cases where the second component has metallic characteristics, i. e., is a conductor of electricity and is a non-metal by comparison only. For example it is possible to prepare bismuth hydride by treating a mixture of magnesium and bismuth with acid[5] but this also may be considered as a proton reaction or ionic reaction rather than one involving elemental hydrogen.

Postulated Reaction Mechanism

A simple yet general reaction mechanism that emerges from a consideration of these observations is

$$M^+X^- + H^+Y^- \longrightarrow XH + M^+Y^-$$
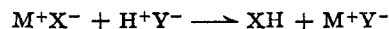
where MX represents a binary compound between metal M and non-metal X in which the bond between M and X is at least partially ionic in character. Y may represent any convenient anion such as OH, Cl or SO_4.

This simple ionic reaction mechanism can be accepted as obvious for such electronegative elements as oxygen and the halogens which are known to be ionic in their binary compounds with metals. In the case of the less electronegative elements such as boron, carbon and silicon, there are certain difficulties which require a satisfactory explanation before this mechanism can be considered as applying to the formation of their hydrides.

The principal difficulty in accepting a simple ionic picture is the wide variation in the nature of the hydride products obtained from compounds of these less electronegative elements. For example, in the hydrolysis of carbides certain compounds will yield almost pure methane, others will give acetylene, while still others may produce complicated mixtures of hydrocarbons both olefin and paraffin.

With the advent of X-ray crystallography it was realized that the type of hydrocarbon produced depended in large measure upon the disposition of the carbon atoms in the crystal lattice. Methanides like beryllium carbide, which yields almost pure methane upon hydrolysis, were found to have structures comprising individual carbon atoms isolated by surrounding metal atoms.[6] Acetylides of the type MC_2 were shown to have carbons present in the crystal lattice in pairs, the acetylenic linkages being preserved during hydrolysis.[7] A third

(5) F. Paneth, Ber., 55, 769 (1922).

(6) M. v. Stackelberg and Quatram, Z. physik. Chem., 27B, 50 (1934).

(7) M. v. Stackelberg, ibid., 9B, 437 (1930).

type of structure probably is present in the magnesium carbide, Mg_2C_3. This carbide is reported to yield pure allylene on hydrolysis indicating by analogy that C_3 groups are present in the structure.[8] Since the compounds showing this behavior are those of electropositive metals it may be presumed that the carbon atoms are present in the structures as complex ions whose valencies correspond both to that indicated by the chemical formulas and to the number of hydrogens added to form the hydrocarbon.

The formation of complex hydrocarbon mixtures shown by a number of pure carbides still may be difficult to interpret. Ferric carbide, with a structure of single carbon atoms surrounded by iron atoms[9] yields a large amount of free carbon upon hydrolysis along with a complicated mixture of various hydrocarbons while nickel carbide, of similar structure, produces little or no free carbon and under certain conditions can be made to yield almost pure methane.[10]

This difference has been attributed to the high efficiency of nickel and the low efficiency of iron as hydrogenation catalysts[11] and it is entirely possible that ferric carbide and nickel carbide may be borderline cases in regard to the electronegativity ratio of their component elements, thus being relatively non-ionic and yielding free carbon initially upon solution. Hydrogenation of the carbon by the metal then may follow. It seems not improbable that this is a valid explanation and that the complicated phenomena observed are a result of the conditions of the hydrolysis reaction rather than complicated carbide structures.

In other cases subsequent reactions suffered by initial products may affect markedly the nature of the final products. For example, calcium carbide yields a high percentage of benzene when treated with high temperature steam.[12] The type of hydrocarbon obtained from nickel carbide also is affected by the reaction conditions.[10]

The carbides not decomposable by water or dilute acids to form hydrocarbons will deposit free carbon or produce carbon dioxide upon breakdown or solution with strong chemical reagents.

Hägg[13] implies from a consideration of atomic radii that the carbides of the transitional elements are non-ionic, most of these compounds are in fact unreactive and do not yield hydrides.[14]

Similarly are structure considerations and the

(8) J. Novak, Z. physik. Chem., 73, 513 (1910).

(9) H. Lipson and N. J. Petch, J. Iron and Steel Inst., 162, 95 (1940).

(10) H. A. Bahr and Th. Bahr, Ber., 63, 99 (1930).

(11) L. J. E. Hofer, "Preparation and Properties of Metallic Carbides," U. S. Bureau of Mines Report No. R13770, July, 1944.

(12) Plauson and Tischenko, German Patent 346,065 (1921).

(13) G. Hägg, Z. physik. Chem., 12B, 33 (1931).

(14) Hägg also considers that the nitrides of the transitional elements are non-ionic but counts their oxides as ionic. Since most nitrides do form ammonia upon hydrolysis this viewpoint is open to question. In view of the known effect of atomic radii upon compound formation and reactivity it is probable that such factors must also be considered in addition to electronegativity in explaining the behavior of borderline cases.

nature of the hydrolysis media important in the synthesis of boranes and silanes. All borides yielding boron hydrides upon hydrolysis appear to be of the general type M_xB_2, which may indicate a reactive boride unit in the structure similar to the carbide ions found in carbide structures. On the other hand, the borides of calcium, strontium and barium, which are inert and, surprisingly enough, do not form boranes, are of the type MB_6 in which the boride units are compact octahedra of six tightly-bonded boron atoms bonded at the corners to neighboring octahedra.[15]

It also is of interest to note that whereas magnesium silicide gives principally monosilane, lithium silicide, Li_6Si_2, yields disilane upon hydrolysis, which may indicate the presence of complex silicide ions in this structure. Similar behavior is observed with germanium compounds.

Since diborane is immediately decomposed by water and monosilane is susceptible to hydrolysis in alkaline or strongly acid solution it is not surprising that in the hydrolysis of borides and silicides the yields of hydrides are quite low and the major reaction products often are polymeric hydride forms.

Discussion

In regard to the ionic nature of the non-metallic components in the binary compounds under discussion it generally is assumed that elements such as oxygen and the halogens are ionic and that hydride formation occurs by ionic reactions. However it may be seen from a consideration of electronegativity values that even with the less electronegative elements such as boron and silicon the chemical bonds probably are partially ionic in their combinations with strongly electropositive elements such as the metals of the first and second groups. Furthermore, the removal of positive metal ions from a crystal lattice during a chemical reaction should leave the non-metal atoms momentarily at least in a highly reactive and ionic condition. For instance, if we remove positively charged magnesium ions from the magnesium silicide lattice by combination with halogen ions there should be left negatively charged silicon atoms to be discharged or removed by reaction, presumably with protons to form silicon hydrides if protons are available under the reaction conditions.

A similar situation should hold for any compound in which the difference in electronegativity between the metal and the hydride forming non-metal is great enough to introduce the necessary degree of ionicity into the compound. Thus with an increasing electronegativity of the non-metal or an increasing electropositivity of the metal an increasing number of compounds will exhibit this behavior.

The hydride products obtained from carbides such as ferric carbide are explainable if we assume that the non-metal atoms in these compounds are only slightly ionic, if at all, and that hydrogena-

(15) M. v. Stackelberg and F. Neumann, Z. physik. Chem., 19B, 314 (1932).

tion of the carbon released during solution is effected by the catalytic properties of the metal component.

If the essential idea of the postulated reaction mechanism is correct we should find, for example, a compound such as magnesium silicide reacting with common sources of both halogen ions and protons to form silanes even in non-aqueous media. The preparation of monosilane by treating magnesium silicide with ammonium bromide in liquid ammonia is one example of this reaction.[16] Other examples have been found by experiment

1. The addition of magnesium silicide to molten ethylamine hydrochloride at 110° resulted in a vigorous reaction and the evolution of spontaneously inflammable silanes.

2. When powdered magnesium silicide was dropped into anhydrous trimethylamine hydrochloride at its melting point (ca. 300°) a violent reaction ensued and polymeric silane products were obtained as well as spontaneously inflammable silanes.

3. Heating magnesium silicide with dry ammonium bromide to a high temperature likewise gave evidence of the formation of polymeric silanes.

(16) W. C. Johnson and T. R. Hogness, THIS JOURNAL, 56, 1252 (1934).

Summary

An examination of the literature on hydride formation has indicated that the formation of volatile covalent hydrides by the hydrolysis of metal-non-metal binary compounds is a general reaction and is essentially an ionic reaction.

The ionic mechanism of reactions resulting in the formation of volatile hydrides is believed to be as follows: the removal of positively charged metal ions from the crystal lattice leaves the non-metal atoms in a more or less ionic condition, a condition in which they must have been to some extent even before reaction. These negatively charged non-metal atoms are in a highly reactive condition and will combine with protons, if protons are available under the conditions of the reaction, to form hydrides, provided that the non-metal to hydrogen bonds are stable. The nature of the volatile hydride products subsequently isolated will depend upon: (1) whether the non-metal atoms were initially present in the crystal structure in combination as complex ion units or present as discrete atoms, and (2) whether the particular hydrolysis medium, or the metal component of the binary compound, exerts any chemical effects on the hydrides thus formed.

Intermolecular Dehydrations by Means of Phosphorus Pentoxide. I. Preparation of Substituted Acetophenones

BY G. M. KOSOLAPOFF

The present investigation is an extension of previous work on intramolecular dehydrations by means of phosphorus pentoxide,[1] with application of the technique of effective utilization of phosphorus pentoxide developed at that time.

It appeared feasible to effect an intermolecular dehydration between aromatic nuclei and aliphatic acid under the influence of a powerful desiccant, such as phosphorus pentoxide, to give a method of synthesis of various substituted acetophenones. It was felt that such a method might be a valuable competitor for the usual Friedel–Crafts type of synthesis in that acids rather than the more expensive acid halides would be used.

The above expectations have been fulfilled in that a number of aromatic compounds have been successfully condensed with acetic acid to yield the corresponding acetophenones in satisfactory yields. In addition, it has been found that further condensation yields by-products in the form of polyacylated materials and other condensation products. The present paper is restricted to the

(1) G. M. Kosolapoff, Doctoral dissertation, University of Michigan, 1936.

description of syntheses of the first class of compounds.

The procedure used for the syntheses was extremely simple. A mixture of the aromatic compound, glacial acetic acid and phosphorus pentoxide, dispersed by filter-aid, was stirred at reflux for thirty to ninety minutes to complete the reaction. The mixture was treated with water and the organic layer was separated and distilled under reduced pressure. The variation of the ratio of the aromatic substance to acetic acid was found to be effective to a certain extent in controlling the extent of polyacetylation. Usually the use of two to three molar amounts of the aromatic constituent vs. one mole of acetic acid was satisfactory. The amount of phosphorus pentoxide necessary for effective condensation was found to be about half of a mole for each mole of acetic acid used.

The above acetylation method varies in its effectiveness with the reactivity of the aromatic substance used as the starting material. In this respect there is a definite analogy with the chloromethylation reaction, in that reactive substances