Summary

The melting point of iron oxides in contact with silica has been determined as a function of the partial pressure of oxygen or the ratio of carbon dioxide to carbon monoxide in the gas phase. With the aid of these and other available data, a large part of the diagram showing the stable phases under various conditions of temperature and gas composition has been constructed for the ternary system iron–silicon–oxygen. The data have been used to interpret the migration of silica through iron oxide to the scale–metal interface during the scaling of steel.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Reactions of Diborane with Hydrocarbons[1]

BY DALLAS T. HURD

A number of experiments have been conducted to delineate the character of the complex reactions that occur between hydrocarbons and diborane at elevated temperatures. In these experiments the effect of the highly reactive diborane on the reaction products has been minimized by using only small amounts of diborane with relatively large amounts of hydrocarbon. Under these conditions several different reactions have been observed:

1. The addition of diborane to olefins occurs with saturation of the double bonds and the formation of trialkyls of boron.
2. Substitution on the benzene ring occurs with the formation of phenyl boron compounds.
3. Diborane reacts with paraffins to form polymeric reaction products containing boron, carbon, and hydrogen. Breakdown and synthesis of hydrocarbon chains effected by the diborane obscures the nature of the reaction.

Experimental

The general technique employed in studying the addition and substitution reactions was to seal mixtures of diborane with various hydrocarbons in heavy-walled Pyrex tubes. The tubes were frozen in liquid nitrogen and evacuated before sealing. The tubes then were encased in protecting tubes of steel pipe and either heated in an oven or allowed to stand at room temperature. After the time allotted for the reaction had elapsed the tubes were immersed in liquid nitrogen to freeze their contents, their tops were cracked off under a blanket of dry nitrogen, and the reaction products together with any unchanged materials were removed from the tubes, generally by distillation on a vacuum chain.

A. Reactions with Olefins. 1. Isobutylene.—The reaction of isobutylene with diborane was studied with mixtures containing from two to ten per cent. by weight of diborane. Within this range of composition no significant differences in the results were observed. Most of the reactions were conducted by heating the tubes at 100° for twenty-four hours but it also was noticed that the addition reaction took place at room temperature although somewhat more slowly. Since no pressure of noncondensable gas developed in the tubes during these reactions it was presumed that the addition of diborane to the olefin was rapid and almost quantitative. Otherwise the pyrolysis of unreacted diborane at the elevated temperature would develop a pressure of hydrogen that would become apparent when the tubes were opened.

Distillation of excess isobutylene from a reaction mixture left a clear colorless oil of low volatility. Upon exposure of this oil to the air it quickly became warm from spontaneous oxidation. Inflammation was observed if a few drops were placed on a filter paper or in a watch glass.

Fractionation of a fresh sample of the oil under a nitrogen atmosphere in a distillation column of approximately twenty plates separated the sample into two fractions of almost equal volume, one boiling at 181.5° and the other at 188.5°. The boiling point calculated from reduced pressure data for tri-*t*-butylboron is 182°[2] and the reported boiling point of tri-isobutylboron is 188°.[3] Each fraction was shaken individually in a separatory funnel with aqueous sodium hydroxide and air until the oil had been oxidized completely and had been dissolved as the sodium salt of the corresponding butylboric acid. The solutions were concentrated by boiling and, after cooling, were neutralized by the addition of hydrochloric acid. This caused the precipitation of the white crystalline butylboric acids. A determination was made of the melting points of the isomeric acids thus isolated and the values obtained checked very closely with those reported in the literature (*t*-butylboric acid, m. p. 113–114°; reported m. p. 113°[2]; isobutylboric acid, m. p. 112–113°; reported m. p. 112°[3]). Although these two butylboric acid isomers have melting points lying within one degree of each other it was clear that the original reaction product comprised a mixture of isomeric tributylboron compounds since oxidation of an unfractionated sample of the oil and isolation of the mixed butylboric acids by the technique described above yielded a crystalline white solid with no sharply defined melting point melting over the range from 80–90°.

2. Ethylene.—Ethylene containing two per cent. by weight of diborane was heated at 100° for four days. The tube then was opened and the unreacted ethylene was removed by distillation on the vacuum chain. A small amount of clear liquid remained in the tube. This liquid inflamed immediately upon exposure to air. Since the liquid had an appreciable volatility it could be analyzed most conveniently on the mass spectrometer. Strong maxima in the pattern indicated large amounts of triethylboron. Examination of a vapor sample taken during the last stages of the removal of ethylene from the sample revealed no volatile ethyldiborane compounds.[4]

B. Reaction with Benzene.—Pure benzene was heated with five per cent. by weight of diborane in sealed tubes or in a stainless steel bomb for twelve hours at 100°. During the course of the reaction it was observed that the benzene gradually developed a dark yellow color. Upon opening the tubes after freezing the contents in liquid nitrogen it

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(1) Presented before the Physical and Inorganic Division, American Chemical Society, New York, September, 1947.

(2) E. Krause and P. Nobbe, *Ber.*, **64B**, 2112 (1931).

(3) E. Krause and R. Nitsche, *ibid.*, **54**, 2784 (1921).

(4) These analyses were performed by Dr. Francis J. Norton.

was noticed that a large pressure of non-condensable gas, presumably hydrogen, had developed. The benzene solution of the reaction products was removed from the tubes in a nitrogen atmosphere.

Evaporation of the unreacted benzene from a sample of the solution left a soft solid material. This solid partially dissolved in water with the evolution of gas to give a milky solution. When this solution was made alkaline with sodium hydroxide and boiled it eventually became clear. After cooling the solution it was neutralized, extracted with ether, and the ether extract was evaporated to yield a white crystalline solid, m. p. 214° (reported m. p. for phenylboric acid 216°[5]). The identity of this compound as phenylboric acid was verified by specific chemical tests for this material, *i. e.*, by the precipitation of white phenylmercuric chloride (m. p. 251°) with mercuric chloride from a very dilute solution, by the thermal dehydration of the acid to its cyclic anhydride (m. p. 190°), and by the slow deposition of a silver mirror from ammoniacal silver nitrate solution.[6]

This experiment established that a substitution reaction occurred between benzene and diborane with the formation of phenylboron compounds.

An examination of the yellow benzene solution removed from the reaction tubes was made with the aid of the mass spectrometer. Samples were concentrated to varying degrees by removing benzene on a vacuum distillation system and analyses were made of the residual solutions. It was found, surprisingly enough, that diborane continued to be given off by the solutions even when most of the benzene had been removed and the samples were highly concentrated. The mass spectrographic analyses showed no evidence of any volatile phenylborane compounds, *i. e.*, phenylboron hydrides. These were indicated indirectly however since the benzene volatilized *in vacuo* from the samples gave upon shaking with water, solutions which responded to the very sensitive mercuric chloride test for phenylboric acid (not shown by benzene or diborane alone).

The residue after complete removal of the benzene was found to be of quite high molecular weight. No mass numbers between 130 and 220 appeared on the mass spectrometer. It was possible to isolate a material crystallizing in long prismatic needles from this residue by sublimation *in vacuo* at 100°. This material, believed to be triphenylboron, reacted rapidly with air to form a substance readily soluble in dilute sodium hydroxide. After neutralization of this solution it was possible to extract phenylboric acid (m. p. 215°) which in turn was verified by the specific tests for this compound as mentioned previously.

C. **Reactions with Paraffins.**—Methane was heated with six per cent. by weight of diborane for seventy-three hours at 180° in a stainless steel bomb. At the end of this time the bomb was frozen in liquid nitrogen and the non-condensable gas was pumped off. Volatilization of the unreacted methane left a small amount of less volatile liquid residue and a solid material containing both boron and carbon. Mass spectrographic analysis of the liquid portion of the reaction product revealed the presence of ethane, propane and butane, in addition to some mass numbers considered explainable as volatile methylboron compounds. Solution of the solid reaction product in water produced a large evolution of gas. The presence of boron bonded carbon in this material could be demonstrated by qualitative analysis.

Thirty-five grams of *n*-pentane and 1.5 g. of diborane were heated in the bomb for sixty-five hours at 180°. The bomb then was cooled in liquid nitrogen to freeze the contents, the non-condensable gas was bled off, and the bomb was evacuated. The bomb then was allowed to warm up slightly and the most volatile fraction of the reaction product was distilled off in the vacuum chain. This volatile material was fractionated further and the components were analyzed in the mass spectrometer. The material comprised roughly 40% methane, 40% ethane, and smaller amounts of other hydrocarbons including pentane.[7] After the bomb had warmed up to room temperature the residual pressure of volatile material was vented and the contents of the bomb were removed. Filtration separated a clear liquid from 3.5 g. of a light yellow powder of unknown composition containing boron bonded carbon. The liquid material was distilled and, with the exception of a very small amount of higher boiling material, the whole amount of liquid boiled at 36° or under.

Diborane and butane reacted only slightly at 100° in twenty-four hours although considerable polymerization of the diborane to decaborane occurred. Analysis of the very small amount of solid residue left after removal of the excess butane revealed only 3% of carbon, the balance being boron and hydrogen. A mixture of butane and five per cent. by weight of diborane heated at 200° for twenty-four hours reacted to yield a light tan powder containing 66% carbon. No analyses were made of the liquid fractions. Large pressures of hydrogen were built up in the tubes during these reactions.

The above experiments show that some substitution to form boron–carbon bonds does occur with diborane and paraffin hydrocarbons although the reactions involving breakdown and synthesis of paraffin chains under the influence of the diborane may be of major importance.

Discussion

There is a considerable amount of evidence on record to show that diborane may take part in many reactions in its monomeric form, that is as borine (BH_3).[8] It seems reasonable, therefore, although not necessary, to assume that in the addition and substitution reactions which diborane undergoes with hydrocarbons the active agent is the BH_3 molecule.

The borine molecule has, like the boron halides and the alkylborons, a strong tendency to accept and coördinate electrons. Thus by a mechanism similar to that proposed for the boron trifluoride activation of olefins a borine molecule could coordinate to one carbon of a carbon–carbon double bond to form temporarily a complex negative ion. Migration of a negative hydride ion (H^-) from the complex ion to the other carbon, positively charged by the withdrawal of electrons from the double bond, would result in a neutral molecule, RBH_2. This process then could be repeated with the remaining hydrogens attached to the boron atom to form eventually a molecule of trialkylboron, R_3B. Alternatively, the newly formed alkylborine molecule (RBH_2) could undergo disproportionation with similar molecules into trialkylboron and borine, a process known to occur readily with the alkyl derivatives of diborane.

Since breakdown of paraffin chains into smaller molecules does occur to a considerable degree under the influence of diborane (such an effect is observed with other strong acceptor molecules such as boron trifluoride and aluminum chloride) the addition or substitution of borine on the hydro-

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[5] E. Krause and R. Nitsche, *Ber.*, **55**, 1261 (1922).

[6] These tests are described in Krause and von Grosse, "Die Chemie der Metall-organischen Verbindungen," Borntraeger, Berlin, 1937, pp. 212–214.

[7] The author wishes to think Dr. Paul Zemany for these analyses.

[8] For example, diborane dissociates into monomeric borine in its reaction with carbon monoxide to form borine carbonyl. See A. Stock, "The Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

carbon fragments could only result in a complicated mixture of compounds. The observed synthesis of paraffin hydrocarbons from methane and the formation of polymeric solids indicates the complexity of these reactions. It is suggested that in the reaction of diborane with olefins or aromatic hydrocarbons this effect will make isolation of the primary reaction products difficult or impossible if the reaction conditions are severe or if relatively large amounts of diborane are used.

The behavior of the reaction products from benzene and diborane suggests that the intermediate phenyldiboranes, if they are formed, are quite unstable and resemble chlorodiborane rather than the alkyldiboranes. Thus monophenyldiborane may exist at room temperature only in equilibrium with both diborane and triphenylboron. This behavior might be predicted in view of the electronegative character of the phenyl group.

This work has been directed toward outlining the general types of reactions that diborane and hydrocarbons may undergo. It is not unreasonable to assume that under different conditions reaction products other than those observed by the author may be obtained. For example, at lower reaction temperatures it may be possible to isolate intermediate alkylation products of diborane.

Summary

The reactions of diborane with hydrocarbons have been investigated at elevated temperatures using low concentrations of diborane. Under these conditions:

1. The addition of diborane to olefins results in the formation of trialkylborons.
2. A substitution reaction occurs with benzene to form phenylboron compounds.
3. The reactions of diborane with paraffins are complex and involve paraffin chain breakdown and paraffin chain synthesis as well as the formation of boron–carbon bonds.

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[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Spontaneous Ignition of Nickel Carbonyl Vapor. The Ignition of *n*-Butane[1]

BY ELMER J. BADIN, PAUL C. HUNTER AND ROBERT N. PEASE

Earlier papers[2] from this Laboratory have described the spontaneous ignition of zinc dimethyl and of boron triethyl vapors in oxygen, and the oxidation of *n*-butane induced thereby. Similar experiments with nickel tetracarbonyl are here reported.

The apparatus for these experiments was of conventional design.[2] It need only be mentioned that a clean, dry reaction bulb (6.5 cm. diameter) was used for each experiment, and that the bulb was thermostatted at 20°. Nickel carbonyl was obtained through the Matheson Company and fractionated in a nitrogen atmosphere before use (b. p. 43.5°). Oxygen and air were dried before using.

Precise measurements of explosion limits were prevented by the occurrence of long and variable induction periods (up to at least 1000 sec.). Thus, out of 6 experiments on 30 mole % nickel carbonyl in oxygen at 110 to 120 mm. total pressure, explosion occurred almost immediately on admitting the oxygen in two cases; after 30 and 325 seconds in two cases; while there was no explosion in 1000 seconds for two other trials. In another set of 12 experiments on 10% nickel carbonyl in dry air between 150 and 200 mm. total pressure, successes and failures (over 1000 seconds) were spread rather uniformly over the whole pressure range.

The reason for this irreproducible behavior is not clear. In some experiments with long induction periods, a film would form slowly at some point on the surface of the bulb. This could indicate dissociation of the carbonyl, since Mittasch's equilibrium data[3] indicate considerable dissociation at equilibrium even at 20° and 180 mm. A free nickel surface would seem to be ideal as a point from which inflammation could spread. Nevertheless, the formation of a white fog in the body of the gas always immediately preceded explosion, as if the initiating reaction were homogeneous. In this connection it is of interest that Berthelot[4] reported explosions of dry nickel carbonyl–oxygen mixtures at room temperature only if the mixture were abruptly expanded in a buret over mercury, or if the buret were shaken violently. This might suggest ionization due to friction between the mercury and the glass container. Though our mixtures were quiescent at the time of explosion, it is conceivable that an extraneous disturbance is involved. The behavior, however, might be still due to indeterminate differences or non-uniformity in the clean Pyrex surfaces used.

In Table I are reported the lowest pressures at which explosion was observed within 1000 seconds. Minimum values were quite low and only moderately different for oxygen as compared to air,

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(2) E. J. Badin, D. R. Walters and R. N. Pease, THIS JOURNAL, **69**, 2586 (1947); R. S. Brokaw, E. J. Badin and R. N. Pease, *ibid.*, **70**, 1921 (1948).

(3) Mittasch, *Z. physik. Chem.*, **40**, 1 (1902).

(4) Berthelot, *Ann. chim. phys.*, [6] **26**, 555 (1892).