

Technical Notes

Selectivity in Sulfonation of Triphenyl Phosphine

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Abstract:

The selectivity of triphenyl phosphine sulfonation using 34% SO₃ to triphenyl phosphine trisulfonate (TPPTS) was studied. Several side products such as mono- and disulfonate, sulfonated phosphine oxide, and sulfonated phosphine sulfides were also observed. Reaction conditions were optimised to give 90% pure TPPTS. Agitation speed, mode of agitation and temperature have a strong influence on activity and selectivity of reaction. The TPPTS formed was tested for its activity in hydroformylation of ethylene and octene-1 in biphasic mode using [Rh(COD)Cl]₂.

Introduction

Biphasic catalysis using metal complex catalysts involving water soluble ligands is considered a major advancement in catalyst product separation techniques. The use of water as a solvent has numerous advantages, particularly considering the environmental issues with conventional organic solvents. In addition the facile separation strategy ensures efficient recycle of catalyst, thereby avoiding highly involved separation techniques, reducing waste, and making the process ecofriendly.^{1–5} Sulfonated phosphines have been applied extensively in a variety of biphasic reactions due to their very high solubility in water. The high solubility of the ligand enables stabilization of the catalyst in the aqueous phase as the ligand-to-metal ratio can be very high [triphenyl phosphine trisulfonate sodium (TPPTS) solubility in water is \cong 1.1, kg/L]. Water soluble sulfonated phosphines are generally synthesized by a sulfonation route which has many advantages such as one-step synthesis, good yields, etc. However, there are many other disadvantages of direct sulfonation besides handling oleum, which also should be considered. The major ones include poor selectivity, formation of side products, sensitivity towards air, etc. Since, TPPTS is a component for catalyst synthesis, a relatively pure compound is desired. However, the synthesis as described earlier in Table 1, also gives numerous by-products

such as triphenylphosphine monosulfonate (TPPMS), triphenyl phosphine disulfonate (TPPDS), triphenylphosphine trisulfonate oxide (OTPPTS), and triphenylphosphine trisulfonate sulfide (STPPTS) in reasonable quantities (see Figure 1). Further, isolation of pure TPPTS is tedious. Herrmann et al. have proposed sulfonation of triphenyl phosphine in superacid medium using SO₃/H₂SO₄/H₃BO₃.¹⁵ This method reduces the formation of OTPPTS considerably. However, selectivity towards TPPTS is very poor. The intermediate TPPDS is formed selectively even under conditions of high temperature (120 °C) and longer reaction times (72 h). TPPTS is formed on further sulfonation of TPPDS, with oleum.

There is thus a definite scope for improvement in the existing procedure for the synthesis of TPPTS by sulfonation. It is also essential to obtain TPPTS in an acceptable yield and purity. The reaction conditions for the synthesis, particularly the reaction period, temperature, and the ratio of triphenyl phosphine to oleum are extremely important. In this study we have investigated the role of mixing, temperature, and reaction time on activity and selectivity to TPPTS. The optimum conditions have been arrived at to obtain TPPTS of suitable purity and high yield.

Experimental Section

Materials. The ligand triphenyl phosphine (PPh₃) was procured from Fluka AG, Switzerland. Sulfuric acid (SD, India), and sodium hydroxide (SD, India) of high purity were purchased and used as received. All operations were performed under argon atmosphere. Oleum of 65% strength was prepared from 20% oleum by distillation. Distilled deionized water was used in all operations. All solvents including water were degassed prior to use.

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Table 1. Sulfonation of triphenyl phosphine

sr no.	TPP, g	H ₂ SO ₄ g	oleum g	temp. °C	time h	product	separation	ref
1	105	960	320 (30%)	15–20	3.5	TPPDS (64%)	extraction with triisooctylamine in toluene	6–8
2	105	960	320 (30%)	20	24	TPPDS (33%) TPPTS (53%)	same as above	8
3	100		1000 (20%)	20–40	15–25	TPPTS	methanol extraction	9
4	8		72 (71%)	20–25	19	TPPTS	tributyl phosphate extraction	10
5	10		38 (20%) 2 (65%)	25	2	TPPMS	ethanol extraction	11
6	20		112 (65%)	22	76	TPPTS	tributyl phosphate extraction	12
7	20		194 (65%)	50	24	OTPPTS	reduced to TPPTS	13
8	10		200 (20%)		150	TPPTS	methanol extraction	14
9	3	40 + H ₃ BO ₃ 4.8	40 (65%)	58	112	TPPDS	methanol extraction	15

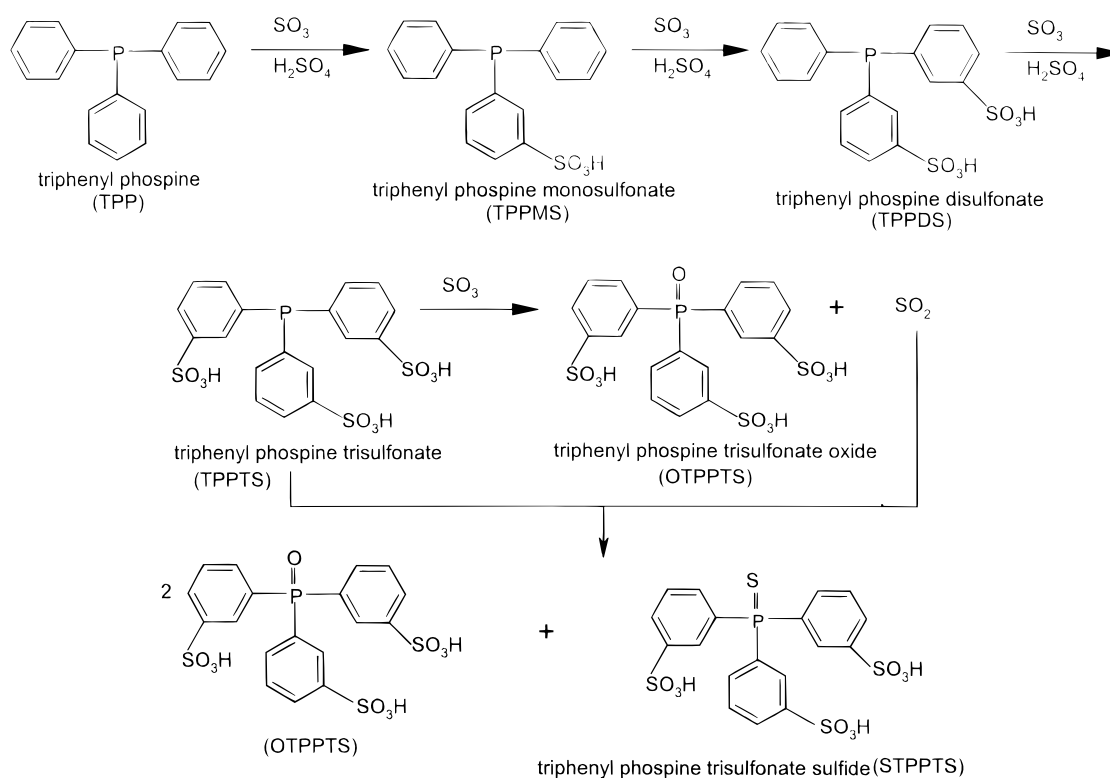


Figure 1. Typical reactions in sulfonation of triphenyl phosphine

Reactor/Apparatus. A double-jacketed 1 L glass reactor equipped with a high-speed half-moon stirrer and a provision for monitoring bulk liquid temperature was used. This reactor was designed so that operations under argon atmosphere were possible. The temperature was controlled by circulation of a constant temperature fluid. A similar reactor of larger volume was used for neutralization of the crude reaction mixture.

Synthesis of TPPTS. The following procedure was standardized for the preparation of TPPTS. Sulfuric acid (98%, AR) 200 g, was introduced into the sulfonation reactor. The acid was cooled to 12–15 °C, and 50 g of solid triphenyl phosphine (190.75 mmol) was introduced at 15 °C over the course of 30–45 min, for proper temperature control. A

homogeneous yellow-colored solution of triphenyl phosphine in sulfuric acid was formed. Then 280 g, (141.48 mL; $d = 1.98$ at 35 °C) of 65% oleum (SO₃ content: 2.275 mol) was introduced into the reactor over a period of 40–45 min, at a temperature of 15 °C. The temperature of the reaction mixture was then raised to 22 °C (± 0.5) and was maintained for 76 h. Thereafter, the temperature of the reaction was lowered to ~ 10 °C and the reaction quenched by slow addition of 50 g of distilled water. The solution of sulfonated triphenyl phosphine in sulfuric acid thus obtained was further diluted to approximately 800 mL by addition of cold water (10 °C). The diluted solution was neutralised (up to a pH of 7–7.2) with a solution of 50% (w/w) degassed sodium hydroxide. The temperature is maintained at about 10 °C

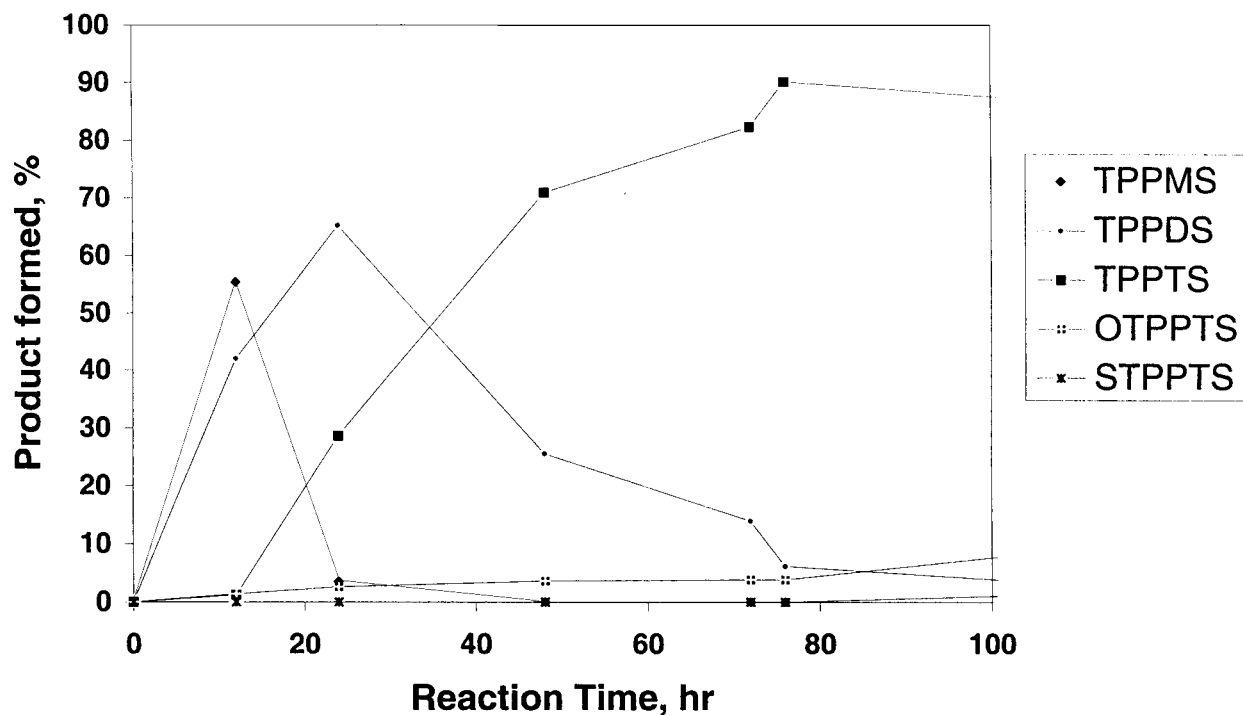


Figure 2. Sulfonation of triphenyl phosphine: Typical concentration–time profile Charge: Triphenyl phosphine: 50 g; Oleum (65% SO₃): 280 g; H₂SO₄: 200 g; Agitation speed: 1000 rpm; Temperature: 22 °C.

during the entire operation. During the course of neutralisation, sodium sulfate precipitated from the solution. This reaction mixture containing sodium sulfate/TPPTS was processed by the method reported by Kuntz.⁹ (This involved concentration of the neutralised solution, and separation of the sodium sulfate by addition of methanol. This exercise was repeated a few times and the final extract was with hot methanol. The methanolic solution was evaporated to dryness. The TPPTS was purified by washing with ethanol and characterised.) For the kinetic studies, periodic samples were withdrawn, quenched with water and D₂O, and ³¹P NMR spectra recorded for the quantification of the products. Typical NMR signals were obtained as ³¹P{¹H NMR (D₂O, 200 MHz, 25 °C), δ -4.8 (P^{III}) and δ 34.2 (P^V) which are consistent with literature.^{14,15}

Results and Discussion

TPPTS was obtained by treating triphenylphosphine with oleum and by subsequent neutralization of the reaction mixture with saturated sodium hydroxide solution. The reaction scheme is shown in Figure 1. The following conditions were chosen from the literature for carrying out the sulfonation reaction¹²

Reaction charge:

- (1) SO₃/TPP = 12 molar ratio
- (2) SO₃/(SO₃ + H₂SO₄ + TPP) = 34% (w/w)
- (3) H₂SO₄/(SO₃ + H₂SO₄ + TPP) = 56% (w/w)

Temperature: 22 °C

Agitation speed: 1000, rpm

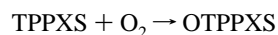
The results are presented in Figure 2. Sulfonation is a

Table 2. Effect of temperature on sulfonation of triphenyl phosphine

serial no	temp. °C	P ^{III} , %			P ^V , %	
		TPPMS	TPPDS	TPPTS	OTPPTS	STPPTS
1	20		10.2	84.6	4.8	
2	22		6.1	90.1	3.8	
3	30		3.4	84.4	12.2	

^a Charge: triphenyl phosphine: 50 g; oleum (65% SO₃): 280 g; H₂SO₄: 200 g; agitation speed: 1000 rpm; time: 76 h.

typical consecutive reaction with sequential formation of mono-, di-, and trisulfonated products. TPPMS is formed very rapidly in the initial stages and passes through a maximum at around 12 h where 55% of TPPMS was observed. The formation of TPPDS was about 42% which increases to 65% in 24 h. Formation of TPPTS was observed at 12 h. At 24 h most of TPPMS is consumed and only TPPDS and TPPTS are major products. At 76 h the maximum TPPTS is formed (90%). At this point 6% TPPDS was also present. The remainder is OTPPTS. On prolonged reaction for 105 h both TPPDS and TPPTS dropped with a subsequent rise in oxide. The formation of STPPTS is also observed in minor quantities (1%). Sulfonated phosphines are very sensitive to traces of oxygen, and they are easily oxidized to the corresponding oxides, formed during synthesis of TPPTS as:



where X = mono-, di-, or trisulfonate.

These oxides are inactive as ligands and thus the presence of these in small quantities in the final TPPTS solution does not pose any problem in catalytic activity. The formation of

Table 3.^a Effect of agitation speed on sulfonation of triphenyl phosphine^a

serial no	agitation speed, rpm	P ^{III} , %			P ^V , %	
		TPPMS	TPPDS	TPPTS	OTPPTS	STPPTS
1	magnetically agitated		55.0	40.3	4.7	
2	300		42.1	58.0	2.3	
3	600		25.1	71.5	3.4	
4	1000		6.1	90.1	3.8	

^a Charge: Triphenyl phosphine: 50 g; oleum (65% SO₃): 280 g; H₂SO₄: 200 g; temperature: 22 °C; time: 76 h.

oxides can be avoided by maintaining an argon atmosphere during sulfonation reaction and by controlling reaction time. The sulfide derivative is also observed after prolonged reaction times. It is formed as per reaction shown in Figure 1. Sulfides are known to poison the catalyst, and formation of these must be avoided.

The selectivity profile of this reaction is extremely sensitive to temperature (Table 2). A lowering of temperature by 2 °C has a pronounced effect on the sulfonation rate, and 10% TPPDS is observed (as against 6% at 22 °C). Likewise TPPTS formation is also reduced. At 30 °C, the oxide formation is high (12% as against 4%) which indicates that high temperatures favour the formation of OTPPTS.

The SO₃/H₂SO₄ mixture is viscous at reaction temperature (22 °C), and thus to ensure the uniform reaction it is necessary to have an efficient agitation. The effect of agitation speed has been given in Table 3. It has been observed that TPPTS selectivity is enhanced with increase in the agitation speed. Although complete conversion of TPPMS is observed under all agitation speed, subsequent sulfonation needs an efficient mixing. This may be due to

non uniform distribution of the highly reactive SO₃ in reaction medium. In a magnetically agitated system very poor selectivity similar to that at lower agitation speed is observed.

Hydroformylation Reactions. The TPPTS synthesised was tested for its activity in hydroformylation. For this purpose a 50 mL stirred reactor was used, as described elsewhere.¹⁶

(i) Hydroformylation of ethylene was carried out under following conditions: temperature: 40 °C, solvent: toluene–water system (aqueous phase hold-up 0.4), catalyst [Rh(COD)Cl]₂: 5.0 × 10⁻⁴ kmol/m³; Rh:TPPTS, 1:6; and a $P_{\text{ethylene}} = P_{\text{CO}} = P_{\text{H}_2}$ of 0.669 Mpa for 1 h. The rate of reaction was found to be 3.45 × 10⁻⁵ kmol/m³/s, with 98% selectivity to propionaldehyde.

(ii) Hydroformylation of octene-1 was also undertaken using the above synthesised TPPTS under the following conditions: temperature: 100 °C, solvent: toluene–water system (aqueous phase hold-up 0.4), catalyst [Rh(COD)Cl]₂: 1.0 × 10⁻² kmol/m³; Rh:TPPTS, 1:6; octene-1 concentration 0.85 kmol/m³; $P_{\text{CO}} = P_{\text{H}_2} = 2.07$ Mpa for 9 h. The rate of reaction was found to be 5.36 × 10⁻⁶ kmol/m³/s, with >95% selectivity to aldehydes, and octene-1 conversion of 23%. An *n/iso* ratio was found to be 1.02.

Conclusions

The consecutive reaction of sulfonation of triphenyl phosphine to TPPTS is found to be extremely sensitive to the reaction temperature and agitation. The reaction time to obtain TPPTS in acceptable yield and desirable purity has been optimized. The TPPTS synthesised in combination with Rh complex catalyst was active for hydroformylation in a biphasic system.

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