nate in a difunctional, trifunctional and tetrafunctional manner with iron(II) and nickel(II). Although many ligands are theoretically capable of coördinating with varying numbers of donor groups, very few instances of this have actually been observed. With the exception of ethylenediaminetetraacetic acid and its derivatives, pyridinaldazine is believed to be unique in the observed degree of flexibility in its mode of chelation.[6]

(6) The authors suggest use of the term "flexidentate" to denote this flexibility in manner of chelation.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE RESEARCH LABORATORY, OLIN MATHIESON CHEMICAL CORPORATION]

Increased Activity of Silica–Alumina Catalysts[1]

BY H. G. WEISS AND I. SHAPIRO

RECEIVED JANUARY 16, 1958

Modification of the active sites on silica–alumina with diborane results in a marked increase in the activity of the catalyst toward cyclization of acetylene to benzene. Isotope studies show the reaction to be rapid, with no intermediates remaining adsorbed on the surface of the catalyst. The results of several reactions on silica gel, alumina and silica–alumina tend to support the concept of alumina as the Lewis acid site in silica–alumina catalysts.

The structure of silica–alumina catalysts has been studied by a number of investigators,[2–5] who have generally agreed to the acid character of the catalytically active sites. The exact nature of these sites is still the subject of speculation.

The chemical altering of active sites has been used in the attempt to clarify further their structure. In this manner the acidity of silica–alumina has been demonstrated by the decrease in activity observed when chemisorbed quinoline poisons the active sites.[6] Reduced activity toward conversion of cetane also has been reported for silica–alumina in which the active sites have been altered with alkali metal ions.[7] Treatment of silica–alumina with water vapor results initially in an increased activity toward hydrogen exchange with isobutane[8]; however, additional water again decreases the activity. Thus, in general, the chemical treatment of the active sites has resulted in diminished activity of the treated catalysts.

In this Laboratory, modification of active sites on silica–alumina with diborane[9] has produced a catalyst having enhanced activity for the cyclization of acetylene to benzene. In an effort to throw more light on the nature of the active sites on silica–alumina, this reaction has been critically examined.

The polymerization of acetylene has been reported by Pease[10] to be a homogeneous bimolecular reaction. Reaction temperatures are of the order of 400 to 600° and a variety of products is obtained. Taylor[11] has amplified these findings and has shown both the polymerization and hydrogenation of acetylene to be bimolecular. In all experiments reported in the literature the prime requisite for initiation of polymerization of acetylene is high temperature.

When acetylene is exposed to silica–alumina cracking catalyst at room temperatures and subatmospheric pressures, no appreciable reaction is noted. However, when the catalyst is first treated with diborane, a rapid reaction occurs as acetylene is passed through this modified catalyst. One unusual aspect of the catalytic reaction reported here, aside from the obvious increase in rate of polymerization, is that only one volatile product, benzene, is obtained from the reaction. Experiments with acetylene and acetylene-d_2 have shown that the polymer-terminating reactions (ring closure) must be rapid, since no intermediate products are found in the catalyst surface.

That boron hydrides have catalytic effects on hydrocarbon polymerization is well known.[12] However, the fact that polymerization of acetylene does not occur on diborane-treated silica gel or alumina is evidence that the hydride itself is not the catalytic agent in the reactions reported here.

Experimental

Reagents. 1. Silica–Alumina.—Houdry Process Corporation synthetic silica–alumina cracking catalyst Type M-46 was heated to 275° *in vacuo* for several hours prior to use.

2. Diborane.—Diborane was prepared in the conventional manner[13] and was purified by low temperature fractionation in the vacuum rack prior to each experiment.

3. Acetylene.—Matheson Co. acetylene was fractionated at low temperature prior to use.

4. Deuteroacetylene.—C_2D_2 was prepared from calcium carbide and deuterium oxide (Stuart Oxygen 99.5% D_2O). Analysis by mass spectrometry showed all samples of deuteroacetylene to contain at least 99.3% D.

5. Silica Gel.—The silica gel used in these experiments has been described previously.[14]

6. Alumina.—Houdry Process Corporation hard alumina catalyst was heated to 275° *in vacuo* for several hours prior to use.

Procedure.—All reactions described here were carried

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(1) Presented at the 132nd Meeting, American Chemical Society, New York, N. Y., September, 1957.

(2) C. L Thomas, *Ind. Eng. Chem.*, **41**, 2564 (1949).

(3) J. D,. Danforth, *J. Phys. Chem.*, **59**, 564 (1955).

(4) T. J. Gray, *ibid.*, **61**, 1341 (1957).

(5) R. G. Haldeman and P. H. Emmett, THIS JOURNAL, **78**, 2917 (1956).

(6) G. A. Mills, E. R. Boedeker and A. G. Oblad, *ibid.*, **72**, 1554 (1950).

(7) J. D. Danforth and D. F. Martin, *J. Phys. Chem.*, **60**, 422 (1956).

(8) R. G. Haldeman and P. H. Emmett, THIS JOURNAL, **78**, 2922 (1956).

(9) I. Shapiro and H. G. Weiss, *J. Phys. Chem.*, **57**, 219 (1953).

(10) R. N. Pease, THIS JOURNAL, **51**, 3470 (1929).

(11) H. A. Taylor and A. Van Hook, *J. Phys. Chem.*, **39**, 811 (1935).

(12) D. T. Hurd, "Chemistry of the Hydrides," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 87.

(13) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, THIS JOURNAL, **74**, 901 (1952).

(14) I. Shapiro and I. M. Kolthoff, *J. Phys. Colloid Chem.*, **52**, 1020 (1948).

out in high vacuum apparatus. The catalyst was contained in a Pyrex reactor between fritted discs. The reactor, which was detachable for filling, comprised part of an all glass circulating system. Reactants were condensed into the system by means of a liquid nitrogen trap and were warmed to room temperature prior to exposure to the catalyst. The pressure changes of the system were followed by means of a mercury manometer. Temperature of the bed was obtained by means of a five-junction thermocouple connected to a Brown Electronic Recorder. Circulation of gases was accomplished with an all glass, magnetic drive, reciprocating pump. All analyses were made using a Consolidated Electrodynamics Corporation Mass Spectrometer, Model No. 21-103, operated at 70 volts ionizing potential. The preparation of the modified catalyst and subsequent exposure to acetylene is the same as that described previously.[15]

Results

Circulation of acetylene at room temperature through a silica–alumina bed results in a slight decrease in pressure of the system. The temperature of the catalyst bed rises slightly above room temperature (*ca.* 2–3°) during circulation and falls to room temperature after the materials are condensed. A trace quantity of product, identified as benzene, is obtained from the reaction.

When diborane is circulated through the catalyst bed, either before or after circulation of acetylene, a small rise in pressure of the system is observed. The catalyst bed temperature rises slightly but rapidly drops to room temperature. No condensable products are found, but hydrogen is produced in a ratio of 2 moles hydrogen per mole diborane consumed. Hydrolysis of the catalyst surface after removal of gaseous diborane from the system yields four additional moles of hydrogen. Thus the remaining hydride hydrogen atoms of diborane are accounted for by hydrolysis.

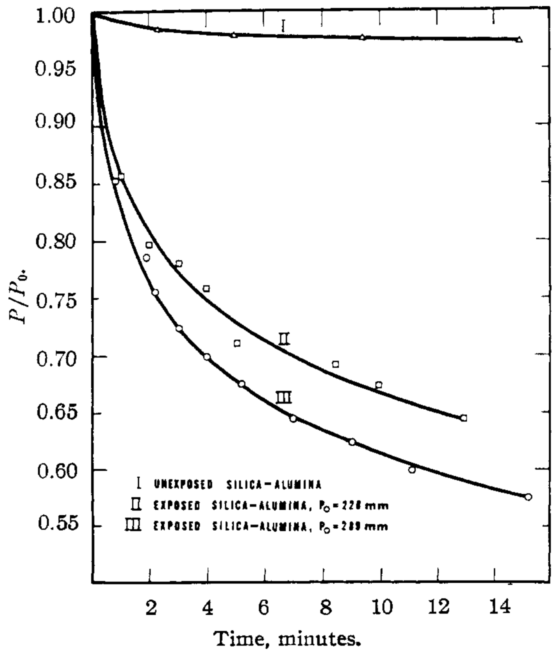

Fig. 1.—Effect of diborane pretreatment of catalyst on relative rate of pressure change.

Circulation of acetylene through diborane-treated silica-alumina results in a rapid reaction in which benzene is formed as the product. The increased rate of cyclization of acetylene on the diborane-exposed silica–alumina is shown by three phenomena. The first, an increased rate of relative pressure change in the system, is shown in Fig. 1. The second, rapid heating of the catalyst bed on exposure to acetylene, is shown in Fig. 2. Curve I, Fig. 1, shows the relative decrease in pressure of the system when acetylene is circulated through the unaltered silica–alumina. This run corresponds to temperature curve I shown in Fig. 2. Curves II and III in Figs. 1 and 2 show pressure and temperature curves for reactions on diborane-treated catalyst. The only difference in these two runs was the initial pressure of acetylene in the system. Had the size of the catalyst bed or the pumping speed for acetylene been changed, other curves displaced from the ones shown in Figs. 1 and 2 would have been obtained. The third phenomenon observed is immediate discoloration of the catalyst bed.

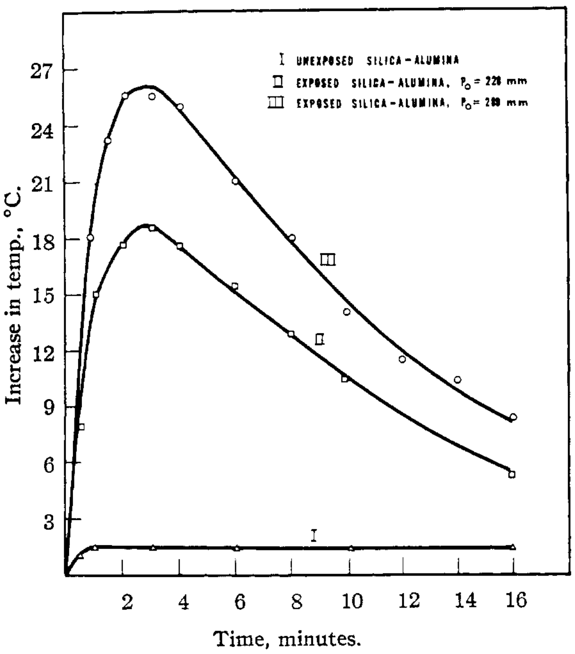

Fig. 2.—Temperature variations in catalyst bed on exposure of C_2H_2 before and after diborane exposure.

Hydrolysis of the diborane-exposed catalyst reduced the catalyst activity to that observed on untreated silica–alumina.

The treatment of a sample of diborane-exposed catalyst with a small quantity of acetylene-d_2 resulted in the formation of benzene-d_6. The benzene-d_6 so obtained contained the same ratio of hydrogen impurity as the initial acetylene-d_2. Subsequent circulation of acetylene over the catalyst without heat treatment between exposures gave benzene plus a trace of benzene-d_6. No benzenes of intermediate deuterium content were obtained.

When mixtures of acetylene and acetylene-d_2 were circulated through the catalyst, the distribution of hydrogen and deuterium in the benzene formed was almost statistical based on the initial H–D ratio. The unconverted acetylene and acet-

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(15) I. Shapiro and H. G. Weiss, This Journal, **79**, 3294 (1957).

ylene-d_2 also contained statistically distributed hydrogen and deuterium.

No decrease in pressure of the system was noted when acetylene was circulated through silica gel, either with or without previous diborane treatment. Neither were there any heat effects nor discolorations of the catalyst observed.

Some acetylene disappeared and the catalyst rapidly became dark in color when acetylene was circulated through diborane-treated alumina. No further reduction of pressure was observed, however, on continued circulation of acetylene through the catalyst; no products other than acetylene were recovered at room temperature. Upon heating the catalyst *in vacuo*, acetylene and a trace of benzene were recovered.

Discussion

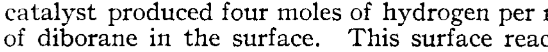
Bound Water in Silica–Alumina.—The surface reaction observed when silica–alumina cracking catalyst is exposed to diborane is the same as that previously reported for silica gel.[9] Hydrogen and diborane measurements show that the ratio of hydrogen formed to diborane consumed on exposure to silica–alumina is 2:1. This value indicates that diborane reacts as BH_3 with the "bound" water in the catalyst, eq. (1). The hydride activity

$$>M—OH + BH_3 \longrightarrow >M—OBH_2 + H_2 \quad (1)$$

of the solid is shown by hydrolysis of the diborane-exposed silica–alumina with water vapor. The hydrolysis reaction produces the equivalent of four moles hydrogen per mole of diborane on the surface. Thus, the 6 to 1 ratio of hydrogen to diborane expected from hydrolysis of the gaseous hydride[16] is obtained. Since the "bound" water in the silica–alumina used in these experiments is of the order of one per cent., it can be seen that the increased activity of the catalyst from exposure to diborane is due to relatively small concentrations of boron hydride on the surface.

Rate of Cyclization of Acetylene.—The small rise in temperature which is obtained when acetylene is circulated through the untreated catalyst is interpreted as heat of cyclization of acetylene. The increased rate of reaction and the rapid temperature rise obtained on the diborane-exposed catalyst are apparently related to one another, and it is reasonable to assume that the increased rate may in part be due to temperature changes. The fact that an increased rate of reaction is observed even after the modified catalyst has cooled to room temperature is evidence that the boron-treated surface is catalytically active in promoting cyclization.

The hydrolysis of the modified silica–alumina catalyst produced four moles of hydrogen per mole of diborane in the surface. This surface reaction can be written as



$$>M—OBH_2 + 2H_2O \longrightarrow >M—O—B\begin{matrix}OH\\OH\end{matrix} + 2H_2 \quad (2)$$

where the hydride ion is completely hydrolyzed. In this form the catalyst activity toward acetylene is approximately the same as on the untreated silica-alumina.

Mechanism of Cyclization.—Initial exposure of the diborane-treated silica–alumina catalyst to acetylene imparts a violet color to the catalyst. In order to determine whether this color might be caused by an intermediate product of the reaction, acetylene and acetylene-d_2 were circulated alternately through the catalyst. It was found that only mixtures of benzene and benzene-d_6 were obtained as products; no partially deuterated benzenes were formed. Identical results were obtained when the catalyst bed was heated to drive off absorbed benzene prior to exposure to acetylene-d_2. It appears, therefore, that no reactive intermediates remain adsorbed on the surface of the catalyst after evacuation at room temperature. From these reactions it is obvious that no exchange of hydrogen takes place between acetylene and benzene-d_6 or between benzene and benzene-d_6 in the presence of the catalyst at room temperature. The source of color on the catalyst still is being investigated.

That the hydride hydrogen does not enter into the reaction is shown by modifying the silica–alumina by treatment with diborane and then exposing the catalyst to a trace of acetylene-d_2. The resultant product contains deuterium in the same quantity as in the initial acetylene-d_2. Hydrolysis of the catalyst using water vapor after exposure to C_2D_2 produced only H_2; no HD or D_2 species could be detected by mass spectral analysis. Since no hydrogen enters the benzene, it is apparent that hydrogen does not add to acetylene in the reaction. If such were the case, exchange of hydrogen between borane and acetylene would be predicted.

The hydrogen–deuterium exchange between acetylene and acetylene-d_2 is rapid on either unexposed or diborane-modified silica–alumina. Species containing all possible hydrogen–deuterium combinations are found in the benzene prepared from such a mixture. The distribution of species in the benzene is a statistical distribution and thus indicates that the rate of exchange is faster than the rate of cyclization. Since exchange between acetylene and acetylene-d_2 occurs on either catalyst while cyclization occurs only on the diborane-modified catalyst, it appears that different sites are active for the two reactions. Thus, the exchange may be effected by adsorption on the bulk of the solid, while cyclization requires chemisorption at "borane sites." The difference in heat effects which are obtained by exposure of diborane to the unexposed and exposed catalysts, tends to support such a mechanism.

Nature of the Active Sites.—Although it is apparent that adsorption at "borane sites" is required for the cyclization reaction, it is interesting to speculate whether attachment occurs directly on boron or on adjacent sites. The known affinity of borane for electrons would appear to be sufficient to cause attachment at these points. However, absence of hydrogen–deuterium exchange between hydride and acetylene-d_2 indicate the contrary. The lack of activity on diborane-treated silica gel is additional evidence that borane itself is not sufficient for catalysis.

The large amount of heat liberated upon exposure

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(16) H. G. Weiss and I. Shapiro, THIS JOURNAL, **75**, 1221 (1953).

of acetylene to the diborane-treated alumina suggests that the alumina plays a part in the cyclization reaction. If this is true, it would tend to substantiate the Danforth[3] concept of alumina atoms as the Lewis acid sites in silica–alumina. Substitution of BH_2 for hydrogen in Al–OH on the silica–alumina surface may result in an increase in acidity of the Lewis acid site due to the borane electron deficiency. In such a case induced polarization of the acetylene molecule would be sufficient to initiate the cyclization reaction. The results of other chemical reactions, which may further elucidate the structure of silica–alumina catalysts, will be reported later.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Fluorocarbon–Phosphinoborines and Related Chemistry[1]

BY ANTON B. BURG AND GOTTFRIED BRENDEL

RECEIVED DECEMBER 16, 1957

The new compound $(CF_3)_2PF$ (m.p. −150°; b.p. −12°) reacts with B_2H_6 at 0° or higher to produce H_2, $(CF_3)_2PH$, BF_3 (also at 0° a partially fluorinated borine), and the new $[(CF_3)_2PBH_2]_3$ (air-stable; m.p. 30.5°; b.p. est. 177°; slow decomp. at 200° converting all B to BF_3). The highly volatile complex $(CF_3)_2PF \cdot BH_3$ is present during the reaction. The reaction between $(CF_3)_2PH$ (m.p. −137°; b.p. 0.9°) and B_2H_6 also produces $[(CF_3)_2PBH_2]_3$; and it was possible to isolate also a trace of $[(CF_3)_2PBH_2]_4$ (m.p. 116°; slightly volatile). Dimethyl ether catalyzes this reaction, and also attacks the reactants to form $B(OCH_3)_3$ and the recently-discovered $CH_3P(CF_3)_2$ (m.p. −105°; b.p. 37.5°). Aqueous HCl attacks $[(CF_3)_2PBH_2]_3$ only very slowly at 150°; methanol–HCl is more effective at 85°, producing H_2, $(CF_3)_2PH$, $B(OCH_3)_3$ and CH_3Cl quantitatively. Aqueous NaOH at room temp. attacks $[(CF_3)_2PBH_2]_3$, forming $3HCF_3$. The ring-stability of $[(CF_3)_2PBH_2]_3$ and $[(CF_3)_2PBH_2]_4$ probably is enhanced by delocalization of B–H electrons for supplementary B–P bonding.

The high stability and relatively inert chemical character of the compound $[(CH_3)_2PBH_2]_3$ (and higher polymers) would accord with the hypothesis that the P–B dative sigma bond is supplemented by an unusual type of pi bonding wherein B–H bonding electrons are partially assigned to phosphorus orbitals above the $3sp^3$ system.[2] This idea seems to gain support from the observation that the HBH and BPB bond angles are near 120° and the PBP angle near 112°,[3] all wider than the usual tetrahedral angle. Any such supplementary B–P bonding should gain importance if the groups on phosphorus were more electronegative: then the sigma bonding would be weaker because of the decreased electron-donor bonding power of phosphorus; but the inductive effect of an increased assignment of B–H electrons to phosphorus would partially compensate for such a weakening of the sigma bonds.

These ideas are supported by the stable existence of the new phosphinoborine low polymers $[(CF_3)_2PBH_2]_3$ and $[(CF_3)_2PBH_2]_4$, which we have made by the reaction of diborane with either $(CF_3)_2PF$ or $(CF_3)_2PH$. They are slightly volatile solids which are observably decomposed as the temperature approaches 200°—in contrast to 400° for the incipient decomposition of $[(CH_3)_2PBH_2]_3$. However, even stability up to 200° would be surprising if the $(CF_3)_2PBH_2$ units were associated only by P–B sigma dative bonding, for the CF_3-substituted phosphines are very weak bases; for example, no evidence could be found for the existence of such borine adducts as $(CF_3)_3PBH_3$ or $(CF_3)_2PH \cdot BH_3$, and $(CF_3)_2PF \cdot BH_3$ apparently exists but is very unstable. The P–B dative bond in $(CF_3)_2PF \cdot BH_3$ doubtless gains strength through the inductive effect of a partial assignment of B–H electrons to weak B to P pi bonds. The same effect would account for the otherwise unexpected existence of $PF_3 \cdot BH_3$.[4] A similar but wider-range delocalization of B–H electrons in the $(PB)_n$ rings would help to explain the stability of the trimer and tetramer of $(CF_3)_2PBH_2$.

The $(CF_3)_2PF$–B_2H_6 reaction converts some of the diborane to boron trifluoride; and at 0° there was evidence of the formation of a very unstable fluoroborine intermediate—probably HBF_2. The disproportionation of this fluoroborine at room temperature apparently is fast and irreversible, for there was no evidence for its presence in the $(CF_3)_2PF$–B_2H_6 reaction at 22°, and no reaction could be observed when diborane and boron trifluoride were left together for long periods of time.

The $(CF_3)_2PH$–B_2H_6 reaction required an accelerator, and dimethyl ether proved to be effective. Very pure $[(CF_3)_2PBH_2]_3$ and $[(CF_3)_2PBH_2]_4$ could be obtained by this method, because B–F bonds were absent. However, the yields were only moderate because the ether was split, with formation of methyl borate and methylation of some of the phosphine to form the interesting compound $CH_3P(CF_3)_2$. This substance has been reported also as a component of a mixture obtained by the reaction of methyl iodide with tris-trifluoromethylphosphine.[5] In the present work it was not difficult to obtain a nearly pure sample because similarly volatile impurities were absent.

Experimental Part

I. Preliminary Syntheses

The New Compound Bis-trifluoromethyl-fluorophosphine.—The iodophosphine $(CF_3)_2PI$ was made by known

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[1] This research was supported by the United States Air Force under Contract AF 33(616)-2743, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] A. B. Burg and R. I. Wagner, THIS JOURNAL, **75**, 3872 (1953).

[3] W. C. Hamilton, *Acta Cryst.*, **8**, 199 (1955).

[4] R. W. Parry and T. C. Bissot, THIS JOURNAL, **78**, 1524 (1956).

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