STUDIES IN THE TETRAARYLBORATES

PART 1. THE PREPARATION AND REAGENT PROPERTIES OF SODIUM TETRAKIS(p-CHLOROPHENYL)BORATE

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The first of the tetraarylborates, tetraphenylborate, was introduced into analytical chemistry in the years $1949-1951^{1-3}$. This compound, as the sodium or lithium salt, was recommended for the precipitation of potassium, rubidium, cesium, protonated basic nitrogen and quarternary ammonium compounds. It soon became available commercially and an extensive literature has subsequently developed on its applications⁴⁻⁶. The reagent has a limited stability in aqueous solution; this fact prompted us to look into the possibilities of preparing a similar molecule that would be more stable. Of the numerous tetraarylborates synthetically possible but hitherto unprepared, the sodium tetrakis(p-chlorophenyl)borate was chosen as the first of a series of molecules in which the substituents on the benzene ring would be varied in such a way as to modify the inductive and resonance effects of the benzene ring on the carbon-boron bond.

EXPERIMENTAL

Synthesis of sodium tetrakis(p-chlorophenyl)borate

Sodium tetrakis(*p*-chlorophenyl)borate is synthesized by the following sequence of reactions.

Cl
$$\longrightarrow$$
 Br + Mg Ether, Cl \bigwedge MgBr
4 Cl \bigwedge MgBr + NaBF₄ Ether, NaB (\bigwedge Cl)₄ + 2 MgF₂ + 2 MgBr₂

To a 1-1 3-necked flask equipped with a stirrer, water-cooled condenser and a dropping funnel, add 9.7 g (0.4 mole) of magnesium turnings. Sweep the assembly with dry nitrogen. Add 250 ml of ether previously dried over sodium to the flask. Dissolve 76.6 g (0.4 mole) of *p*-bromochlorobenzene in 100 ml of dry ether and arrange for dropwise addition into the flask. Add approximately 10 ml of the *p*-bromochlorobenzene solution to the flask and stir the solution. Bring to reflux temperature. The

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reaction generally starts within 20 min. Add the remaining 90 ml of solution dropwise over a period of 1 h. Continue the reflux and stirring for an additional hour.

To the cold solution of p-chlorophenyl Grignard reagent, add 11.0 g (0.1 mole) of sodium borofluoride which has been previously dried at 110° for 1 h. Blanket with nitrogen; stir and reflux for 2 h while maintaining the blanket of nitrogen. Pour the contents of the reaction flask into 400 ml of ice-cold saturated sodium chloride solution. A white precipitate of inorganic material forms in the aqueous layer. Separate the ether layer with a separatory funnel and extract the aqueous phase 3 times with 50-ml portions of ether. Add these to the previously separated ether layer. The reaction mixture need not be worked up immediately and may be left standing several days before adding it to the sodium chloride solution. Evaporate the major portion of ether under vacuum at room temperature and the remainder under vacuum at 40°. A yellow viscous liquid remains. Pour this into 300 ml of dry xylene and cool in an ice bath. The crystals of the mixed salts, sodium-magnesium tetrakis(p-chlorophenyl)borate, will separate. The yield is about 25 g.

To prepare the pure sodium salt, pass 3 g of the mixed salt in 100 ml of water through an ion-exchange column of Dowex 50W-X4, in its sodium form, at a rate of 3-5 ml per min. It is best to prepare the column with 4% sodium hydroxide. It appears that the acid residue left on the column after the usual HCl-NaCl cycle decomposes the borate. Saturate the eluate, which amounts to about 175 ml, with sodium chloride and extract with three 50-ml portions of ether. Combine the extracts and evaporate under vacuum. Pour the clear viscous liquid into 200 ml of dry xylene. Cool in an ice bath and collect the resulting crop of crystals. Yield: 1.9 g. An analysis of the dried sodium salt yielded the following results: C 59.13%, H 3.49%, Cl 29.73%; calculated: C 60.00%, H 3.36%, Cl 29.54%.

Reagent properties of the tetrakis(p-chlorophenyl)borate anion

A 1% solution of the reagent as the mixed Na-Mg salt was used for qualitative testing. About 2 ml of the reagent were added to 2 ml of the 0.1 M test solution. The following ions gave heavy precipitates: K⁺, NH₄⁺, Rb⁺, and Cs⁺, while Ba²⁺, Cu²⁺, Ni²⁺, Ca²⁺, Cd²⁺ and Co²⁺ gave no precipitates.

The reagent was also tested for its ability to precipitate quaternary ammonium compounds and other compounds containing a basic nitrogen which had been protonated. Precipitates in such cases are of interest for possible quantitative methods as well as for qualitative identification purposes. Sodium tetraphenylboron has been extensively used as a reagent for the preparation of derivatives of compounds of these types⁷. The nitrogen-containing compound was dissolved in dilute hydrochloric acid and a 1% solution of the reagent was added. The following compounds gave heavy precipitates: 1-phenyl-ethylamine, N-ethylamine, diethylamine, dibenzylamine, atropine, hexamethylenetetramine, 1,6-diaminohexane, glycine and tetrabutylammonium chloride, while pyridine and quinine gave light precipitates. A few of the precipitates were filtered, dried, and analyzed for nitrogen and melting points were taken on a melting point block. The results are summarized in Table I.

The reagent was then tested for its ability to precipitate the potassium ion by mixing 2 ml of a 1% solution of the reagent with 2 ml of test solution. For a comparison tetraphenylborate was used in a similar series of tests. The results are summarized in Table II.

TABLE 1

ANALYSIS OF REPRESENTATIVE PRECIPITATES

Material tested	M.P.(°)	%N			
		Calculated	Found		
Benzidine	173-176	4.24	4-43		
n-Butylamine	117-118	2.63	2.52		
Brucine	148-149	3.29	3.24		
Quinine	146-151	3.58	2.79		

TABLE II

COMPARISON OF SODIUM TETRAKIS(p-CHLOROPHENYL)BORATE AND SODIUM TETRAPHENYLBORATE AS A PRECIPITANT FOR POTASSIUM

Reagent	Concentration of potassium ion (mg/ml)							
	2.0	0.2	0.15	0.10	0.01	0.005	0.002	
	Heavy	Heavy	Slight	Trace	None	None	None	
Na*(CI~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	- Immediate	Immediate	Immediate	Slow				
Na+ ()4B-	Heavy Immediate	Heavy Immediate	Slight Immediate	Slight Immediate	Slight Immediate	Trace Slow	None	

TABLE III

SOLUBILITY OF POTA3SIUM TETRAKIS(p-chlorophenyl)borate in water at 25° at different ph values

pH of solution	Solubility (mole/l)
3.7	6.0 · 10 ⁻⁴
6.7	0.5 · 10-4
6.8	7.5 . 10-4

The solubility values were obtained by determining the potassium in the supernatant liquid by flame photometry. These values are shown in Table III.

The reagent solutions of sodium tetrakis(p-chlorophenyl)borate were tested for stability by observation of the appearance of cloudiness and by checking the activity of the solution against the potassium ion. It was noted that alcoholic solul tions of 25% and above by volume remained clear and appeared to be stable for severaweeks. Aqueous solutions tested concurrently developed a turbidity after 5 days and were inactive after sixteen days.

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Sodium tetrakis(p-chlorophenyl)borate as a reagent for potassium

The procedure described by $Gloss^8$ in the determination of potassium by sodium tetraphenylborate was selected for the study of the precipitation of potassium with sodium-magnesium tetrakis(*p*-chlorophenyl)borate. A 2% solution of the reagent in water was prepared from the sodium tetrakis(*p*-chlorophenyl)borate. To this was added I g of reagent-grade aluminium hydroxide and the solution filtered and the filtrate reserved for analytical use.

Duplicate 10.00-ml aliquots of a standard solution of potassium chloride (2 mg/ml) were pipetted into 250-ml beakers and water was added to bring the volume to 100 ml. They were heated to 70°, and 40 ml of a 2% reagent solution was added slowly to each beaker. The heavy white precipitate which formed immediately was allowed to stand for 30 min, and finally cooled in an ice bath for 30 min. The precipitate was filtered through a fine-porosity, sintered-glass crucible. Four 5-ml portions

TABLE IV results of quantitative tests using sodium tetrakis(*p*-chlorophenyl)borate

K+ taken(mg)	K+ found (mg)		
47.0	.15.0		
47.6	44.9		
47.6	44.9		
47.6	45.1		
20.0	19.7		
20.0	19.5		
20.0	19.0		
21.4	21.0		
21.4	21.0		
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of ice-cold water were used for transferring and washing the precipitate. The precipitate was dried for 30 min at 110°, cooled in a desiccator and weighed. The recovery of potassium was calculated using the theoretical gravimetric factor 0.07882. The results are summarized in Table IV.

DISCUSSION

The potassium salt was examined for thermal stability by drying at 110°. After the initial constant weight was established, no further weight was lost during a normal drying interval. Constant weight was usually achieved in about 30 min. Drying for periods of 54 h resulted in losses of less than one part per thousand. The precipitate appeared somewhat more crystalline in character than potassium tetraphenylborate. It flocculated more readily, settled more rapidly and was generally easier to handle than potassium tetraphenylborate. It should be an excellent reagent for use in qualitative analysis schemes. The compound has the serious disadvantage as a precipitation reagent for potassium of yielding a compound of potassium of moderate solubility ($6.5 \cdot 10^{-4}$ mole/l at 25° at pH 6.5).

As shown in Table I the compound has possibilities as a reagent for the formation of derivatives of quarternary ammonium and protonated basic nitrogen compounds. A few of the compounds tested yielded precipitates which were not suitable for derivative purposes. Notable among these were aniline and atropine. Compounds containing two basic nitrogens formed mono or di salts. Benzidine produced a compound that was difficult to recrystallize; this analyzed as the mono salt. These derivatives were characterized by several phase changes before the final melt was achieved.

SUMMARY

Sodium tetrakis(p-chlorophenyl)borate was synthesized. It formed precipitates with K+, Rb+, Cs+, quarternary ammonium and protonated basic nitrogen compounds. The potassium salt was more soluble than potassium tetraphenylborate but flocculated more readily and filtered more easily. The salts formed with nitrogen compounds offer possibilities as derivatives suitable for qualitative analysis.

RÉSUMÉ

donne des précipités avec le potassium, le rubidium, le caesium, l'ammonium quaternaire et des composés azotés basiques. Le sel de potassium est plus soluble que le tétraphénylborate de potassium, mais il flocule plus facilement et il se filtre plus aisément.

ZUSAMMENFASSUNG

Es wurde Natriumtetrakis(p-chlorophenyl)borat hergestellt, das mit K+, Rb+, Cs+, quaternärem Ammonium und protonisierten basischen Stickstoffverbindungen Niederschläge bildet. Das Kaliumsalz war löslicher als das Kaliumtetraphenylborat, flockte jedoch leichter aus und liess sich besser filtrieren. Die mit Stickstoffverbindungen gebildeten Salze bieten sich für die qualitative Analyse an.

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