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Evaluation of Kinetic Parameters from the Synthesis of Triaryl Phosphates Using Reaction Calorimetry

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Abstract:

Triaryl phosphates were prepared by a "one-pot" methodology through the reaction of sodium phenoxides with phosphorus oxychloride. This system can be described as a semi-batch reaction, where the phenoxides were synthesized inside the reactor and a solution of phosphorus oxychloride in toluene was added continuously through a pump. These highly exothermic reactions were performed in a Mettler RC-1 reaction calorimeter. The aim of this work was to evaluate the reaction rate and the reaction rate constant through the study of the rate of heat release. Although the phenoxides react almost immediately with phosphorus oxychloride, it was possible to notice the slight differences among the sodium phenoxides studied. The phenoxide bearing an electron-donating group (methoxy) was the most reactive, and the one bearing an electron-withdrawing group (nitro) was the least reactive one. The reactions could be considered to be feed-controlled. It was demonstrated that the reaction temperature does not affect the reaction rate and reaction rate constant in the same way that the feed rate of the phosphorus oxychloride does.

Introduction

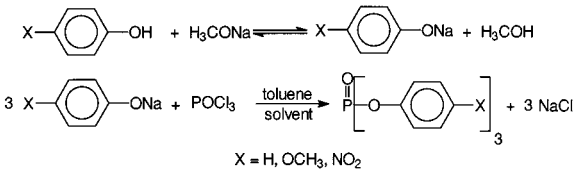
The triaryl phosphates are thermically stable compounds and can be used in different industrial applications suchas plastifiers, lubricants, hydraulic fluids, and flame retardants.[1]

They can be obtained by a "one-pot" synthesis through the reaction of phenoxides with phosphorus oxychloride[2] as shown in Scheme 1.

The main purpose of this work was to apply a mathematical model to obtain an estimation of the kinetic constants and reaction rates through the interpretation of calorimetric data from the triaryl phosphate synthesis.

The classic methods for the evaluation of kinetic constants are based mainly on following the concentration profiles through the reaction by chromatographic techniques.[3] The implementation of these techniques would be very difficult in this case, since the reaction of phenoxides and phosphorus oxychloride is extremely fast, taking place almost immediately when the reagents are mixed.

Scheme 1



Experimental Section

Toluene (0.8 L) was introduced manually in the RC-1 reactor vessel at room temperature (27 °C). The reaction medium was stirred at 150 rpm during the experiment. Phenol (0.25 mol) was added, and the reaction temperature was raised to 30 °C. A solution of 5.75 g (0.25 mol) of sodium dissolved in 100 mL of methanol was added. The difference between the jacket and the reaction temperatures ($T_j - T_r$) was set to 20 °C to remove all the methanol−toluene azeotrope (64 °C) by distillation. The distillation continued until the temperature reached toluene's boiling point (110 °C). A volume of toluene equal to the distilled volume of azeotrope (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. To determine the total heat-transfer coefficient U and the heat capacity of the reaction medium C_p, a set of temperature ramps and calibrations was performed.

During a period of 5 min, 170 mL of a 0.5 M solution of phosphorus oxychloride in toluene was added to the reactor through a pump. In each experiment, 0.083 mol of phosphorus oxychloride was added (144 g). A final set of U and C_p determinations was carried out.

Discussion

A mass balance for a semi-batch reactor was used to obtain an expression for the reaction rate constant (k). The synthesis reactions were carried out in a Mettler RC-1 reaction calorimeter. A complete description of this reactor can be found in the literature.[4]

The obtained data from reaction calorimetry are based on the heat flow, which is calculated from the overall heat-transfer coefficient, the wetted area and the temperature difference between the reactor wall and the fluid circulating through the vessel jacket.[5]

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(1) Quin, L. D. *A Guide to Organophosphorus Chemistry*; John Wiley & Sons Inc.: New York, 2000.
(2) Da Silva, J. F. C.; Nakayama, H. T.; Neto, C. C. *Phosphorus Sulfur* **1997**, *131*, 71−82.
(3) Levenspiel, O. *Chemical Reaction Engineering*; Wiley: New York, 1972.
(4) Crevati, A.; Mascarello, F.; Lenthe, B.; Minder, B.; Kikic, I. *Ind. Eng. Chem. Res.* **1999**, *38*, 4629−4633.
(5) Leggett, D. J. *Thermochim. Acta* **2001**, *367/368*, 351−365.

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Since the heat flow is closely related to the kinetics,[6] it was possible to obtain an estimate of the reaction rate constant, in a noninvasive in-situ way.[7]

The synthesis of triaryl phosphates employed is an irreversible second-order reaction that can be represented as $3A + B \rightarrow C + 3D$, as expressed in Scheme 1, where A = the sodium phenoxide, B = phosphorus oxychloride, C = the triaryl phosphate, and D = sodium chloride.

The rate law (R_A)[8] for this reaction can be expressed as:

$$-R_A = kC_AC_B \tag{1}$$

Since B is fed to the reactor initially containing only A, the number of mols of A remaining in the reaction mass at any time can be found from the mass balance

$$N_A = N_{A0} - N_{A0}X \tag{2}$$

The molar balance of A gives:

$$-R_AV = \frac{dN_A}{dt} \tag{3}$$

A substitution of eq 2 in eq 3 gives

$$-R_AV = \frac{N_{A0}dX}{dt} \tag{4}$$

For B, it is possible to write:

$$N_B = F_{B0}t - N_{A0}X/3 \tag{5}$$

The concentrations of A and B are:

$$C_A = N_A/V_r = N_{A0}(1 - X)/V_r \tag{6}$$

$$C_B = N_B/V_r = (F_{B0}t - N_{A0}X/3)/V_r \tag{7}$$

Substituting C_A and C_B in the rate law gives the expression:

$$-R_A = \frac{k[N_{A0}(1 - X)][F_{B0}t - N_{A0}X]}{V_r^2} \tag{8}$$

The combination of eqs 4 and 8 permits to write:

$$N_{A0}\frac{dX}{dt} = \frac{k[N_{A0}(1 - X)][F_{B0}t - N_{A0}X]}{Vr} \tag{9}$$

$$k = \frac{dX}{dt}\frac{V_r}{(1 - X)[F_{B0}t - N_{A0}X/3]} \tag{10}$$

By applying eq 10, the reaction rate constant k was estimated through the calorimetric data supplied by the reactor calorimeter RC-1. The reaction rate was calculated by expression 4.

When phosphorus oxychloride is added to the phenoxide, two simultaneous phenomenona take place: the solubilization of $POCl_3$ and the chemical reaction. This way, one might suppose, the heat generated by the chemical reaction could suffer interference from the rate of heat released or consumed.

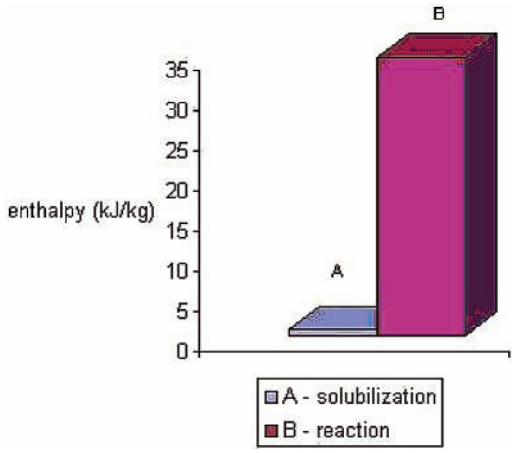

Figure 1. **Comparison between the solubilization of phosphorus oxychloride in the reaction media and the total heat involved in the process.**

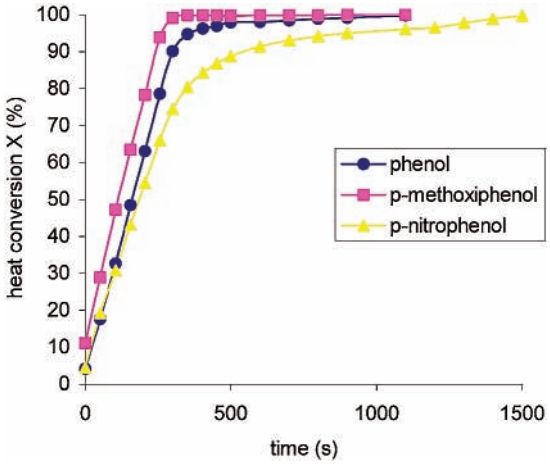

Figure 2. **Heat conversion of the reaction of the sodium phenoxides with phosphorus oxychloride.**

Figure 1 shows a comparison between the solubilization enthalpies of the 0.5 M phosphorus oxychloride solution in toluene and the heat of reaction obtained.

The solubilization enthalpy of the phosphorus oxychloride solution in toluene is very small if compared with the heat of reaction. Thus, all the data supplied by the RC-1 system regarding the heat generated are mainly related to the heat of reaction since the heat due the solubilization is insignificant.

The percentage of the total heat released from the reaction of the sodium phenoxides with $POCl_3$, expressed as heat conversion, are presented in Figure 2.

The terms dX/dt, $(1 - X)$ and $N_{A0}X/3$, from eq 10, were calculated from the points present in the conversion curves. All the data was obtained in intervals of 4 s, so that the term dX/dt was calculated by: $dX/dt = (X_{i+1} - X_i)/4$.

The reaction volume, V_r, and the quantity of B added ($F_{B0}t = Cm/d$), can be obtained by the RC-1 evaluation program.

The estimation of the reaction rate and the reaction rate constant during the addition of the phosphorus oxychloride

(6) Landau, R. N. *Thermochim. Acta* **1996**, *289*, 101−126.
(7) Landau, R. N.; Blackmond, D. *Chem. Eng. Prog.* **1994**, 43−48.
(8) Foegler, H. S. *Elements of Chemical Reaction Engineering*; Prentice Hall International, Inc.: New York, 1992.

Table 1. **Calculated parameters for the systems studied**

product	reaction rate constant k (L/mol·s)	reaction rate dX/dt (s^{-1})	heat of reaction (kJ/kg)
triphenyl phosphate	56.88 ± 15	0.273 ± 0.005	34.95
tris(p-methoxyphenyl)phosphate	139.00 ± 20	0.315 ± 0.003	40.94
tris(*p*-nitrophenyl)phosphate	26.77 ± 10	0.208± 0.004	31.78

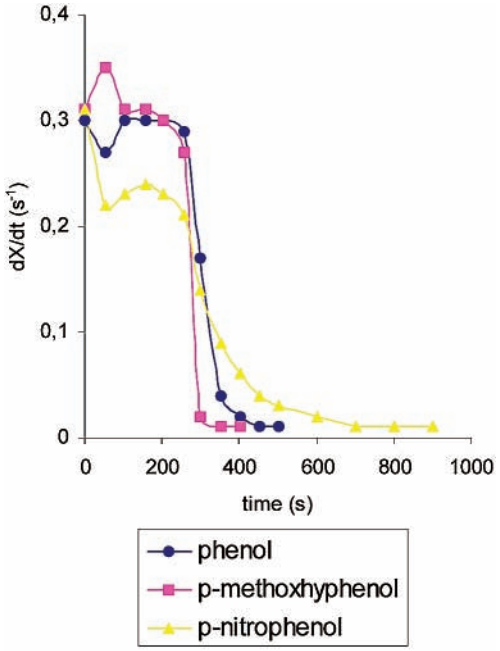

Figure 3. **Comparison of the reactivity for the phenoxides in study. The reactor temperature was 45 °C.**

solution were performed by applying eqs 4 and 10, respectively. The results are summarized in Table 1.

Even though the values of reaction rate are very similar, the difference between them can be better understood in Figure 3.

It is possible to notice that each curve has a higher peak in the beginning. This peak happens because the pipe linking the pump and the reactor must be filled with the phosphorus oxychloride solution before the addition starts. After the pipe is full, the pump is turned on, and it immediately throws the solution before establishing a regular flow.

The first important point to observe in these curves is the fact that the curve of the most reactive system (the *p*-methoxyphenoxide, which has an electron-donating group) is located in a level above the other curves, and the *p*-nitrophenoxide (which has an electron-withdrawing group) has the lower value.

Second, when the feed of phosphorus oxychloride solution is interrupted (approximately 300 s), the decay of the reaction rate is much more abrupt for the *p*-methoxyphenoxide than for the phenoxide or for the *p*-nitrophenoxide.

Furthermore, the reaction rate of the *p*-methoxyphenoxide system is the first to be extinguished, closely followed by the phenoxides system. The system employing *p*-nitrophenoxide is the last one to be extinguished. This clearly indicates this system as the least reactive one.

These three aspects clearly show that, despite the fact that the reactions are feed-controlled and that the reactions happen

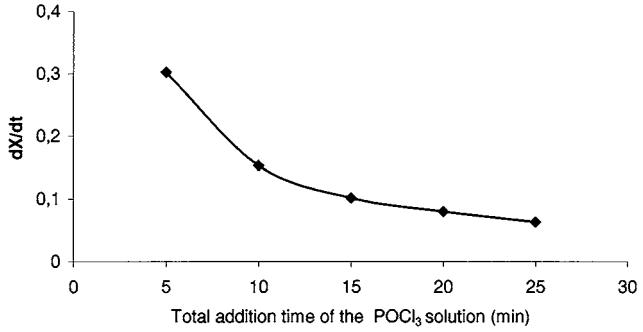

Figure 4. **Feed rate influence in the reaction rate of the sodium phenoxide with the $POCl_3$ solution at 45 °C.**

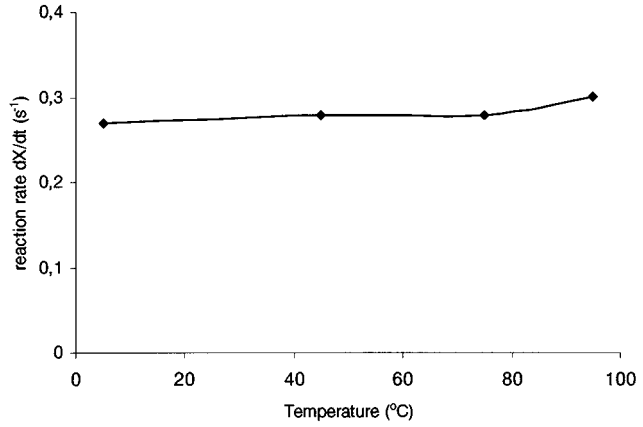

Figure 5. **Temperature influence of T_r on the reaction rate for the triphenyl phosphate synthesis. The total feed time of the $POCl_3$ solution was 5 min.**

almost immediately when the phosphorus oxychloride is added into the reactor, it is possible to notice that the *p*-methoxyphenoxide is indeed the most reactive and the *p*-nitrophenoxide the least reactive one.

To examine if the rate of heat release could be influenced by the rate of mixing, the synthesis of triphenyl phosphate was conducted at two other stirring speeds: 75 and 225 rpm. The profiles of the heat conversion curves were the same as that of the one obtained at 150 rpm. This behavior clearly shows that there is no mass-transfer influence due to the rate of mixing and that the rate of heat release depends only on the kinetics of the reaction.

The influence of the total time of addition of phosphorus oxychloride was also studied; it was observed that the faster the addition of the phosphorus oxychloride solution the higher the values of reaction rate obtained, as shown in Figure 4.

The influences of the temperature on the reaction rate and on the reaction rate constant in the synthesis of triphenyl phosphate using a constant addition time of 5 min are shown in Figures 5 and 6, respectively.

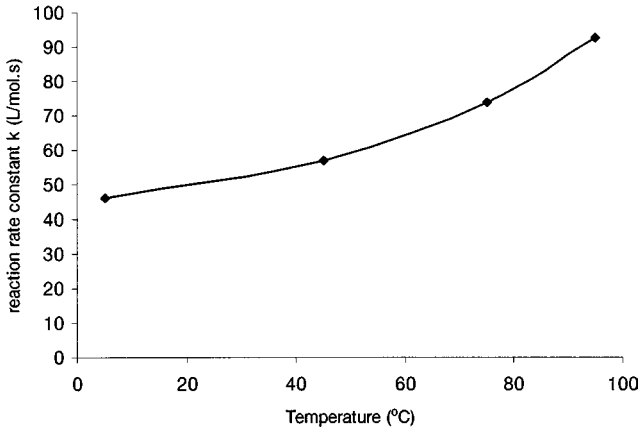

Figure 6. **Influence of T_r on the reaction rate constant for the triphenyl phosphate synthesis. The total feed time of the $POCl_3$ solution was 5 min.**

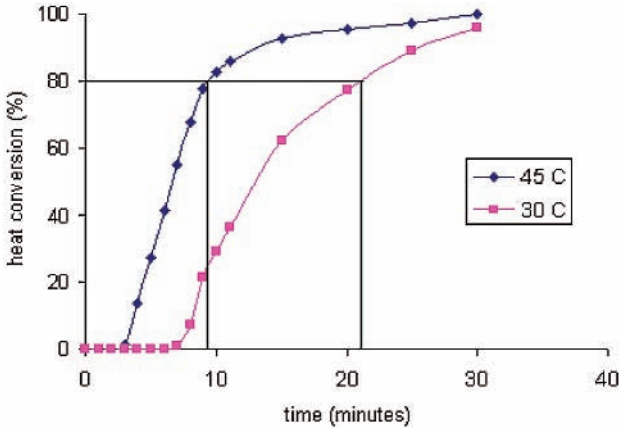

Figure 7. **Temperature influence for the tris(*p*-nitrophenyl)-phosphate synthesis. The total addition time was 5 min.**

The important thing to notice in these two graphics is that the reaction rate increases are basically the same when the temperature is increased from 5 to 95 °C but the reaction rate constant k increases about 100%. This difference is explained by the fact that the reaction is feed-controlled; thus, the reaction rate increases mainly due to the feed rate, but the reaction rate constant k, also known as the Ahrrenius constant, is a parameter that increases exponentially with the temperature.

To verify the influence of the temperature in the less reactive systems, the synthesis of tris(*p*-nitrophenyl)phosphate in two different temperature levels was studied as shown in Figure 7.

The reaction rate constant k and the reaction rate dX/dt calculated for the synthesis on tris(*p*-nitrophenyl)phosphate were: $k = 16.5$ (L/mol·s) and $dX/dt = 0.0834$ (s^{-1}) for 30 °C and $k = 26.8$ (L/mol·s) and $dX/dt = 0.208$ (s^{-1}) for 45 °C. These results clearly indicate an important influence of the temperature for the least reactive system that was not observed for the more reactive ones. Notice that the time necessary to achieve 80% of heat conversion at 45 °C is 10 min and at 30 °C it is about 20 min..

Conclusions

(1) The reaction rate of the synthesis of triaryl phosphates depends mainly on the addition rate of the phosphorus oxychloride solution. Except for the effect of *p*-nitrophenoxide, the influence of the temperature on the reaction rate is small, if compared with the effect of the rate of addition of the phosphorus oxychloride solution.

(2) All the phenoxides studied react almost immediately with phosphorus oxychloride. Considering $(dX/dt)_{heat} = (dX/dt)_{molar}$ and applying eq 4 to calculate the reaction rate and eq 10 to calculate the reaction rate constant k, with all data based on heat conversion, it was possible to detect the slight differences that exist among the phenoxides reactivity due the presence of electron-donating and -withdrawing groups.

Nomenclature

C = concentration (mol/L)
C_p = heat capacity of reacting mixture at constant pressure ($J \cdot kg^{-1} \cdot K^{-1}$)
d = density (kg/L)
dX/dt = rate of heat release (s^{-1})
$F_{B0}t$ = number of mols of B added until time t
R_A = reaction rate
k = reaction rate constant for a second-order reaction ($L \cdot mol^{-1} \cdot s^{-1}$)
N_A = number of mols of A in the reactor at any given moment t
N_{A0} = the initial number of mols of A in the reactor
$N_{A0}X$ = number of mols of A that react until time t
$N_{AO}X$ = number of mols of B that react until time t
N_B = number of mols of B in the reactor at any given time t
R = gas constant
T = temperature (°C)
T_r = reaction temperature (°C)
t = time (s)
U = global heat-transfer parameter ($W \cdot m^{-2} \cdot K^{-1}$)
V_r = reaction volume (L)
X = molar conversion of compound A
X_i = fraction of heat release at time, t_i
X_{i+1} = fraction of heat release at time, t_{i+1}

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