

# Determination of kinetic parameters and Hammett $\rho$ from the synthesis of triaryl phosphites using reaction calorimetry

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## Abstract

Triaryl phosphites bearing electron donating and electron withdrawing substituents were prepared through the reaction of sodium phenoxides with phosphorus trichloride. The reactions were performed in a Mettler RC1 reaction calorimeter. The main purpose of this work was the determination of Hammett  $\rho$  from the synthesis of substituted triaryl phosphites through the interpretation of calorimetric data. The phenoxide bearing a methoxide group was the most reactive, and the one bearing the nitro group was the least reactive. It was demonstrated that the reaction rate depends mainly on the addition rate of phosphorus trichloride solution. A good correlation between the Hammett parameters ( $\sigma_p^+$ ) was obtained, indicating a reaction mechanism in which a decrease of the negative charge occurs in the transition state.  
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## 1. Introduction

Aromatic phosphites are used as stabilizers for polymers and to prepare phosphates through oxidation [1]. A “one-pot” methodology developed for the preparation of triaryl phosphates [2] was applied to the synthesis of triaryl phosphites bearing electron donating and electron withdrawing substituents. The irreversible second-order reaction associated to the synthesis of triaryl phosphites follows the multi-step mechanism outlined in Scheme 1.

The most commonly used relationship to obtain the systematic description of the influence of substituents in the reactivity pattern of molecules is the Hammett equation [3,4].

The main purpose of this work was the determination of Hammett  $\rho$  from the synthesis of substituted triaryl phosphites through the determination of kinetic constants and reaction rates through the study of the rate of heat release [5]. The determination of the kinetic parameters based on the study of the rate of heat release was recently reviewed [6].

## 2. Experimental procedure

### 2.1. Experimental apparatus

The reactions were carried out in a Mettler–Toledo RC1 reaction calorimeter. A complete description of the calorimetric principles used in the calculations performed in this equipment can be found in the literature [7]. Infrared spectra were recorded on a Nicolet 740 FT-IR spectrophotometer.  $^1\text{H}$ NMR and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker HC200 at 200 and 81 MHz, respectively.  $\text{CDCl}_3$  was used as solvent, and the chemical shifts were expressed in  $\delta$  (ppm) unit, using TMS as internal reference for  $^1\text{H}$  spectra and  $\text{H}_3\text{PO}_4$  (85%) as external reference for  $^{31}\text{P}$ .

### 2.2. Triaryl phosphites synthesis

Toluene (0.8L) was manually introduced into the 2.0L reactor vessel at 25 °C. The reaction mixture was stirred during the experiment at 150 rpm using an anchor agitator. A 0.25 mol of the phenol was added, and the reaction temperature was raised to 30 °C. A solution containing 5.75 g

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### Nomenclature

$C$	concentration ( $\text{mol L}^{-1}$ )
$C_p$	heat capacity of reacting mixture at constant pressure ( $\text{J kg}^{-1} \text{K}^{-1}$ )
$dX(t)/dt$	rate of heat release ( $\text{s}^{-1}$ )
$F_{B_0}t$	number of moles of B added until time $t$
$k$	reaction rate constant for a second-order reaction ( $\text{L mol}^{-1} \text{s}^{-1}$ )
$N_{A_0}$	the initial number of moles of A in the reactor
$R_A$	reaction rate
$t$	time (s)
$T$	temperature ( $^{\circ}\text{C}$ )
$T_r$	reaction temperature ( $^{\circ}\text{C}$ )
$U$	global heat-transfer parameter ( $\text{W m}^{-2} \text{K}^{-1}$ )
$V_r(t)$	reaction volume (L)
$X(t)$	thermal conversion
$X_i$	fraction of heat release at time $i$

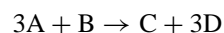
(0.25 mol) of sodium in 100 mL of methanol was added. The excess methanol was removed as a toluene–methanol azeotrope ( $64^{\circ}\text{C}$ ) by distillation until the temperature reached toluene's boiling point ( $110^{\circ}\text{C}$ ). A volume of toluene equal to the distilled volume of azeotrope (200–250 mL, in average) was added to the reactor after the distillation was finished. This procedure was necessary to ensure that the reaction mass could be considered as a constant throughout all the experiments to compare different values of reaction enthalpies. An electrical calibration heater was used to apply a known heat generation rate to the reactor. On the assumption that no reaction occurs, the applied calibration power (20 W) can only be dissipated via the wall. This allows the global heat transfer coefficient ( $U$ ) to be determined. The specific heat capacity of the reaction mass was determined performing temperature ramps [8]. The reaction temperature was kept at  $45^{\circ}\text{C}$  followed by the addition of 170 mL of a 0.5 M solution of phosphorus trichloride in toluene (0.085 mol) was added to the reactor through a pump, during a period of 5 min. A final set of  $U$  and  $C_p$  determinations was carried out to make the

heat of reaction calculation possible. Toluene was removed by distillation. The resulting mixture of solids (NaCl and the triaryl phosphite) was washed with water to remove the sodium chloride. After drying, the products were obtained in yields ranging from 70 to 87%. The product characterizations were achieved by FT-IR,  $^1\text{H}$  and  $^{31}\text{P}$  NMR as presented in Table 1.

### 3. Results and discussion

Triaryl phosphites were prepared by the reaction of sodium phenoxides with phosphorus trichloride. The synthetic reactions of tris(*p*-nitrophenyl) phosphite, tris(*p*-chlorophenyl) phosphite, triphenyl phosphite and tris(*p*-methoxyphenyl) phosphite were carried out in a Mettler RC1 calorimeter where kinetic evaluations based in the heat flow can be estimated in a noninvasive in situ way. The products characterizations are summarized in Table 1.

The multi-step mechanism shown in Scheme 1 can be simplified and mathematically expressed as:



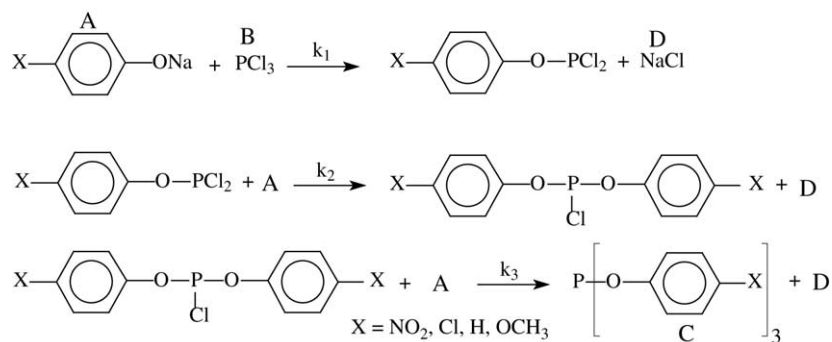
where A = the sodium phenoxide, B =  $\text{PCl}_3$ , C = triaryl phosphite and D = NaCl.

The reaction rate ( $R_A$ ) and the reaction rate constant ( $k$ ) for the triaryl phosphite synthesis were calculated using expressions (1) and (2), respectively [10]:

$$-R_A V_r(t) = N_{A_0} \frac{dX(t)}{dt} \quad (1)$$

$$\frac{dX(t)}{dt} = k \frac{(1 - X(t))[F_{B_0}t - N_{A_0}X(t)/3]}{V_r(t)} \quad (2)$$

The percentage of the total heat released from the reactions of the sodium phenoxides with  $\text{PCl}_3$ , expressed as thermal conversion are presented in Fig. 1. The data were measured in 4 s intervals, so that the term  $dX/dt$  was calculated by the expression  $dX/dt = (X_{i+1} - X_i)/4$ . The other terms in Eq. (2) and the values of heat of reaction were obtained by the RC1 evaluation program from Mettler [11]. The kinetic parameters ( $k$ ) and  $dX/dt$  and the reactions enthalpies are shown in Table 2.



Scheme 1.

Table 1  
Characterization of the products shown in Scheme 1

X	NMR		FT-IR P–O–C (cm <sup>-1</sup> )	mp (°C)	
	<sup>1</sup> H NMR, δ (ppm)	<sup>31</sup> P NMR, δ (ppm)		Found	Literature [9]
NO <sub>2</sub>	8.3, 7.3	124.8	1169, 1201	168–171	170–171
Cl	7.0	127.0	1192, 1230	47–48	49–51
H	7.3	127.8	1186, 1228	29–31	26–29
OCH <sub>3</sub>	3.8, 6.8, 7.1	129.4	1179, 1234	–	17–19

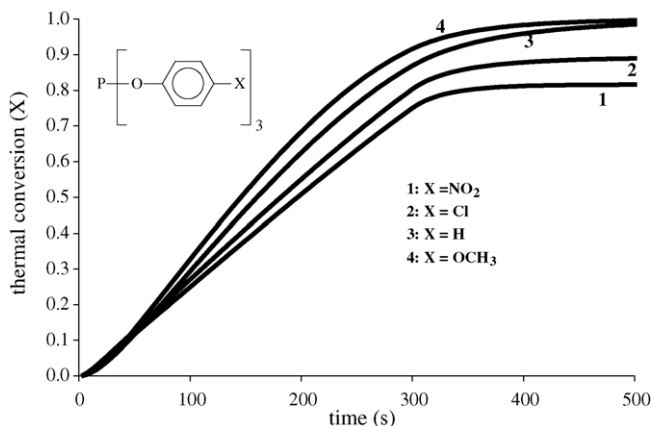


Fig. 1. Experimental thermal conversions from calorimetric data for the reactions of the substituted sodium phenoxides with PCl<sub>3</sub> at 45 °C.

The results shown in Fig. 1 made it possible to differentiate the reactivities of the phenoxides studied. Notice that the time necessary to achieve a value of thermal conversion, for example 70%, is increased from the sodium phenoxide bearing the most electron-donating substituent (OCH<sub>3</sub>) to the phenoxide bearing the most electron-withdrawing group (NO<sub>2</sub>).

To check if the studied reaction could be considered as feed controlled, the influence of the total time of ad-

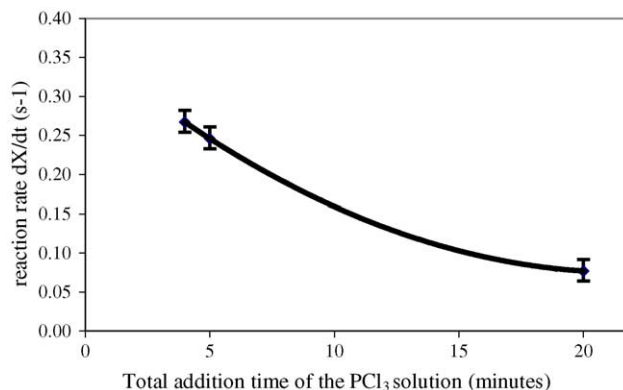


Fig. 2. Influence of the feed rate in the reaction rate of sodium *p*-nitrophenoxide with PCl<sub>3</sub> solution at 45 °C.

dition of phosphorus trichloride solution was evaluated, as shown in Fig. 2. It was observed that the faster the addition of PCl<sub>3</sub> solution, the higher the values of reaction rate obtained.

Using the results presented in Fig. 2, it was possible to estimate the value of the reaction rate for this reaction under batch conditions. Using the polynomial equation of the curve shown above, for example, for an addition time of PCl<sub>3</sub> of 10 s, the calculated value for  $dX/dt$  was  $0.3588 \text{ s}^{-1}$ . When this

Table 2  
The calculated kinetic parameters for the triaryl phosphite synthesis during PCl<sub>3</sub> addition at 45 °C

Substituent (X) in Scheme 1	Reaction rate constant, $k$ (L mol <sup>-1</sup> s <sup>-1</sup> )	Reaction rate $dX/dt$ (s <sup>-1</sup> )	Heat of reaction (kJ)/mol of the phenol
NO <sub>2</sub>	82 ± 7	0.246 ± 0.003	58.4
Cl	103 ± 6	0.254 ± 0.004	111.6
H	110 ± 10	0.255 ± 0.006	117.2
OCH <sub>3</sub>	190 ± 10	0.303 ± 0.005	125.6

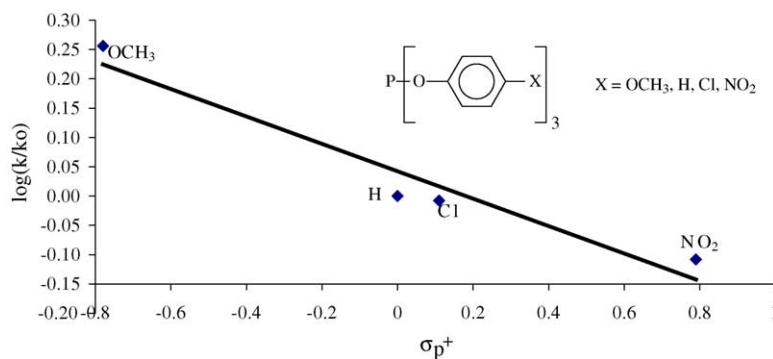


Fig. 3. Hammett plot for the triaryl phosphites.

batch experiment was performed, a reaction rate of  $0.371 \text{ s}^{-1}$  was found.

The effect of the substituents present in the aromatic ring of the sodium phenoxides used in the synthesis described in this paper, were evaluated using the Hammett equation:

$$\log(k) - \log(k_0) = \sigma\rho \quad (3)$$

where  $k$  is the reaction rate constant obtained for the synthesis of a substituted sodium phenoxide with  $\text{PCl}_3$  and  $k_0$  the reaction rate constant for the reaction of the sodium phenoxide with  $\text{PCl}_3$ . The best results for the Hammett plot were those obtained for the  $\sigma_p^+$  parameters as presented in Fig. 3.

The negative value of  $\rho(-0.2337)$  is in total agreement with the reaction rate decrease observed when the electron-withdrawing power of the substituents increases. The good correlation with  $\sigma_p^+$  values ( $r^2 = 0.9369$ ) is in accordance with the decrease of the negative charge in the transition state. These results are in agreement with a mechanism of nucleophilic substitution on phosphorus that would be favored when the nucleophilicity of the phenoxide increases.

#### 4. Conclusions

- (1) The reaction rate for the synthesis of triaryl phosphites depends mainly on the addition rate of phosphorus trichloride solution.
- (2) The tendency shown in the Hammett plot, pointed out to a reaction mechanism where a decrease of the negative

charge occurs in the transition state. The negative value of  $\rho$  confirm the decrease of the reactivity as the electron-withdrawing power of the substituents increases.

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