

Boron Hydride on Polymeric Matrix

INTRODUCTION

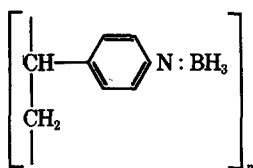
As a result of the successful utilization of catalysts formed by a metal bound to a polymeric matrix, the study of such systems which can find application for the synthesis of organic compounds has received increasing attention.

Among others, we can mention complexes of poly(vinyl alcohol) and polyacrylonitrile with platinum and palladium¹ or polyamides (nylon 3) with platinum,² which are used as catalysts for selective hydrogenation reactions, and complexes of poly(vinylpyridine) (at various degrees of crosslinking with divinylbenzene) with cobalt-carbonyl, as catalysts for hydroformylation reactions.

In the present work, we have synthesized a borane-poly(vinylpyridine) complex and determined its properties, keeping in mind the possibility of its utilization for the hydrogenation of many classes of organic compounds, such as aldehydes, ketones, etc.

Much emphasis has been given recently to the chemistry of boron hydrides, mainly because of their high reactivity with organic compounds. Diborane can be used in many ethereal solvents, such as diglyme and THF, but precautions must be taken owing to its gaseous state at room temperature.

It is known that borane easily reacts with tertiary amines and pyridine,^{3,4} giving rise to quite stable compounds of the type —N—BH_3 . We can therefore assume that an analogous reaction takes place with P-4VP, and we can tentatively assign to the reaction product the following formula:



EXPERIMENTAL

Materials

Diborane was generated as described by Brown,⁵ and solutions of borane in THF were prepared and standardized.

Tetrahydrofuran (THF) was purified according to the method of Fever and Savides.⁶

The vinylpyridine monomer (Merk-Schuchardt, purity greater than 95%) was distilled over CaH_2 in an inert atmosphere; bp $64^\circ\text{C}/15$ mm Hg (lit.⁷ $65^\circ\text{C}/15$ mm Hg).

CH_2Cl_2 was distilled over molecular sieves.

Polymerization Procedure

Commercially available samples usually contain about 2.7% water; therefore a sample was prepared by modification of the method in the literature.⁷ 4-Vinylpyridine (1.39M) and benzoyl peroxide (0.0105M) were dissolved in toluene under nitrogen; the inert atmosphere was maintained during the entire procedure in order to assure anhydrous conditions. The polymer gradually precipitates as the reaction proceeds. The final product was filtered, washed many times with anhydrous benzene and *n*-hexane, and stored under nitrogen.

The intrinsic viscosity of the polymer in alcohol is 1.11 at 25°C ; it corresponds to a $\overline{PM}_v = 229,000$, according to the relationship $[\eta] = 2.5 \times 10^{-4} \times \overline{PM}_v^{0.69}$.

X-Ray analysis indicated an amorphous structure, in agreement with the data in the literature.⁸ The UV absorption spectrum shows a maximum at 225 nm. The analytical data and the IR spectrum are the expected ones for a poly(4-vinylpyridine).

Synthesis of Borane-P-4VP Complex

P-4VP (0.4950 g = 4.71 mmoles) was dissolved in 400 ml CH_2Cl_2 . To this solution, 20 ml 2.22M borane (14.83 mmoles) in THF was added slowly with vigorous stirring at room temperature. The P-4VP- BH_3 complex separates as a white powder. After 24 hr at room temperature, it was filtered, washed with THF, and dried for 4 hr in a drying pestle (80°C, 0.5 mm Hg). Yield, 0.5327 g (95%).

The same complex can be obtained in a heterogeneous reaction by suspending P-4VP in 200 ml THF and then following the same procedure previously described. However, the product obtained in the homogeneous phase is more finely divided than that obtained under heterogeneous conditions.

Apparatus

The IR spectra were recorded on Perkin-Elmer Spectrophotometers Models 337 and 225. Samples of the complex were prepared by placing a dispersion of the powder in Nujol between two KBr windows. P-4VP films were cast on a KBr plate by evaporation of solutions in CHCl_3 and CH_2Cl_2 .

The x-ray powder spectra of P-4VP (Fig. 1) and P-4VP- BF_3 (Fig. 2) were obtained with a Philips diffractometer connected to a proportional counter and a multichannel analyzer; the x-irradiation was $\text{CuK } 1.54 \text{ \AA}$.

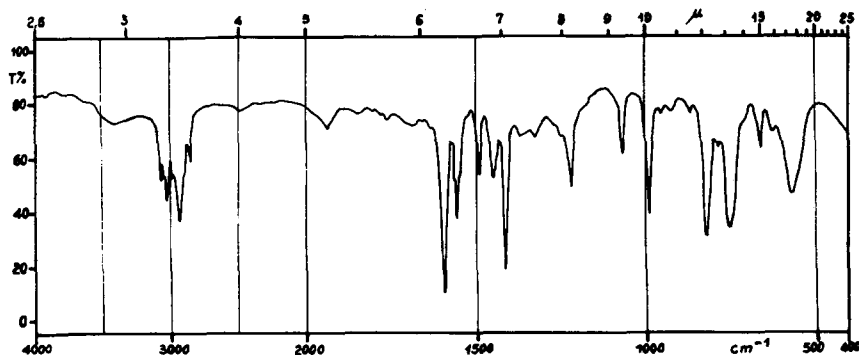


Fig. 1.

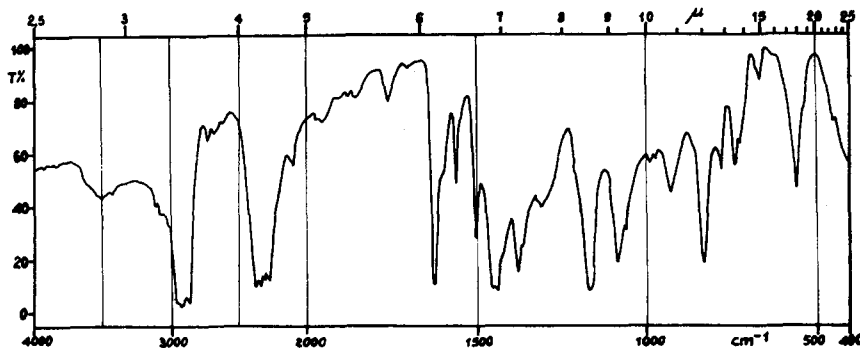


Fig. 2.

RESULTS AND DISCUSSION

IR Spectra of P-4VP-BF₃ Complex

From a comparison of the IR spectra of the complex P-4VP-BF₃ (Fig. 2) and of P-4VP (Fig. 1) it can be seen that new bands appear while some bands of the polymer disappear or are shifted. The complex has an intense and broad absorption between 2380 and 2250 cm⁻¹, with two maxima at 2280 and 2350 cm⁻¹. Using the spectrophotometer Model 225, a better resolution is obtained, and maxima are observed at 2390, 2380, 2350, 2310, and 2270 (shoulder) cm⁻¹. This absorption belongs to the region in which the stretching of the B-H bond was observed for gaseous B₂H₆,⁹ as well as for carbonylborane (maxima¹⁰ at 2434 and 2380 cm⁻¹), for CH₃N → BH₃ (maxima^{11,12} at 2360 and 2260 cm⁻¹), and for pyridine → BH₃ (maxima^{12,13} at 2350 and 2280 cm⁻¹).

The maximum of P-4VP at 1450 cm⁻¹ is not visible in the spectrum of the complex, possibly because of the overlap of the Nujol absorption. On the other hand, the strong band at 1414 cm⁻¹ can be shifted in the complex to 1459 cm⁻¹. The same shift was observed for the pyridine → BH₃ complex.¹²

The spectrum of P-4VP shows a maximum at 1219 cm⁻¹ (1220 cm⁻¹ for 4-ethylpyridine).¹³ In our complex, this band forms the shoulder of the much stronger absorption at 1170 cm⁻¹. In pyridine → BH₃, the corresponding maximum is at 1165 cm⁻¹; it was attributed to a bending of the B-H bond.¹² Moreover, P-4VP has an absorption at 1067 cm⁻¹ (1068 for 4-ethylpyridine). In the same region, the P-4VP-BH₃ complex shows two maxima at 1088 and 1060 cm⁻¹, while in pyridine → BH₃, these two maxima are at 1090 and 1060 cm⁻¹. They were assigned to the stretching of the B-N bond and to the bending in the plane of the unsaturated C-H bonds, respectively.¹²

The relatively intense band at 990 cm⁻¹ for the polymer (994 for 4-ethylpyridine)¹³ has been assigned to a breathing mode of the aromatic ring.¹⁴ This band does not appear in the spectrum of the complex, while there is a very low absorption at 925 cm⁻¹, wagging vibration of the BH₃ group.^{14,15}

The spectral changes we observe, going from the polymer to its reaction product with boron hydride, and the analogies between the spectrum of this reaction product and the known spectrum of the pyridine → BH₃ complex lead us to assume that P-4VP reacts with borane in a similar manner.

Diffractometric Analysis

In Figure 3 we report the most significant features of the x-ray powder spectra of P-4VP and P-4VP-BH₃. The spectra are quite similar and suggest an amorphous structure for both. However, in the P-4VP-BH₃ spectrum, the two maxima are shifted about 1.5° toward lower angles, and the principal maximum is broader than in the spectrum of the polymer.

From the approximate¹⁶ $R = 1.25 d_{\text{Bragg}}$, the average interatomic distances R can be calculated: they are 9.38 and 5.66 Å for P-4VP and 11.33 and 5.96 Å for P-4VP-BH₃. These differences are consistent with a structure in which BH₃ is bound to the pyridine nitrogen. The average distance N-B was calculated to be 1.43 Å.¹⁷ The increase of 1.5 Å in the average distance among the polymeric chains in the amorphous state is therefore well justified. At the same time, the higher dispersion of the van der Waals distances and their small mean increment (from 5.66 Å to 5.96 Å) appear justified.

CONCLUSIONS

From the reaction of diborane and P-4VP, a polymeric compound can be obtained for which we suggest the structure reported in the first part of this article. The IR and x-ray data support this hypothesis.

Regarding its reactivity, P-4VP-BH₃ decomposes rapidly in aqueous solutions of strong mineral acids, with the evolution of a stoichiometric amount of H₂; however, in MeOH and H₂O it is comparatively more stable than diborane itself. It behaves as a mild reducing agent toward ketones and aldehydes, and the reaction rates increase going from THF to protic solvents such as MeOH.

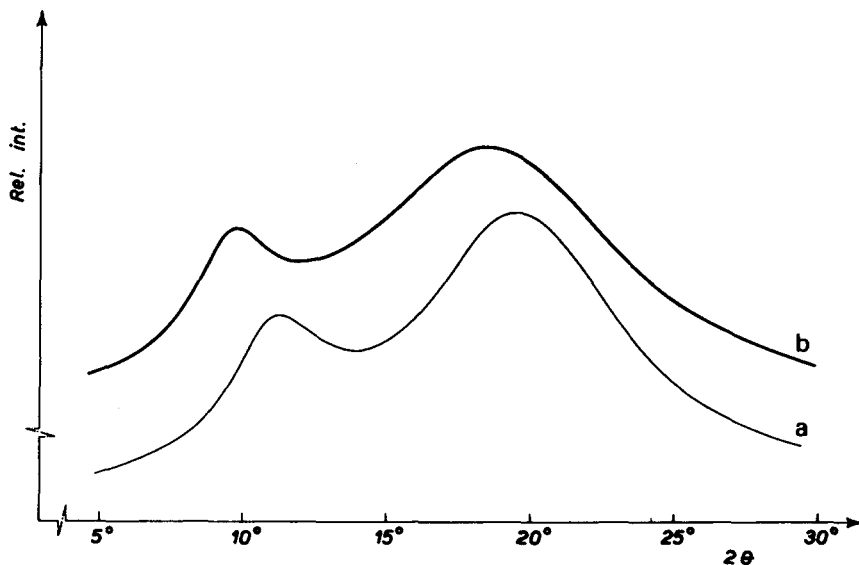


Fig. 3.

A more detailed study of the stoichiometry and stereoselectivity of the reaction with carbonyl compounds is under investigation.

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