

POTENTIOMETRIC STUDIES ON THE REACTION BETWEEN SULPHUR MONOCHLORIDE AND SODIUM TETRAHYDROBORATE

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ABSTRACT

Potentiometric titrations have been carried out between sulphur monochloride and sodium tetrahydroborate in diglyme-tetrahydrofuran-benzene mixed solvent employing glass-platinum electrode couple. The titration of sulphur monochloride (taken in the titration cell) with sodium tetrahydroborate (dispensed from the burette) exhibits three inflexions in the potential curve whereas the reverse titration shows only two potential jumps.

PRELIMINARY investigations in this laboratory have shown that a variety of inorganic sulphur compounds are quantitatively reduced by sodium tetrahydroborate¹. A potentiometric study of the reaction between sulphur monochloride and sodium tetrahydroborate has been carried out and the results are presented in this communication.

EXPERIMENTAL

Solvents.—Solvents like diglyme (Ansul), tetrahydrofuran² and benzene³ are purified by standard methods and preserved in dry condition.

Reagents.—Commercial sample of sodium tetrahydroborate (~ 85%, B.D.H.) is purified by recrystallisation from pure pyridine⁴. The purity of such a sample was found to be at least 99.9% as assayed by chloramine-T method⁵. A standard solution of the purified sample is prepared by dissolving 0.02 g in 25 ml of diglyme. A known weight (0.150 g) of sulphur monochloride is dissolved in 50 ml of benzene and the concentration of the reagent is checked by two independent methods⁶. All transfer operations are carried out inside a dry box in an atmosphere of nitrogen.

Procedure.—2 to 5 ml of the solution of sulphur chloride is taken in a 50 ml glass titration cell fitted with an appropriate lid carrying the electrodes and provided with two inlets for the burette tip and nitrogen and an outlet for nitrogen. The solution is diluted with 10 ml of tetrahydrofuran. The contents are stirred by means of a magnetic stirrer. The tetrahydroborate solution is dispensed from a microburette, protected from atmospheric moisture. The titrations are carried out under the blanket of dry nitrogen. The progress of the reaction is followed by potential measurements with an Electronic Model Cambridge pH Meter employing a glass-platinum (10 mm × 10 mm) electrode couple. The results of potentiometric titrations are shown in Fig. 1.

RESULTS AND DISCUSSIONS

It can be seen from the figure that there is a drop in potential with the progressive addition of

sodium tetrahydroborate to sulphur chloride solution. Three distinct inflexions can be demarcated on the titration curve corresponding to the three stages of reduction. The first significant drop in potential (*a*) occurs when the amount of tetrahydroborate added is equal to half the amount of sulphur chloride taken. The second fall in potential (*b*) is noticed when the mole ratio of tetrahydroborate added to sulphur chloride taken is 2 : 1 and the final fall (*c*) occurs at the mole ratio of 3 : 1. The titration results are quite reproducible as can be seen from the results presented in the Table. However, it has to be pointed out that considerable time (5 to 30 minutes) is required for the attainment of equilibrium after each addition of the reagent. It takes nearly four hours to complete one potentiometric titration.

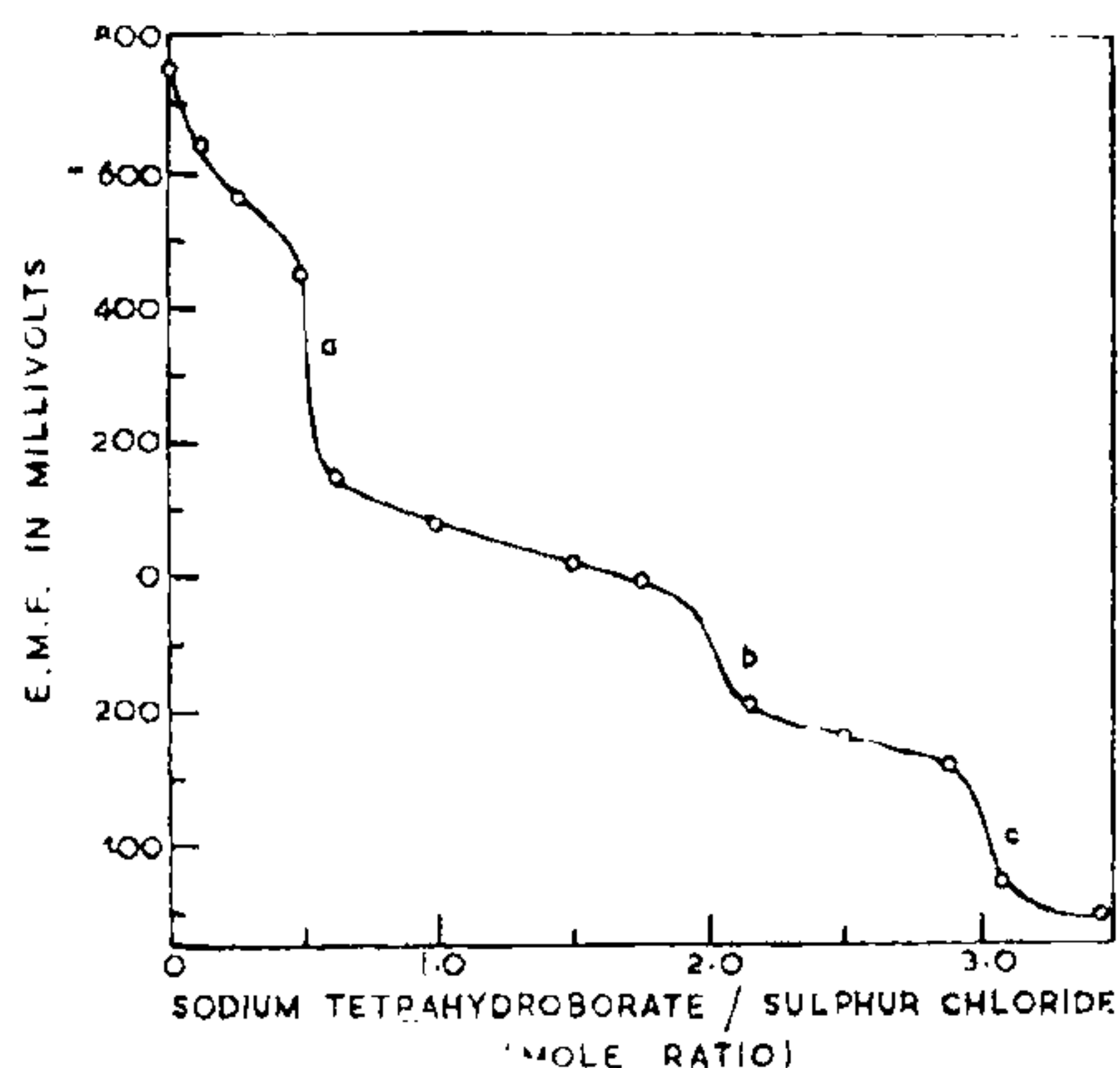


FIG. 1. Potentiometric curve for the titration of Sulphur Monochloride with Sodium Tetrahydroborate.

It is interesting to observe that only two jumps in the potential are observed (Fig. 2) in the reverse titration, viz., when sulphur chloride solution is progressively added to the solution of tetrahydroborate taken in the cell. There is an

TABLE I
Reduction of sulphur monochloride with sodium tetrahydroborate

Direct titration			Reverse titration		
Amount of sulphur chloride taken	Amount of tetrahydroborate added corresponding to 3 stages	Mole ratio of $S_2Cl_2 : NaBH_4$	Amount of tetrahydroborate taken	Amount of sulphur chloride added corresponding to 2 stages	Mole ratio of $S_2Cl_2 : NaBH_4$
Moles $\times 10^6$	Moles $\times 10^6$		Moles $\times 10^6$	Moles $\times 10^6$	
182.5	92.7 (a)	1 : 0.50	153.0	51.1 (d)	1 : 3.00
	361.3 (b)	1 : 1.98		78.5 (e)	1 : 1.95
	534.0 (c)	1 : 2.93			
179.7	85.7 (a)	1 : 0.48	214.2	71.9 (d)	1 : 2.98
	353.3 (b)	1 : 1.97		107.8 (e)	1 : 1.99
	524.6 (c)	1 : 2.92			

initial drop in the potential value with the first addition of the reagent. The potential then rises gradually and shows the first inflexion (d) when the mole ratio of sulphur chloride added to tetrahydroborate taken corresponds to 1 : 3. A steady value in the potential is reached after the second stage of reduction (e) when the mole ratio of sulphur chloride consumed to tetrahydroborate taken is 1 : 2. Even very large excess of further additions of sulphur chloride will not change the potential considerably indicating that sulphur chloride will not react further with tetrahydroborate.

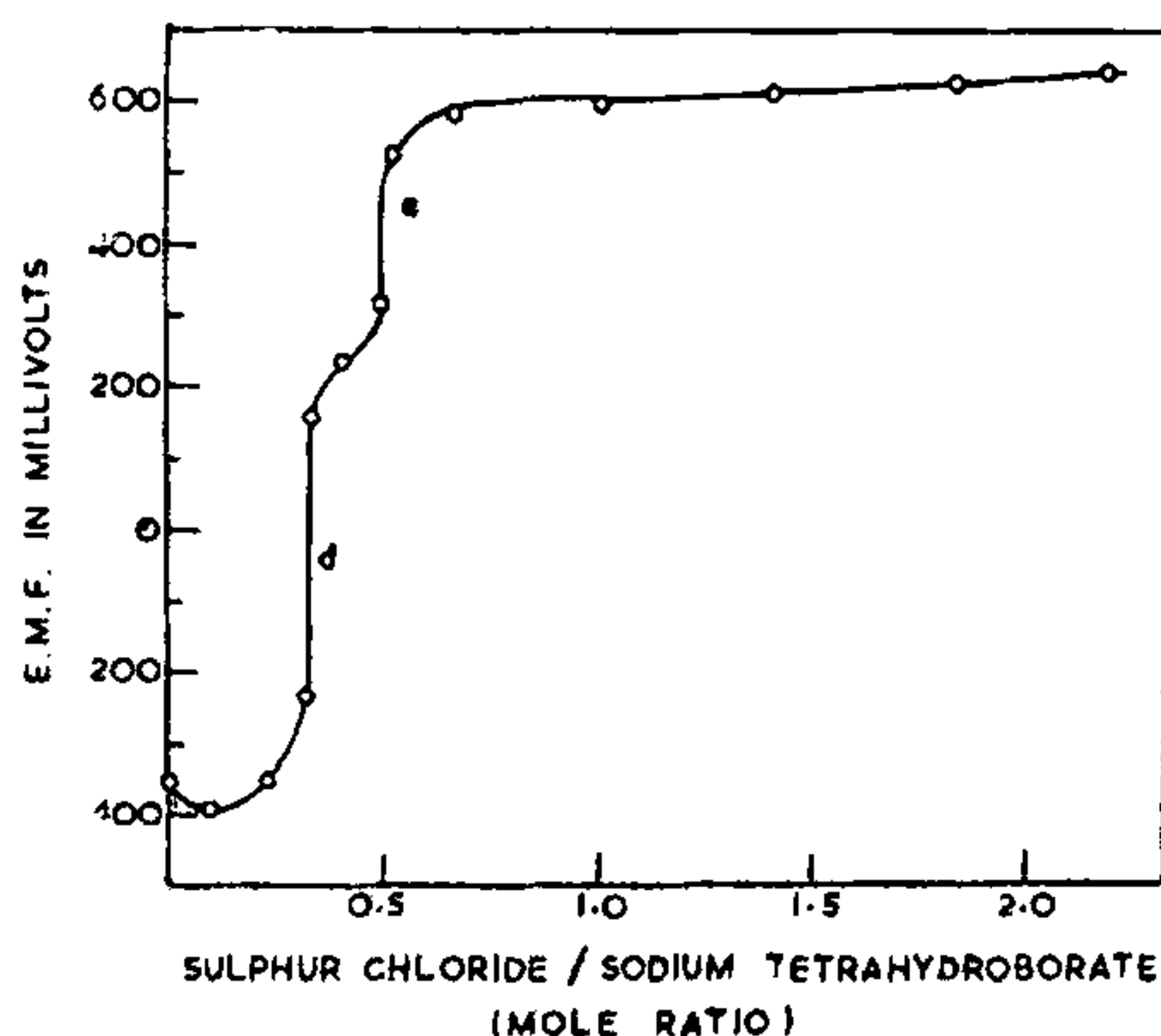


FIG. 2. Potentiometric curve for the titration of Sodium Tetrahydroborate with Sulphur Monochloride.

The results of these two sets of experiments complement each other. It can be seen that stage 'b' of direct titration and stage 'e' of reverse titration exhibit the same stoichiometric proportions (1 : 2) for the reactants while stage 'c' of direct titration and stage 'd' of reverse titration have similar molar ratios (1 : 3) for the reactants. It is, therefore,

likely that similar products are obtained at these stages, viz., at 'b' and 'e' and at 'c' and 'd'. These two stages of the reaction are, perhaps, reversible as it is possible to arrive at these stoichiometric quantities starting from either with a large excess of tetrahydroborate or with a large excess of sulphur chloride and treating it with the other reagent. In the presence of large excess of sulphur chloride, tetrahydroborate gives such products, as observed at 'a', which react with further quantities of tetrahydroborate irreversibly to give rise to the products of stage 'b'. In the reverse titration, since we start with a large excess of tetrahydroborate, we first notice stage 'c' and then stage 'b'. In the reverse titration, however, since 'b' and 'a' are not reversible we do not observe a jump corresponding to 'a' of the direct titration.

It is rather difficult to identify the products of reaction corresponding to the different stages of potentiometric titration. Complex thiohydroborates, boron hydrides, hydrogen and hydrogen chloride could be the possible products of reaction.

The potentiometric results are highly valuable and give a clue for the possible formation of different kinds of intermediate compounds which have to be isolated and identified by actual analysis. It will then be possible to work out the mechanism of the reduction process. Further work is in progress.

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