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Sulfonation of Triphenylphosphines and Separation of Sulfonated Triphenylphosphines by Crystallization and Solvent Extraction

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Abstract: The effect of sulfonation conditions on the formation of sulfonated triphenylphosphines and their separation from the post-reaction mixture, containing concentrated sulphuric acid, was studied. The solvent extraction was found to be a suitable technique to separate sulfonated triphenylphosphines from concentrated sulphuric acid, and the purity and yield was higher than obtained by crystallization from various solvents. Tributyl phosphate was a suitable extractant. Sodium salts of sulfonated triphenylphosphines could then be recovered as precipitates by treating the organic phase with the sodium hydroxide solution and separation by crystallization. The solvent extraction simplified the separation process. The separation process was much faster, less chemicals were required, and lower amounts of wastes were produced.

Keywords: Sulfonation, triphenylphosphine, crystallization, extraction

INTRODUCTION

Hydroformylation is an exothermic reaction between an olefin, carbon monoxide, and hydrogen. It was developed by Otto Roelen in 1938, in the laboratory of Ruhrchemie AG (1).

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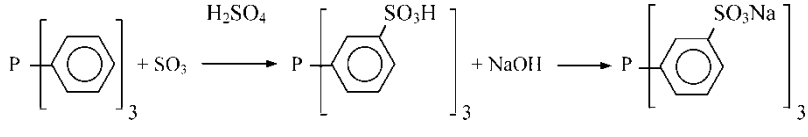
The industrial process, called *oxo synthesis*, gives aldehydes with normal and branched alkyl chains which are then hydrogenated to yield corresponding alcohols. The most desired option is the formation of the isomer with the straight-chained alkyl group. Hydroformylation of propylene is usually carried out with the use of the rhodium-type catalyst dissolved in the reaction medium. The products are separated by distillation (2). The use of water-soluble rhodium-based complexes requests to carry out the hydroformylation process of olefins in the aqueous-organic system. The organic phase contains the raw materials and the reaction products, while the water-soluble catalyst and phosphine ligand remain in the aqueous phase (3–6). The products are then recovered by separation of phases.

Water-solubility of complex compounds can be obtained when sulfonated triarylphosphines are used both for the preparation of the rhodium-based complex and as the free ligand present in excess concentration in the reaction system (5, 6). Among the water-soluble phosphines, hydrophilic trisodium salt of tri(m-sulfophenyl)phosphine (NaTPPTS) is advantageous as a modifying ligand. In 1984, Ruhrchemie developed an industrial process for hydroformylation of propylene, with the use of NaTPPTS. Disodium salt of phenyl[di(m-sulfophenyl)]phosphine (NaTPPDS) can also be used for that purpose. That reagent exhibits lower hydrophilic performance as it contains only two sulfonated groups.

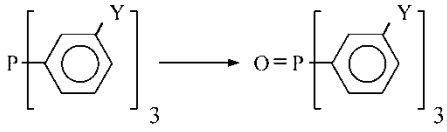
The syntheses of tri(m-sulfophenyl)phosphine (TPPTS) and of phenyl[di(m-sulfophenyl)]phosphine (TPPDS) were already described in reports, Scheme 1 (3, 7–9).

Sulfonation of triphenylphosphine has, however, some peculiarity connected with the necessity to obtain a pure product suitable for the synthesis of the rhodium catalyst. Sulfonation of triphenylphosphine is a subsequent process giving mono-, and trisulfonated derivatives. The sulfonyl group is an electron withdrawing substituent and the next group is introduced to the next aromatic ring. The final product contains a high level of the derivative three and/or two sulfonyl groups. Moreover, sodium salts of tri(m-sulfophenyl)phosphine and of phenyl[di(m-sulfophenyl)]phosphine should be isolated with acceptable yields.

Phosphines undergo easy oxidation to phosphine oxides and the undesirable side reactions can be eliminated or suppressed to acceptable levels. 9–20% of phosphine oxides have been reported, depending on experimental conditions, Scheme 2 (8).



Scheme 1.



Where: Y = H, SO_3H or SO_3Na.

Scheme 2.

Phosphine oxides having alkyl groups as hydrophobic substituents are well known extractants, e.g. CYANEX® 921, CYANEX® 923 and CYANEX® 925, and are used for the separation of several inorganic and organic substances (10–12 and bulletins of the American Cyanamid Company). However, oxides are highly undesirable impurities in phosphines employed to modify the rhodium catalyst.

The separation technique must take into account that

i) the fuming sulphuric acid is used as the reaction medium and its neutralization gives some amounts of undesirable sodium sulfate,
ii) the sodium salts of sulfonated phenylphosphines must be separated with acceptable yields, and
iii) their oxidation to phosphines should be reduced to a possibly low level.

The separation can be achieved by crystallization from various solvents or by the combination of solvent extraction and crystallization (13, 14). The second option permits to avoid the formation of large amounts of sodium sulphate.

The goal of the work was to study sulfonation of triphenylphosphine and to compare the applicability of crystallization and solvent extraction as techniques suitable to separate sulfonated triphenylphosphines from the post-reaction mixture which contains concentrated sulphuric acid.

EXPERIMENTAL

Sulfonation of TPP

12.0 g of TPP was introduced into a reaction flask and 39 g of concentrated sulphuric acid was slowly dropped under argon, keeping the temperature below 20°C. After dissolution of TPP, 11.3–27.1 g oleum containing 65% free SO_3 (SO_3/TPP = 2–28 mol/mol) was added dropwise over 2–70 h, keeping the temperature below 15°C and stirring vigorously the reaction mixture.

Separation by Means of Crystallization

Sodium Salt of Diphenyl(m-Sulfophenyl)Phosphine (NaTPPMS)

The sulfonation reaction was carried out at the SO_3/TPP mole ratio = 2 mol/mol. The post-reaction mixture was cooled down to 10°C and placed on the ice bath ice containing 200 g of ice. 40% NaOH solution was then dropped into it to achieve the equilibrium pH near 11 and 2 L of methanol were added. The precipitated sodium sulphate was filtered off. Methanol was distilled off at 40°C under reduced pressure of 200 mm Hg and cooled down to room temperature. The precipitate was filtered off, washed twice with 100 cm^3 of water and dried at 30°C under reduced pressure (0.1 mm Hg).

Disodium Salt of Phenyl[di(m-Sulfophenyl)]Phosphine

The post-reaction mixture was cooled down to 10°C and placed on the ice bath containing 400–1,000 g of ice. 40% NaOH solution was then dropped into it up to the equilibrium pH value equal to 11. After 4 h, the precipitate was filtered off, washed twice with 100 cm^3 of ice water and dried in a vacuum at a temperature below 35°C. The precipitate was dissolved in 250–800 cm^3 of water, the solution was slowly heated up to boiling and filtered off. The filtrate was cooled down to room temperature and the precipitate of NaTPPDS was separated. The salt was washed with 20 cm^3 of water and dried at 30°C under reduced pressure (0.1 mm Hg).

Trisodium Salt of Tri(m-Sulfophenyl)Phosphine

Water was distilled off from the filtrate obtained above after the crystallisation of NaTPPDS at temperature below 75°C under the pressure of 200 mm Hg, and the residue dissolved in 800–1,600 cm^3 of ethanol under reflux. After filtration, the new filtrate was concentrated by distillation to the volume of 250 cm^3 and cooled down to room temperature. The precipitate of NaTPPTS was washed with 25 cm^3 of ethanol and dried in vacuum at 30°C under reduced pressure. When necessary, sodium salts of sulfonated phenylphosphines were re-crystallized.

Separation by Extraction and Crystallization

The post-reaction (post-sulfonation) mixture was cooled down to room temperature and it was processed in extraction procedures. Extraction was carried out twice with new portions of tributyl phosphate (80 g each time). The combined extracts of tributyl phosphate (TBP) were washed with 50% sodium hydroxide to the equilibrium pH value of 11. The precipitate was separated by filtration and further treated as described above for crystallization procedures.

Analytical Procedures

The phosphorus(III) content was determined by the iodometric method, i.e. titration of excess iodine with sodium thiosulfate. The total content of phosphorus (sum of P^{3+} and P^{5+}) was determined by the Pushel method. The content of sulfur was determined by the Grote method.

IR spectra were taken with the use of the FTIR Mattson 3000 Spectrophotometer equipped with Galaxy 3020 software, Unicam. A ^{13}C NMR spectrometer, Unitry Inova 300, Varian, was used to register ^{13}C NMR spectra.

RESULTS AND DISCUSSION

The TPP was first dissolved in concentrated sulphuric acid and then treated with fuming sulphuric acid, containing 60% free sulphur trioxide, at the temperature below 15°C and under the argon atmosphere. The sulfonation occurred at the 3 position to yield derivatives with 1, 2, and 3 sulfonyl groups. The extent of the reaction was mainly controlled by the SO_3/TPP ratio and reaction time. The composition of the post-reaction mixture was not studied but the mixture was separated by means of two techniques (crystallization and extraction-crystallization) and the separated components were characterized.

The main problem in the crystallization operation was the separation of sodium sulfate formed by neutralization of fuming sulphuric acids used in a large excess. Sulfonated phosphines could be, however, concentrated by solvent extraction.

Both sulfonated phosphines and sulfuric acid could be extracted with solvating and basic extractants, including TBP, trialkylphosphine oxides (CYANEX reagents), and trialkyamines (ALAMINE reagents, from Cognis). The use of trialkylphosphine was disregarded because undesirable phosphorus (V) compounds could be introduced as unwanted impurities to NaTPPDS and NaTPPTS. Some separation problems (hazy phases and/or formation of emulsion) are also observed for these extractants. Trialkylamines are protonated with sulphuric acid and strongly extract mineral acids, even above the typical mole ratio. They had to be used in a hydrocarbon diluent and an addition of the hydrophobic modifier was necessary to avoid the formation of stable emulsions. As a result, the use of individual TBP was selected. However, the reagent underwent slow hydrolysis giving butanol and partial esters. The negative effect of this process on the purity of NaTPPTS was not observed.

Sulfonated phosphines were less hydrophilic than sulphuric acid and their extraction with TBP was preferred. The distribution coefficient, calculated as the ratio of P^{3+} content in the TBP phase and sulphuric acid phase, amounted to nearly 30 for SO_3/TPP ratio equal to 10–15 mol/mol (Table 1).

Table 1. Extraction of sulphonated triphenylphosphine with tributyl phosphate

SO_3/TPP ratio [mol/mol]	SO_3 content [%]	P^{3+} content [%]		Distribution coefficient[a]
		TBP phase	Sulfuric acid phase	
5	5	0.920	Traces	>30
10	10	0.900	0.030	30.0
15	15	0.950	0.035	27.1
25	20	0.485	0.088	5.5
35	25	0.220	0.220	0.8

[a]Calculated as the ratio of phosphorus(III) content.

It meant that sulfonated phosphines were transferred to the TBP phase at nearly 97%. However, the distribution coefficient amounted to 0.75 for the SO_3/TPP ratio equal to 35 mol/mol what indicated extraction of acid instead of sulfonated phosphines. The high value of the distribution coefficient was obtained for the SO_3/TPP ratio equal to 5 mol/mol but this ratio did not permit to obtain high yields of desired di- and tri-sulfonated phosphines.

The stripping of sulfonated phosphines was achieved when the TBP phase was washed with 50% NaOH. Sulfonated phosphines precipitated as sodium salts (equilibrium pH of the aqueous phase, 11). It was also possible to precipitate both sodium sulfate and sodium salts of sulfonated phosphines. Sodium sulfate was then separated from phosphines by dissolution of precipitate in water and precipitation of the inorganic salt with methanol.

Figure 1 shows the effect of SO_3/TPP ratio on the yield of the separated sodium salts of sulfonated phosphines.

The NaTPPMS was isolated with a low yield of 5% at the SO_3/TPP ratio up to 2 mol/mol. No important difference between the performance of the crystallization and solvent extraction-crystallization systems was observed. The purity of NaTPPMS amounted to 95 and 96.5%, while the P(III) content reached 8.1 and 8.2%, for the salts recovered in the crystallization and extraction methods, respectively. The products with higher sulfonation degrees were not isolated from such mixtures.

The NaTPPDS and NaTPPTS were isolated at the SO_3/TPP ratio above 6 mol/mol. For the SO_3/TPP ratio equal to 6 mol/mol, the maximum yield of NaTPPDS was about 70% and 75% for crystallization and extraction-crystallization procedures, respectively, and it monotonously decreased to 4% at the SO_3/TPP ratio equal to 48 mol/mol. The yield of the separated NaTPPTS increased from 5% to 33% and 43% for crystallization and extraction-crystallization procedure, respectively, when the SO_3/TPP ratio changed from 7 to 30 mol/mol. However, at higher SO_3/TPP ratio the post-reaction mixture became brown and lower amounts of sulfonated phenylphosphines were separated (5% and 20% of NaTPPDS and NaTPPTS). It is obvious

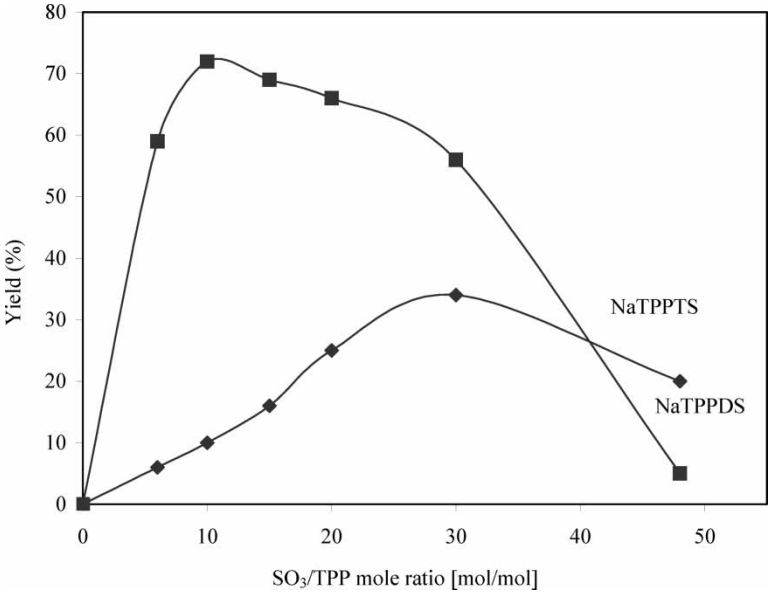


Figure 1. Effect of the SO_3/TPP ratio on the yield of the separated sodium salts of phenyl(di(m-sulphophenyl))phosphine and tri(m-sulphophenyl)phosphine (crystallization technique, time of sulphonation 20 h).

that the determined yields did not characterize the composition of the post-reaction mixture and higher yields could be expected for more efficient separation techniques.

The reaction medium and then the crystallization procedures, although carried out under argon blanketing, could cause oxidation of TPP and its sulfonated derivatives to appropriate phosphine oxides that crystallize together with phosphines. The process could be monitored by determination of the total phosphorus and phosphorus(III) contents in the isolated products. The theoretical content of P^{3+} amounted to 8.5%, 6.6%, and 5.5% for NaTPPMS, NaTPPDS and NaTPPTS, respectively. In the last two cases the values close theoretical were obtained for the SO_3/TPP ratio equal to 7–15 mol/mol (Fig. 2). An exception was NaTPPMS, which was separated only for the SO_3/TPP ratio equal to 2 with 8.2% of the determined P^{+3} content, as already mentioned above.

The increase of the ratio to 48 mol/mol caused the decrease of the P^{3+} content close to 4 and 2% for NaTPPDS and NaTPPTS, respectively, indicating enormous loss of desired oxides caused by the oxidation and degradation.

The impact from the reaction time on the separated sodium salts and the content of phosphorus(III) in NaTPPDS and NaTPPTS is demonstrated in Figs. 3 and 4.

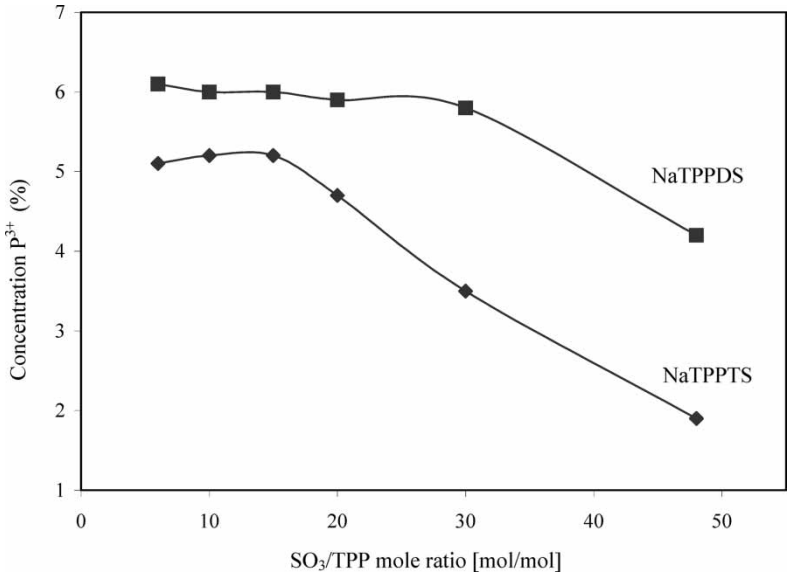


Figure 2. Effect of the SO_3/TPP ratio on the content of phosphorus(III) in the separated sodium salts of phenyl(di(m-sulphophenyl))phosphine and tri(m-sulphophenyl)) phosphine (crystallization technique, time of sulphonation 20 h).

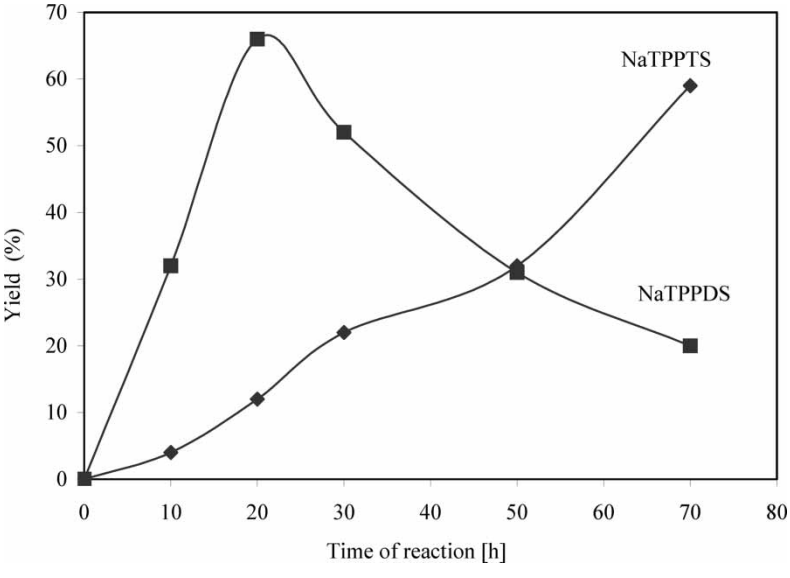


Figure 3. Effect of reaction time on the yield of the separated sodium salts of phenyl (di(m-sulphophenyl))phosphine and tri(m-sulphophenyl)) phosphine (crystallization technique, SO_3/TPP ratio = 15 mol/mol).

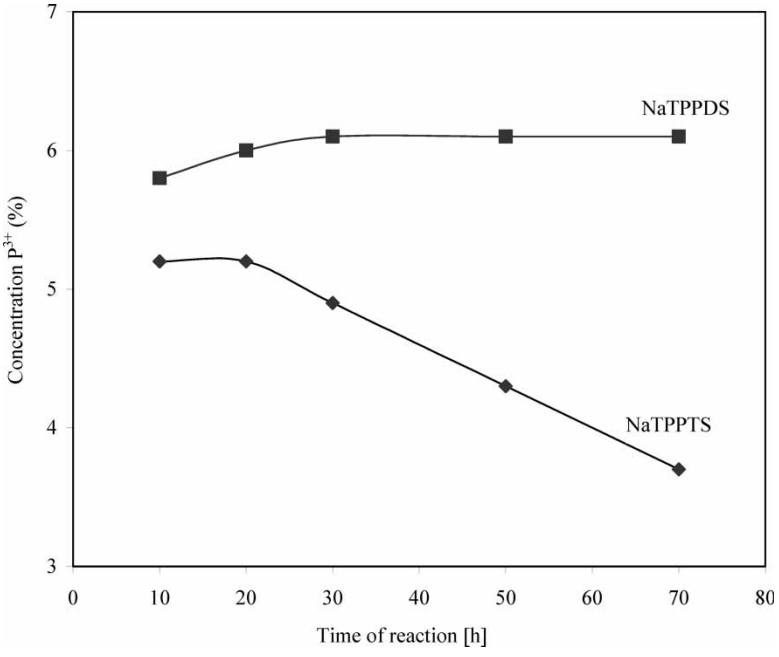


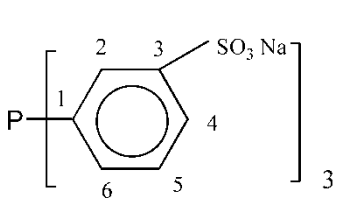
Figure 4. Effect of reaction time on the content of phosphorus(III) in the separated sodium salts of phenyl(di(m-sulphophenyl))phosphine and tri(m-sulphophenyl))phosphine (crystallization technique, SO_3/TPP ratio = 15 mol/mol).

The effect of the reaction time was typical for subsequent reactions, i.e., the yield of NaTPPDS had a maximum (66% for 20 h), while the yield of NaTPPTS increased with time up to 59% for 70 h. However, a significant oxidation/degradation was also observed and the content of phosphorus(III) decreased from 5.3% to 3.7%. Taking this into account, it was decided that the time of reaction could not exceed 30 h with the yield of NaTPPTS somewhat above 20% obtained for the SO_3/TPP ratio equal to 7–15 mol/mol. The purity calculated as the ratio of P^{3+}/P_{total} was estimated as equal to 88% and 98% for crystallization and extraction-crystallization, respectively.

The following conditions were selected for NaTPPDS; the SO_3/TPP ratio equal to 10 mol/mol and the time of reaction about 20 h. The maximum yield amounted to 72% and the purity of the separated sodium salt was 92% and 97% for crystallization and extraction-crystallization, respectively.

IR Spectroscopy of Separated Salts

NaTPPTS: 3472 cm^{-1}, 2958–2857 cm^{-1} $\nu_{=CH\ aromatic}$; 1436 cm^{-1} $\delta\nu_{P\text{-}C\ aromatic}$; 1219 cm^{-1}, 1185 cm^{-1}, 1053 cm^{-1}, 1037 cm^{-1}, 674 cm^{-1} and 623 cm^{-1} $\nu_{S=O}$;



C1: 128+9+0 137 (138.5)
C2: 128+5+0 133 (132.7)
C3: 128+0+16 144 (145.2)
C4: 128+0+0 128 (128.8)
C5: 128+0+0 128 (131.9)
C6: 128+5+4 137 (138.4)

Figure 5. The constitution formula of trisodium salt NaTPPTS and the chemical shifts identified in a ^{13}C NMR spectrum and calculated theoretically ($SO_3/TPP = 15$ by moles; sulfonation time, 20 h; spectrum recorded in D_2O).

788 cm^{-1} and 697 cm^{-1} δ_{CH} 1,3 disubstituted aromatic ring and 627 cm^{-1} $\nu_{C=C\ aromatic}$.

NaTPPDS: 3472 cm^{-1}, 2958–2857 cm^{-1} $\nu_{=CH\ aromatic}$; 1436 cm^{-1} $\delta\nu_{P\text{-}C\ aromatic}$; 1219 cm^{-1}, 1185 cm^{-1}, 1053 cm^{-1}, 1037 cm^{-1}, 674 cm^{-1} and 623 cm^{-1} $\nu_{S=O}$; 788 cm^{-1} and 697 cm^{-1} δ_{CH} 1,3 disubstituted aromatic ring and 627 $\nu_{C=C\ aromatic}$; 730–745 cm^{-1} δ_{CH} monosubstituted aromatic ring.

^{13}C NMR Spectroscopy of Separated Salts

NaTPPTS: 138.4 ppm (d: 138.54, 138.39, $J_{C\text{-}P}$ 11.0 Hz); 132.7 ppm (d: 132.6, 132.8, $J_{C\text{-}P}$ 22.5 Hz); 145.2 ppm (d: 145.1, 145.3, $J_{C\text{-}P}$ 7.2 Hz); 128.8 ppm (s); 132.3 ppm (d: 132.1, 131.7, $J_{C\text{-}P}$ 6.5 Hz) and 139.0 ppm (d: 138.49, 138.26, $J_{C\text{-}P}$ 17.6 Hz).

The values found for chemical shifts are close to those calculated theoretically for individual carbon atoms in the aromatic ring of NaTPPTS (Fig. 5). The values for chemical shifts as determined experimentally for the analysed salts have been specified in brackets.

The solvent extraction technique also permitted for separation of sodium salts of methyl di(m-sulfophenyl)phosphine and tri(p-fluor-m-sulfophenyl)phosphine with the yield and purity higher than available form the crystallization procedure.

The solvent extraction simplified the separation process. The separation could be obtained faster, with the use of lower amounts of chemicals and with the production of lower volumes of wastes.

CONCLUSION

Solvent extraction is a suitable technique to separate sulfonated triphenylphosphines from fuming sulphuric acid with the purity and yield higher than obtained by crystallization from various solvents. TBP is a suitable extractant for that purpose. Sodium salts can then be recovered as precipitates by treating the organic phase with the sodium hydroxide solution.

The solvent extraction simplifies the separation process. The separation can be obtained faster, and the amounts of chemicals used and the volumes of wastes generated are lower.

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