

CONDUCTOMETRIC TITRATIONS OF ORGANIC BASES WITH BORON TRIBROMIDE IN APROTIC SOLVENTS

by

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INTRODUCTION

The literature contains a number of references¹⁻⁵ to the titration of Lewis acids and bases in non-aqueous solvents. MANDELL⁶ has reported a reaction between boron tribromide and nitrobenzene. Little use has been made of boron tribromide as an acid in non-aqueous solvents. In the present work, conductance titrations have been carried out to determine the nature of the reaction of boron tribromide with organic bases. Several anhydrous aprotic solvents were selected as reaction media.

EXPERIMENTAL

Materials

Thionyl chloride was distilled in an all glass still as described by LUDER^{4,5}. Pyridine, quinoline and isoquinoline were dried over sodium hydroxide pellets and distilled through a Vegreux column collecting only a small central portion. The products were stored in a dispensing flask with a sodium hydroxide magnesium perchlorate drying tube. Nitrobenzene was stored over sodium carbonate and treated in a similar manner. Thiophosphoryl chloride (Westvaco Chemical Division — Food Machinery and Chemical Corp.) was used as received after drying and storing in a dispensing flask. Boron tribromide was prepared by a modification of a procedure suggested by GAMBLE *et al.*⁷.

The boron tribromide was distilled twice and the colorless liquid stored in a special dispensing burette with a drying tube and Teflon stopcock.

Other reagents were stored in specifically designed Florence flasks with side arm burettes joined to the side. A drying tube was stoppered into the neck of the flask. Delivery of the reagent was accomplished through a Teflon stopcock thus avoiding any errors due to stopcock grease or other contaminants.

Procedure

A standard type conductance cell⁸ was employed which had about a 40 ml capacity. Platinum electrodes were placed in side arms imbedded in the side of the cell in the conventional manner. A third side arm was fused to the conductance cell for the purpose of passing dry nitrogen over the solution during the titration. The conductance measurements were carried out in a constant temperature bath accurate to $250^{\circ}\text{C} \pm 0.05$. Nitrogen dried by successive passage through Drierite, magnesium perchlorate and phosphorous pentoxide was passed over the surface of the reactants. A plastic cover was fitted over the cell. A burette tip was inserted through a hole in the cover. The titrant was added in known amounts directly to the cell and conductance measured at five minute intervals by means of a Surfass conductivity bridge.

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RESULTS

Fig. 1 shows the reaction between pyridine and quinoline with boron tribromide using nitrobenzene as a solvent. In this case the organic base was added to a solution of boron tribromide in nitrobenzene. The reaction between the solvent and boron tribromide was found to yield a 1:1 addition compound which is highly dissociated

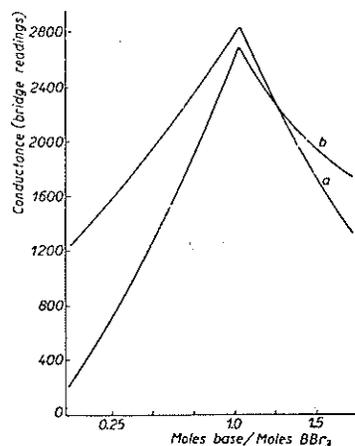
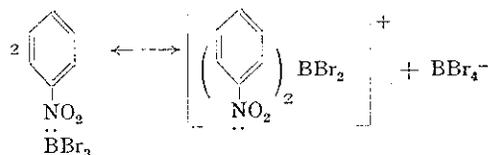


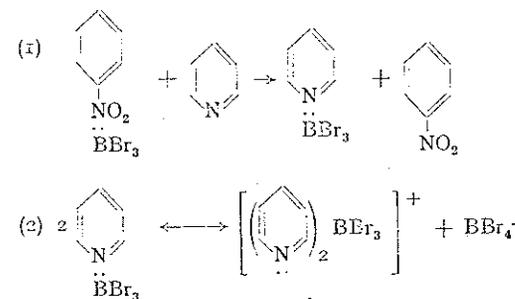
Fig. 1. Nitrobenzene
a) Pyridine, b) Quinoline

and soluble in excess nitrobenzene. On addition of quinoline or pyridine the stronger base displaced the weaker base, nitrobenzene, from its complex with boron tribromide. The initial conductance arose from the dissociation of the addition compound formed in the interaction between the boron tribromide and the nitrobenzene. The dissociation of the addition compound may be visualized in the following reaction:



Addition of pyridine (curve a) and quinoline (curve b) changed the reaction so that the favored reaction was between the boron tribromide and the organic base. This formed a more ionogenic compound than the nitrobenzene addition compound as follows:

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The conductance reached a limiting value corresponding to the formation of a 1:1 complex and then fell off beyond the end-point. This suggests a reversal of process number 2 in excess boron tribromide with a subsequent lessening in ionization. The reduced conductance may be attributed both to the lowering of the dielectric of the system and therefore a decrease of the ionization of the addition compound. Curve 1b shows a larger rate of change of conductance with concentration for the quinoline as compared to that of pyridine. This behavior correlates with the higher base strength of quinoline and possible steric effects introduced by the second ring.

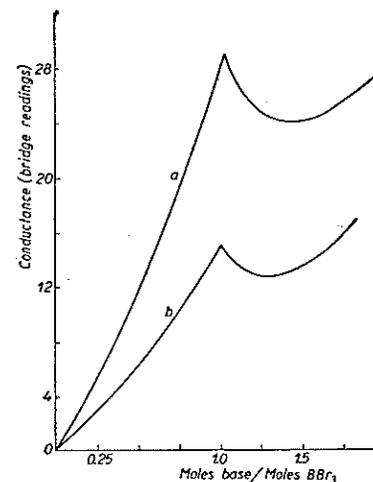


Fig. 2. Thiophosphorylchloride
a) Isoquinoline, b) Quinoline

In Fig. 2 the results of titrating boron tribromide dissolved in thiophosphoryl chloride with isoquinoline and quinoline are noted. The initial zero conductance suggests that there was no reaction between the two acid molecules. The rising

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portion of the curve indicates compound formation between the strongly acidic boron tribromide and the organic base with subsequent ionization as in Fig. 1. At the end-point the conductance reached a maximum. The reaction was stoichiometric and corresponded to the formation of a 1:1 complex. Beyond the equivalence point the conductance dropped sharply then rose slowly. The rise in conductance beyond the end-point was the result of a slow reaction between the organic base and the solvent. The difference in base strength of the isoquinoline and quinoline is shown by the difference in conductance values. The isoquinoline complex was more highly ionized suggesting that isoquinoline is a stronger Lewis base than quinoline in the solvent thionyl chloride.

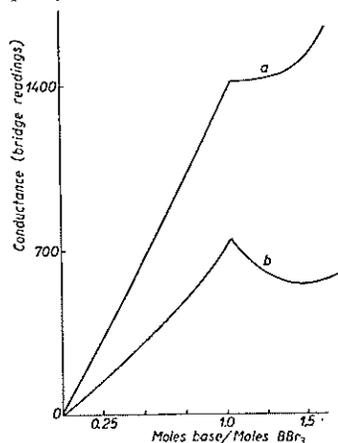
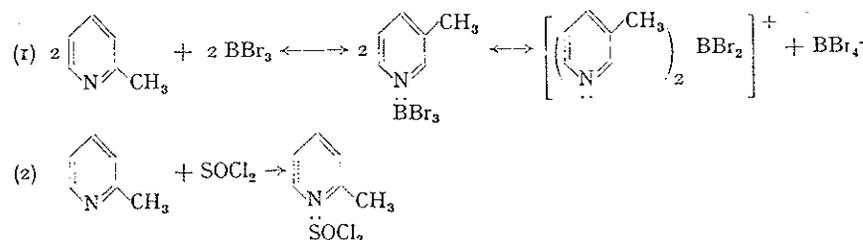
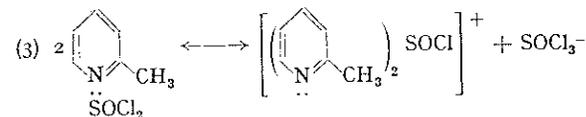


Fig. 3. Thionyl chloride
a) α -Picoline, b) Isoquinoline

Fig. 3 shows the titrations of boron tribromide dissolved in thionyl chloride with the bases, α -picoline and isoquinoline. The preferential reactions were between the bases and the stronger acid, boron tribromide. The completion of these reactions was, in each case, marked by an end-point corresponding to a break in the conductance curve at a 1:1 molecular ratio. Further addition of base resulted in a reaction of the base with the solvent acting as an acid. These successive reactions are illustrated in the following:



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The reaction of the base with the solvent is seen to be a function of the base strength, the stronger base α -picoline showing a strong reaction with solvent beyond the equivalence point.

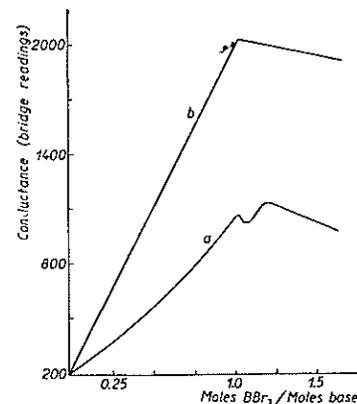
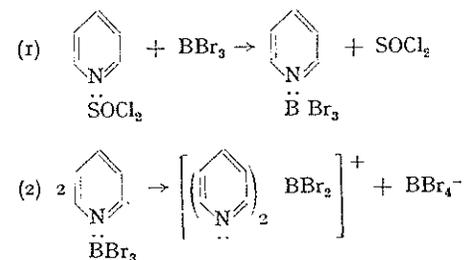


Fig. 4.
a) Pyridine 0.32M, b) 2-Methyl-5-ethyl-pyridine 0.15M

Fig. 4 shows the titration of pyridine and 2-methyl-5-ethyl-pyridine with boron tribromide in thionyl chloride. In this case the base was dissolved in the solvent and the boron tribromide used as a titrant. This gave a more uniform and accurate result because the base-solvent reaction was completed before the boron tribromide was added. A similar reaction has been described previously⁴. The addition of boron tribromide resulted in the displacement of the weaker acid from the complex as shown in the following:



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The pyridine curve in Fig. 4 shows an unexplained dip and then a rise to a leveling off point that is not present in the other curves. This behavior was reproducible but has not been explained. The 2-methyl-5-ethyl-pyridine proved to be the stronger base, probably due to inductive effects being stronger than steric effects.

The present results (Fig. 3 and 4) support the postulate of LUDER⁹ that the high dielectric constant of the thionyl chloride promotes ionization of a salt composed of large ions.

SUMMARY

Conductance curves are presented for the reactions between organic bases and boron tribromide in the non-aqueous solvents, thionyl chloride, nitrobenzene and thiophosphoryl chloride. Interpretations of the data on the basis of the electronic theory are suggested. The reactions are stoichiometric and should find application in analytical chemistry.

RÉSUMÉ

Des courbes de conductance sont présentées pour les réactions se produisant entre les bases organiques et le tribromure de bore, dans les solvants non aqueux: chlorure de thionyle, nitrobenzène et chlorure de thiophosphoryle. Des interprétations des résultats sont proposées, se basant sur la théorie électronique. Les réactions sont stochiométriques et peuvent être appliquées à la chimie analytique.

ZUSAMMENFASSUNG

Die Leitfähigkeitskurven der Reaktionen zwischen organischen Basen und Bortribromid in den nicht wässrigen Lösungsmitteln Thionylchlorid, Nitrobenzol und Thiophosphorylchlorid werden beschrieben. Die Ergebnisse werden auf Grund der Elektronentheorie ausgelegt. Die Reaktionen verlaufen stöchiometrisch und sollten in der analytischen Chemie Anwendung finden.

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