vapor pressure of the compounds in question. (Model B Infra-Red Spectrophotometer, Baird Associates Inc., Cambridge, Mass.) The spectra of the pure compounds compare favorably with those found by Hobbs.[5] They indicate that the absorption band at 750 cm.$^{-1}$ is characteristic of the mixed halide.

The mass spectra of these compounds will be reported in another publication.

AMES, IOWA

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[5] W. E. Hobbs, "The Infrared Spectrum of Chromyl Fluoride," U. S. A.E.C. Report No. K-1325, July, 1957.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The Complexes of Pyridinaldazine with Iron(II) and Nickel(II). II

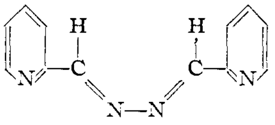
BY WILMER J. STRATTON AND DARYLE H. BUSCH

RECEIVED JANUARY 28, 1958

Pyridinaldazine (PAA) has been shown to react with iron(II) and nickel(II) to form compounds of the type $[M_2(PAA)_3]X_4$ which are believed to involve a dinuclear cation, with each ligand coördinated in a tetrafunctional manner. In solution the iron(II) compound has been shown to dissociate one metal ion, approaching an equilibrium according to the equation $[Fe_2(PAA)_3]^{+4} \rightleftarrows [Fe(PAA)_3]^{+2} + Fe^{+2}(aq)$. Each ligand is then coördinated in a difunctional manner. Evidence for the $[Fe(PAA)_3]^{+2}$ ion has been obtained from a continuous variations study of the absorption spectrum and from a mole ratio study of the magnetic susceptibility. Preliminary kinetic data for the above reaction were obtained from both absorption spectra and magnetic susceptibility data, and the equilibrium constant has been evaluated. A further equilibrium has been shown to exist according to the equation $2[Fe(PAA)_3]^{+2} + Fe^{+2}(aq) \rightleftarrows 3[Fe(PAA)_2]^{+2}$. The rate at which this second process occurs is much slower than that associated with the first reaction.

Introduction

The preparations of the complexes of iron(II) and nickel(II) with 2-pyridinaldazine (structure I) have been described in an earlier paper.[1] Compounds of the type $[M(PAA)_2]X_2$ can be prepared by the addition of pyridinaldazine (PAA) to an aqueous solution of the metal salt, followed by heating on a steam-bath for a few minutes. Compounds were prepared in which M was iron(II) or nickel(II) and X was the iodide, perchlorate or fluoroborate ion. These compounds were of the expected type in which each ligand is presumed to coordinate in a tridentate manner, with one of the azine nitrogens being used in coördination (structure II). The iron compounds were found to be essentially diamagnetic, and conductivity data were in agreement with the formulation of the compounds as electrolytes of the MX_2 type.



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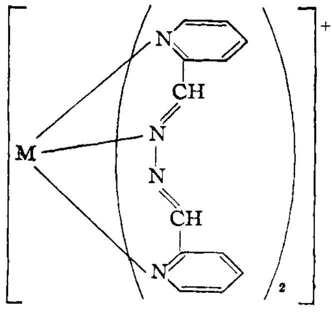

II

If, however, solutions of ligand and metal ion are kept at room temperature and crystallized by cooling fairly rapidly, compounds with the empirical formula $M_2(PAA)_3X_4$ are obtained. The iron compounds were found to be diamagnetic in the solid state, indicating that both metal ions are involved in coördination. The structure of these $M_2(PAA)_3X_4$ compounds presents an intriguing problem, and this paper is devoted to some studies which have been undertaken in an effort to elucidate their nature. The authors have previously suggested that the structures of these substances probably involve a dinuclear cation, $[M_2(PAA)_3]^{+4}$. Magnetic susceptibilities of the iron compounds, conductivity data and the existence of salts with anions of poor coördinating ability all support this hypothesis. Conductivity data in 10^{-3} M solutions were interpreted as representing the MX_4 electrolyte type with a large unsymmetrical cation, but it was pointed out that the same data would also support a structure involving free metal salt, $[M(PAA)_3]X_2 \cdot MX_2$. The diamagnetism of the crystalline iron compounds seemed to rule out the latter structure, however.

Experimental

Spectrophotometric Measurements.—All measurements of spectra in the visible region were carried out with a Cary Recording Spectrophotometer, Model 10, using matched one centimeter quartz cells.

Magnetic Measurements.—The magnetic measurements were carried out with a Gouy type balance, using a Consolidated Engineering Corporation magnet and power supply which were operated at a field strength of approximately 8000 gauss. The study of susceptibility as a function of mole ratio was made using a balance of 0.1 mg. sensitivity, while the study of susceptibility as a function of time was carried out with a balance of 0.01 mg. sensitivity. Both studies used 25 ml. of solution in a tube of 19 mm. diameter fitted with a standard taper cap.

Results

Visible spectra are shown in Fig. 1 for $Fe_2(PAA)_3I_4$ (curve A, 1×10^{-4} M), and $[Fe(PAA)_2]I_2$ (curve B, 2×10^{-4} M). Curve C was obtained using the solution of $Fe_2(PAA)_3I_4$ (10^{-4} M) after it had stood for 70 hr. and is assumed to represent an equilibrium mixture of complexes. A spectrum similar to C may be obtained by allowing a dilute solution of $Fe(PAA)_2I_2$ to reach equilibrium.

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[1] W. J. Stratton and D. H. Busch, THIS JOURNAL, **80**, 1286 (1958).

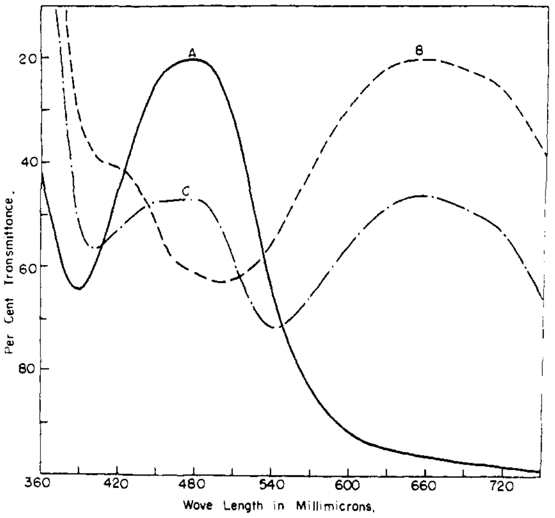

Fig. 1.—Absorption spectra of iron(II)-pyridinaldazine solutions in the visible region.

Figures 2 and 3 show the manner in which the spectra of the iron–pyridinaldazine solutions change with time. The spectrum obtained by dissolving a sample of the crystalline red compound having the empirical formula $Fe_2(PPA)_3I_4$ (10^{-4} M) and carrying out the measurements quickly is shown in the dotted curve of Fig. 2. The absorption maximum occurs at about 510 mμ. If this same solution is allowed to stand several hours, the color gradually changes from red to orange, and the spectrum becomes as shown in the solid curve of Fig. 2, with an absorption maximum at about 475 mμ. By recording the spectrum at two-minute intervals and plotting the wave length of the point of maximum absorption as a function of time, a graph was obtained which then was extrapolated to a wave length of approximately 522 mμ at zero time. (The data for this were taken over a 20 minute period). This change is shown in another way in Fig. 3, where absorption is plotted as a function of time at 475 mμ. It is observed that the absorption increases rapidly and then levels off to an equilibrium value. At 22°, this reaction is 99% complete in 2 hr. After a relatively long period of time (not shown), the absorption at 475 mμ decreases slowly, with simultaneous increase in absorption at 650 mμ, corresponding to conversion to the blue[$Fe(PAA)_2]I_2$) compound. This second process occurs much more slowly, having gone less than 3% toward equilibrium when the first reaction is 99% complete.

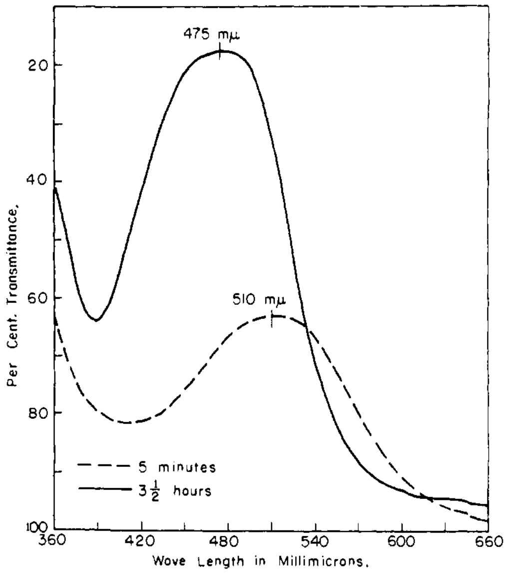

Fig. 2.—Absorption spectra in the visible region of $Fe_2(PAA)_3I_4$ in 10^{-4} molar solution at 5 minutes and 3.5 hours after mixing.

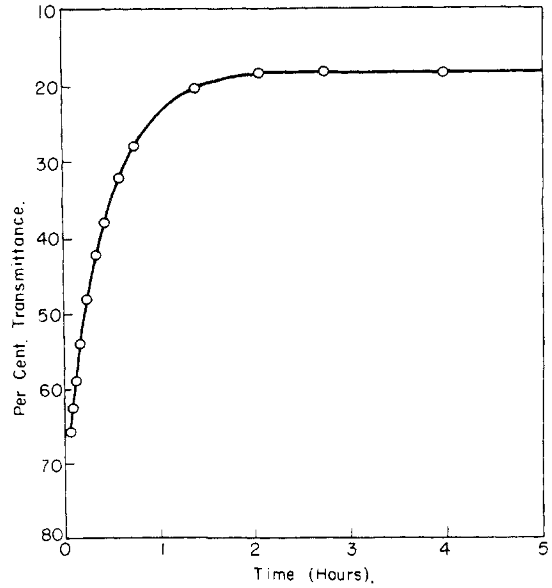

Fig. 3.—Time dependence of optical density in $1 \times 10^{-4}M$ $Fe_2(PAA)_3I_4$, 22°, λ 475 mμ.

In order to obtain the ratio of ligand to metal in the dissolved complex, a continuous variations study[2] was carried out. Stock solutions of iron(II) sulfate and pyridinaldazine, both 5×10^{-4} M, were prepared and mixed in various ratios. Because of the manner in which the spectra change with time (as discussed above), the solutions were allowed to stand 4 hr. after mixing before recording their spectra. The results of this study, using λ 480 mμ are shown in Fig. 4. It is observed that, in approximately 10^{-4} M solutions, the principal species present at equilibrium has three moles of ligand associated with one mole of metal salt.

It was felt desirable to determine the ligand-to-metal ratio at considerably higher concentrations than 10^{-4} M in order to minimize the effect of the solvent in the determination of the product formed. Although the spectrophotometric method cannot be used conveniently at higher concentrations, the determination of magnetic susceptibility as a function of mole ratio was found to be a suitable method for this determination. Solutions were prepared containing 0.072 M iron(II) sulfate and varying amounts of pyridinaldazine, using approximately 17% by weight of ethanol to keep the pyridinaldazine in solution. The magnetic susceptibilities of

[2] W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

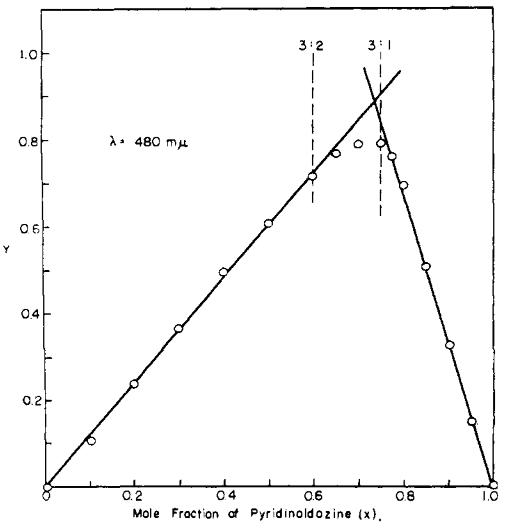

Fig. 4.—Continuous variations graph of pyridinaldazine (x) and iron(II) ($1 - x$) in 10^{-4} M solutions, 4 hours after mixing.

the solutions were determined, and the gram susceptibilities of the ferrous ion were calculated for each solution using the following equation, where χ_{soln}, χ_s, χ_{PAA}, $\chi_{\text{Fe}^{++}}$ and $\chi_{\text{SO}_4^=}$ represent the gram susceptibilities of the solution, solvent, ligand, ferrous ion and sulfate ion, respectively, and F_s, F_{PAA}, $F_{\text{Fe}^{++}}$ and $F_{\text{SO}_4^=}$ represent the weight fractions of solvent, ligand, ferrous ion and sulfate ion, respectively.

$$\chi_{\text{Fe}^{++}} = \frac{\chi_{\text{soln}} - F_s\chi_s - F_{\text{PAA}}\chi_{\text{PAA}} - F_{\text{SO}_4^=}\chi_{\text{SO}_4^=}}{F_{\text{Fe}^{++}}}$$

Knowing the gram susceptibilities of water[3] and ethanol,[4] the gram susceptibility of the solvent was calculated to be -0.724×10^{-6}. The molar susceptibility of iron(II) was then calculated by multiplying the experimentally determined susceptibility of Fe^{++} by the atomic weight. The gram susceptibility of pyridinaldazine, determined in the course of the present work, is -0.28×10^{-6}, and the molar susceptibility of the sulfate ion was taken as -40×10^{-6}.[5] The results are shown in Fig. 5. It is observed that the susceptibility drops from a value of 11×10^{-3} (that of the hydrated ferrous ion) to zero when three ligand molecules are present for each ferrous ion. These results indicate that three ligand molecules are coördinated with each ferrous ion in a diamagnetic complex.

Parallel to the change in absorption spectra with time, the magnetic susceptibilities of solutions of the complexes also have been observed to exhibit a time dependence. A sample of $\text{Fe}_2(\text{PAA})_3\text{I}_4$ was dissolved in 0.01 M solution, and the susceptibility of the solution was determined at various time intervals. The results shown in Fig. 6 were obtained, after correcting for the diamagnetic susceptibilities of water, ligand and anion by the method used previously. It is observed that the susceptibility increases from 3.17×10^{-3}, 14 minutes after dissolving, to an equilibrium value of 5.84×10^{-3}, which corresponds to 3.8 Bohr Magnetons per two iron(II) ions. The curve may be extrapolated to zero time, giving a result not inconsistent with the observed susceptibility of $\text{Fe}_2(\text{PAA})_3\text{I}_4$ in the solid state.

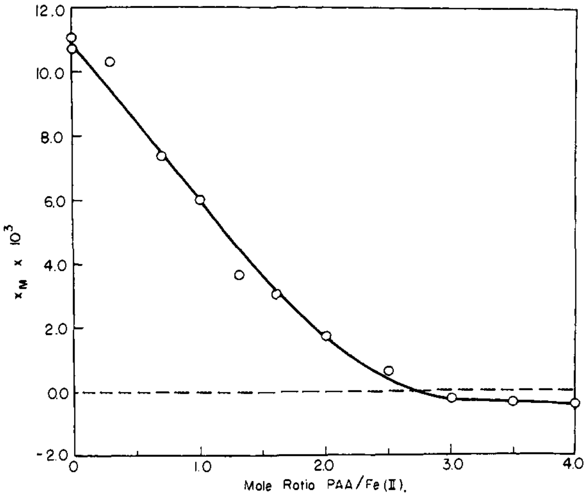

Fig. 5.—Molar magnetic susceptibility of iron(II) *vs.* mole ratio of pyridinaldazine to iron(II), 0.072 M FeSO_4.

Discussion

It has been shown by means of a spectrophotometric continuous variations study that the principal species present in 10^{-4} M solution is $[\text{Fe(PAA)}_3]^{+2}$. The same species also has been found from a study of magnetic susceptibility in solutions 100 times more concentrated. This would appear to be inconsistent with the evidence presented in the previous paper[1] for the existence of dinuclear cations of the type $[\text{M}_2(\text{PAA})_3]^{+4}$. Most significantly it appears to contradict the diamagnetism of the iron compounds which contain two metal ions and three ligand molecules. It is to be noted that the solution magnetic study was carried out at a concentration similar to the concentrations used in the preparative work; thus, concentration differences cannot explain the paradox.

The answer to this apparent anomaly is believed to lie in the unusual time dependences of absorp-

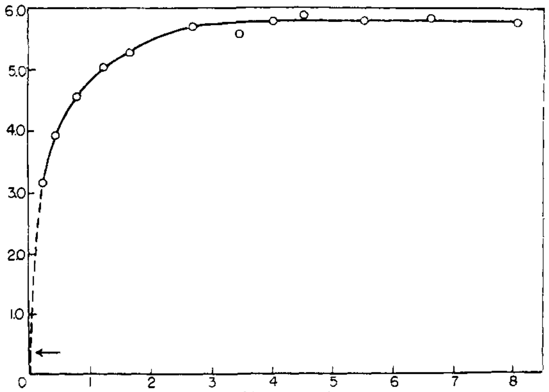

Fig. 6.—Time dependence of molar magnetic susceptibility of iron(II) in 0.01 M $\text{Fe}_2(\text{PAA})_3\text{I}_4$, 30°, arrow indicates susceptibility in the solid state.

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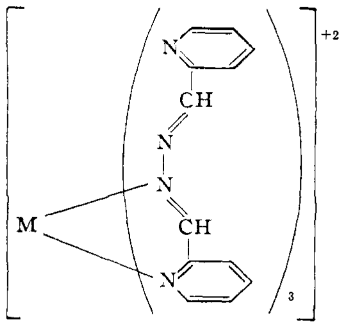
[3] P. W. Selwood, "Magneto Chemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 86.

[4] "International Critical Tables," Vol. VI, McGraw-Hill Book Co., New York, N. Y., p. 361.

[5] Selwood, ref. 3, p. 78.

tion spectra and magnetic susceptibility as reported above. The shift in wave length is interpreted to indicate a change in the nature of the chemical species present. The continuous variations study which was carried out four hours after mixing the solutions indicates that the equilibrium species in dilute solutions is the 3:1 cation. A complex cation of this type is quite likely in view of the structure of the ligand. The probable structure is shown below (structure III).



III

Since the empirical formula of the solid compound clearly indicates that three ligands are associated with two metal ions, it seems reasonable that a dinuclear cation might actually be the substance initially present in solution. This then loses one metal ion, forming the 3:1 cation and free metal salt. The slight shift in the wave length of absorption would be consistent with this dissociation process. (Efforts to obtain evidence for the 3:2 species at short time intervals by the method of continuous variations have given inconclusive results.)

The observed change in magnetic susceptibility with time gives further and more direct evidence for this dissociation process. In solution the gradually increasing paramagnetism corresponds to slow dissociation of one iron ion from the dinuclear cation, the process envisioned being described by the equation

$$[Fe_2(PAA)_3]^{+4} \rightleftharpoons [Fe(PAA)_3]^{+2} + Fe^{+2}(aq)$$

An equilibrium constant for this process may be calculated from the magnetic data, using the familiar formula

$$K_{eq} = \frac{Mx^2}{(1 - x)}$$

where M is the molar concentration of $[Fe_2(PAA)_3]^{+4}$ and x is the degree of dissociation into $[Fe(PAA)_3]^{+2}$ and hydrated ferrous ion. From the magnetic data given above, the extent of dissociation at 0.01 M is 0.53; the value of the equilibrium constant is therefore approximately 6×10^{-3}. This dissociation constant is unusually large for complexes of iron(II) with aromatic ammines and probably arises as a consequence of coulombic repulsion between the two metal ions, as well as from the steric strain involved in a molecule of this complexity.

The proposed formulation for the 3:2 compounds as $[M(PAA)_3]X_2{\cdot}MX_2$ was previously ruled out in favor of the formulation as a dinuclear cation.[1] It now appears that both structures are correct, the latter existing in the solid state and the former being formed from it in solution. It is to be noted that conductivity data for 10^{-3} M solutions could not be used to distinguish between the two possibilities, and one may now conclude that the solutions being studied were, in fact, mixtures, corresponding to partial dissociation of the dinuclear cation into the 3:1 complex cation and hydrated ferrous ion.

In addition to the equilibrium mentioned in the preceding discussion, a further equilibration occurs at long times in accordance with the equation

$$2[Fe(PAA)_3]^{+2} + Fe^{+2}(aq) \rightleftharpoons 3[Fe(PAA)_2]^{+2}$$

This second process has been identified unambiguously by spectral measurements (Fig. 1). The two processes are easily distinguished because of the great difference in the rates of equilibration.

A reasonable structure for the $[M_2(PAA)_3]^{+4}$ ion is shown in structure IV and in Fig. 7.

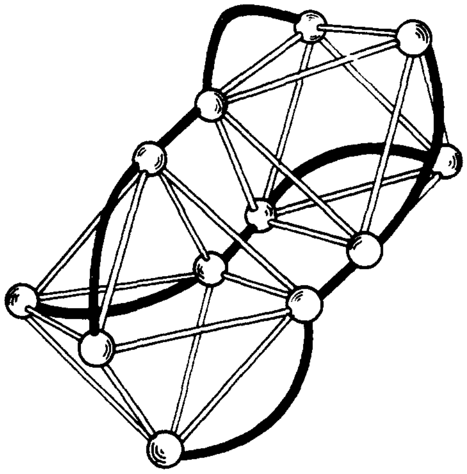
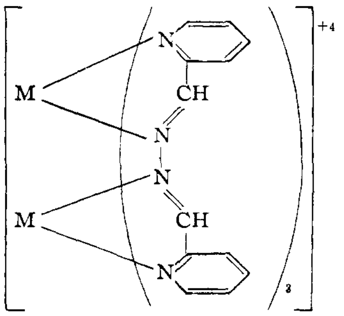


Fig. 7.—Proposed structure for $[M_2(PAA)_3]^{+4}$.



IV

The octahedral configurations about each metal ion are depicted in Fig. 7 by the open lines, with the shaded lines indicating the ligand molecules. (The two metal ions at the centers of the octahedra are not shown.) Each of the three ligand molecules is presumed to coördinate in a bidentate manner with each of the two metal ions; thus the two octahedra are joined by three nitrogen–nitrogen bridges. It is seen from the drawing that the octahedra have a pair of adjacent, parallel faces, separated by the N–N bond distance.

Pyridinaldazine has thus been shown to coördinate 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. Hàldeman 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).