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A Comparison between Kinetic Parameters from the Synthesis of Tris(*p*-nitrophenyl)phosphite and Tris(*p*-nitrophenyl)phosphate Using Reaction Calorimetry

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Abstract:

Tris(*p*-nitrophenyl)phosphite was prepared by a modification of a "one-pot" methodology developed for the preparation of triaryl phosphates. This exothermic reaction was performed in a Mettler RC-1 calorimeter. The principal aim of this work was to compare the reactivity of phosphorus trichloride and phosphorus oxychloride in their reactions with sodium *p*-nitrophenoxide. The reaction rate and the reaction rate constant for the synthesis of tris(*p*-nitrophenyl)phosphite were evaluated and compared to the obtained values for the tris(*p*-nitrophenyl)phosphate synthesis. Phosphorus trichloride was found to react faster than phosphorus oxychloride, but the reaction with the phosphorus oxychloride proved to be more exothermic.

Introduction

A modification of a "one-pot" methodology developed for the preparation of triaryl phosphates[1] was applied to the synthesis of tris(*p*-nitrophenyl)phosphite through the reaction of sodium *p*-nitrophenoxide with phosphorus trichloride.

The main purpose of this work was the comparison of the reactivity of phosphorus trichloride with that of phosphorus oxychloride in relation to sodium *p*-nitrophenoxide and to check if the mathematical model developed for the evaluation of the kinetic parameters from the synthesis of triaryl phosphates[2] could be applied to this synthesis.

Discussion

The synthesis reactions were carried out in a Mettler RC1 reaction calorimeter where kinetic evaluations based in the heat flow can be estimated in a noninvasive in-situ way.[3]

The irreversible second-order reactions applied to the synthesis of tris(*p*-nitrophenyl)phosphite and tris(*p*-nitrophenyl)phosphate are outlined in Scheme 1.

Following the methodology showed in Scheme 1, tris(*p*-nitrophenyl)phosphite and tris(*p*-nitrophenyl)phosphate were obtained in 87% and 95% yields, respectively. The enthalpy for the reactions of sodium *p*-nitrophenoxide with 175 mL of 0.5 molar solutions of PCl_3 and $POCl_3$ were −14.59 kJ and −20.29 kJ, respectively. The percentages of the total heat released from these reactions, expressed as heat conversion, are shown in Figure 1.

The synthesis of tris(*p*-nitrophenyl)phosphate is more exothermic than the synthesis of tris(*p*-nitrophenyl)phosphite, but the heat conversion curve shows clearly that, for a specified value of time, the percentage of the total heat released is higher for the reaction of sodium *p*-nitrophenoxide with PCl_3 than for the reaction using $POCl_3$, indicating that the reaction synthesis of the phosphite should be faster.

To verify this observation, the reaction rate and the reaction rate constant k for the tris(*p*-nitrophenyl)phosphite synthesis was estimated using the expressions 1 and 2, respectively.[2]

$$-R_A V = N_{A0}\, dX/dt \tag{1}$$

$$k = \frac{dX}{dt}\,\frac{Vr}{(1 - X)[F_{B0}t - N_{A0}X/3]} \tag{2}$$

The terms dX/dt, $(1 - X)$, and $N_{A0}X/3$, from eq 2, were calculated from the points in the conversion curves. All the data were obtained in intervals of 4 s, so that the term dX/dt was calculated by $dX/dt = (X_{i+1} - X_i)/4$. These results are summarized in Table 1.

The total heat transfer coefficients were nearly the same for both reactions. The intervals presented in Table 1 correspond to the values measured before and after the additions of PCl_3 and $POCl_3$. The rate of dissipative flow was greater than the rate of heat production. The graphs showing these observations are shown as Supporting Information.

The reaction rate constant for the phosphite synthesis ($k_{phosphite}$) was 4 times greater than the reaction rate constant for the phosphate synthesis ($k_{phosphate}$). If these values correspond to the real behavior of the studied reactions, the addition of a solution containing the same molar proportion of PCl_3 and $POCl_3$ over a suspension of sodium *p*-nitrophenoxide would furnish the phosphite and phosphate in yields of 80% and 20%, respectively. This experiment was performed, and the crude product, a mixture of tris(*p*-nitrophenyl)phosphite and tris(*p*-nitrophenyl)phosphate, was analyzed by ^{31}P NMR; the percentage area of tris(*p*-nitrophenyl)phosphite and tris(*p*-nitrophenyl)phosphate signals in the ^{31}P NMR were 77.6 and 22.4%, respectively. These results are in very good agreement with the predicted values of $k_{phosphite}$ and $k_{phosphate}$ given by the mathematical

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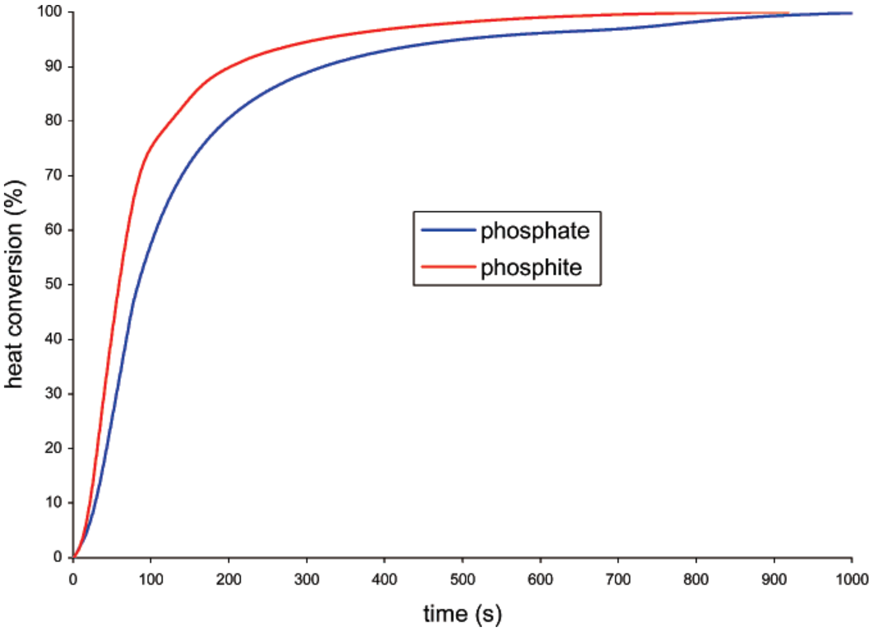

Figure 1. **Heat conversion for the reactions of sodium *p*-nitrophenoxide with PCl_3 (phosphite) and $POCl_3$ (phosphate).**

Scheme 1

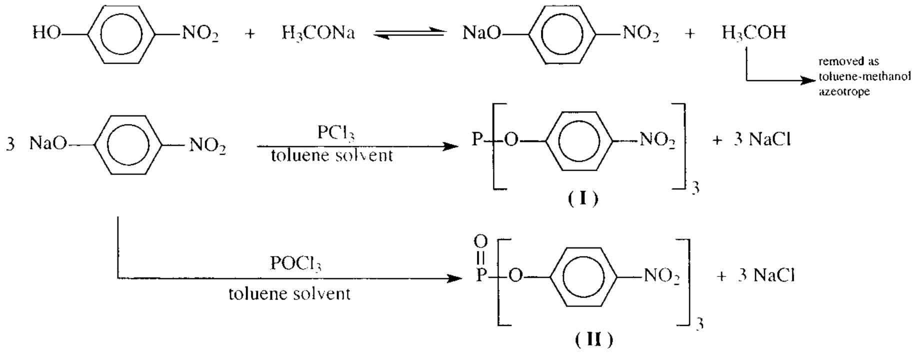

Table 1. **Calculated parameters for systems studied at 45 °C**

product	total heat transfer coefficient, *U* (W/m^2 K)	reaction rate constant, *k* (L/mol s)	reaction rate d*X*/d*t* (s^{-1})	heat of reaction (kJ/kg)
I	143.4−137.5	81.97 ± 10	0.281 ± 0.004	−14.10
II	127.3−133.8	20.81 ± 10	0.200 ± 0.004	−19.55

model as expressed in eq 2. This result validates the mathematical model used to evaluate the kinetics of the studied reactions.

Conclusions

(1) Tris(*p*-nitrophenyl)phosphite was successfully prepared using the one-pot methodology developed for the synthesis of triaryl phosphates.

(2) Phosphorus trichloride was found to react approximately 4 times faster with sodium *p*-nitrophenoxide than with phosphorus oxychloride, as expressed by the ^{31}P NMR results. These experimental values were in total agreement with the predicted values indicated by the reaction rate constants $k_{\text{phosphite}}$ and $k_{\text{phosphate}}$ furnished by the mathematical model used.

Experimental Section

General. Infrared spectra were recorded on a Nicolet 740 FTIR spectrophotometer. ^1H NMR and ^{31}P NMR spectra were recorded on a Brucker HC200 at 200 and 81 MHz, respectively. $CDCl_3$ was used as solvent, and chemical shits were expressed in δ (ppm) units using TMS as internal reference for ^1H spectra and H_3PO_4 (85%) as external reference for ^{31}P.

Tris(*p*-nitrophenyl)phosphite. Toluene (0.8 L) was manually introduced into the RC-1 reactor vessel at 25 °C. The reaction mixture was stirred during the experiment at 150 rpm using an anchor agitator. *p*-Nitrophenol (34.7 g) was added, and the reaction temperature was raised to 30 °C. A solution of 5.75 g (0,25 mol) of sodium in 100 mL of methanol was added. The excess methanol was removed as a toluene−methanol azeotrope (64 °C) by distillation until the temperature reached toluene's boiling point (110 °C). The reaction volume was completed to 0.8 L by the addition of 0.2 L of toluene. 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. The reaction temperature was kept at 45 °C, and then, 170 mL of a 0.5 M solution of phosphorus trichloride in toluene 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. Toluene was removed by distillation. The resulting mixture of solids (sodium chloride and tris(*p*-nitrophenyl)phosphite) was washed with water to remove the sodium chloride. After drying, the product was obtained in 87% yield, mp 171−172 °C (lit.[4] 170−171 °C).

Tris(*p*-nitrophenyl)phosphate. The unique modification in the previous procedure was the addition of a phosphorus oxychloride solution instead of the phosphorus trichloride solution. The product was obtained in 95% yield, mp 153−156 °C (lit.[5] 153−155 °C).

NOMENCLATURE

C = concentration (mol L^{-1})
C_p = heat capacity of reacting mixture at constant pressure (J kg^{-1} K^{-1})
d = density (kg/dm^3)
$\mathrm{d}X/\mathrm{d}t$ = rate of heat release (s^{-1})
$F_{\mathrm{B0}}t$ = number of mols of B added until time t
R_A = reaction rate
k = reaction rate constant for a second-order reaction (L·mol^{-1} s^{-1})
N_i = number of mols of i in the reactor at any given moment t
N_{A0} = the initial number of mols of A in the reactor
$N_{\mathrm{A0}}X$ = number of mols of A that react until time t
$N_{\mathrm{AO}}X$ = number of mols of B that react until time t
R = gas constant
T = temperature (°C)
T_r = reaction temperature (°C)
t = time (seconds)
U = global heat-transfer parameter (W m^{-2} K^{-1})
V_r = reaction volume (L)
X = molar conversion of compound A
X_i = fraction of heat release at time i

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Supporting Information Available

^{31}P NMR of tris(*p*-nitrophenyl)phosphite, tris(*p*-nitrophenyl)phosphate, and their mixture. Graphs showing that the heat dissipative flow is greater than the rate of production of heat for the synthesis of tris(*p*-nitrophenyl)phosphite and tris(*p*-nitrophenyl)phosphate. This material is available free of charge via the Internet at http://pubs.acs.org.

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