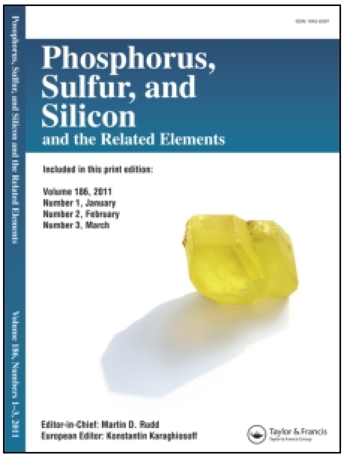

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Monitoring the Phosphorylation of Phenol with Diethyl Chlorophosphate in Aqueous Medium in the Presence of Sodium Hydroxide by in Situ Fourier Transform Infrared Spectroscopy

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MONITORING THE PHOSPHORYLATION OF PHENOL WITH DIETHYL CHLOROPHOSPHATE IN AQUEOUS MEDIUM IN THE PRESENCE OF SODIUM HYDROXIDE BY IN SITU FOURIER TRANSFORM INFRARED SPECTROSCOPY

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In situ Fourier transform IR spectroscopy has been found to be an appropriate tool for monitoring the title reaction resulting in the formation of diethyl phenylphosphate.

Keywords Heterogeneous phase; in situ Fourier transform IR spectroscopy; monitoring; phenol; phosphorylation

INTRODUCTION

In situ Fourier transform (FT) IR spectroscopy is a current method for monitoring organic chemical transformations.[1–8] The time-dependent IR spectra allow the establishment of formal kinetics, detection of intermediates, and optimization of the reaction investigated. Hence, in situ FT-IR spectroscopy is a useful tool in environmentally friendly chemistry. No matter if the reaction mixtures are homogeneous or heterogeneous, they can be studied by the ReactIR 1000 spectrometer supplied with an attenuated total reflection (ATR) probe in the range of –80 to 250°C, even under pressure. In situ FT-IR spectroscopy is becoming a routine method in the pharmaceutical and fine chemical, and even in the plastics industries. In earlier studies, esterifications[6] and oximation reactions[7,8] were investigated. On the one hand, a formal equilibrium constant was determined,[6] while on the other hand, intermediates were pointed out under suitable reaction conditions.[7,8] The reactions were, in all cases, optimized. In situ FT-IR spectroscopy has been applied only rarely in organophosphorus chemistry.[5] We decided to monitor an esterification involving a Schotten–Baumann phosphorylation of phenol. This type of reaction is important in the industrial synthesis of organophosphorus insecticides.[9,10]

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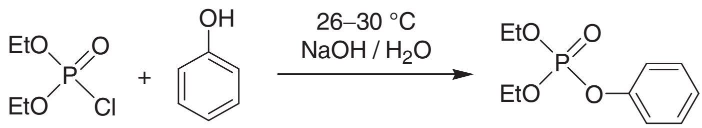
RESULTS AND DISCUSSION

The model reaction to be studied involved the phosphorylation of phenol with diethyl chlorophosphate in the presence of aqueous sodium hydroxide to yield diethyl phenylphosphate (Scheme 1). Under Schotten–Baumann conditions, minor hydrolysis of the phosphoryl chloride is inevitable.



Scheme 1

First the phosphorylation was carried out to prepare diethyl phenylphosphonate using 1.1 eq. of diethyl chlorophosphate and 1.05 eq. of sodium hydroxide in 10% aqueous solution at 5–26°C. According to GC analysis of the crude product, the proportion of $(EtO)_2P(O)OPh$ and $(EtO)_2P(O)OH$ was 9:1. Diethyl phenylphosphate was obtained in 68% yield after the workup procedure.

The next step was to register the IR spectra of the reaction components (phenol, sodium phenolate, diethyl chlorophosphate, and diethyl phenylphosphate). This was done by inserting the probe into the water solution of phenol and sodium phenolate, or placing some oily chlorophosphate and diethyl phenylphosphate on the head of the probe. The spectra obtained are shown in Figure 1, while selected absorptions together with expected

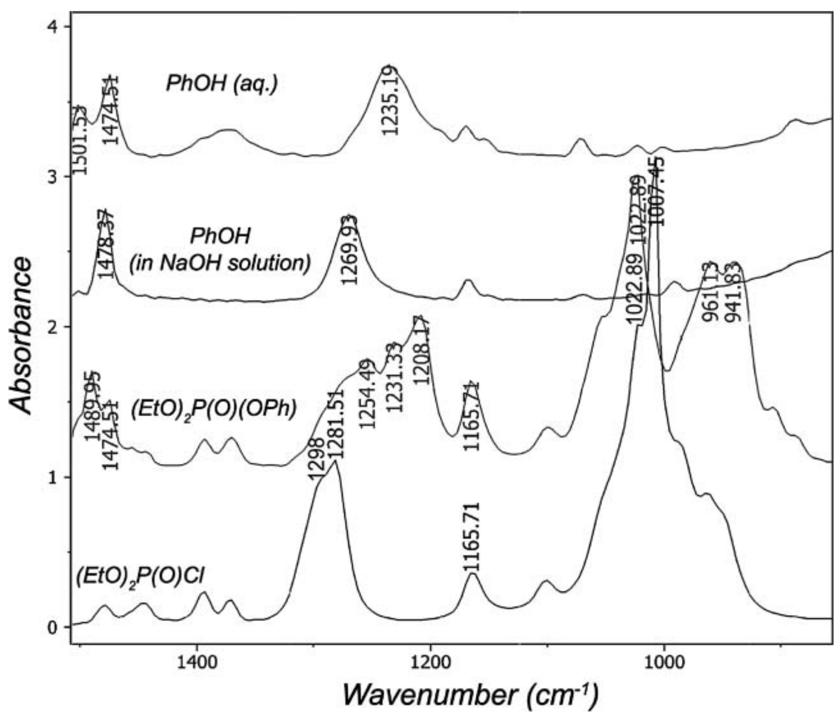


Figure 1 IR spectra for the reaction components measured neatly.

Table I IR absorptions expected and measured for $(EtO)_2P(O)Cl$ and $(EtO)_2P(O)Ph$ (cm^{-1})

	Range[11]	$(EtO)_2P(O)Cl$ (neat)	$(EtO)_2P(O)Ph$ (neat)
$\nu_{P=O}$	1175–1350	1282 (1298)[a]	1180–1320[b]
$\nu_{P–O–C}$ (alkyl)	990–1050	1007, 1023	1023
$\nu_{P–O–C}$ (aryl)	1180–1240	—	1180–1320[b]

[a]Shoulder.
[b]A broad signal results from $\nu_{P=O}/\nu_{P–O–C}$ (aryl) vibrations.

ranges are listed in Table I. Diethyl chlorophosphate revealed intensive absorptions at 1007/1023 and 1282 cm^{-1} due to $\nu_{P–O–C}$ (alkyl) and $\nu_{P=O}$ stretching vibrations, respectively. At the same time, the IR spectrum of the mixed ester showed intensive signals at 1023 and in the range of 1180–1320 cm^{-1}, due to the $\nu_{P–O–C}$ (alkyl) and $\nu_{P=O}/\nu_{P–O–C}$ (aryl) stretching vibrations, respectively. The ester also had absorptions at 961 and 942 cm^{-1}.

Then the phosphorylation reaction was repeated by inserting the probe into the reaction vessel. The mixture of phenol in water was kept at ∼2°C by an ice-water bath. Then diethyl chlorophosphate was added with intensive stirring over ca. 5 min, followed by the addition of aqueous sodium hydroxide over ca. 20 min so that the temperature did not rise above 5°C. Then the bath was removed, and the mixture was stirred further at 26°C for 4 h until completion of the phosphorylation. The reaction was monitored by in situ FT-IR spectroscopy (Figure 2). Appearance of the mixed ester could be seen easily in the 3D diagram, making use of the frequencies at 1208, 961, and 942 cm^{-1} mentioned above. Decreasing bands at 1007 and 1282 cm^{-1} characteristic to the phosphoryl chloride could not be observed in the 3D diagram at the start of the reaction. The broad absorption at 1208 cm^{-1} is the result of the combination of the $\nu_{P=O}$ and $\nu_{P–O–C}$ stretching vibrations of the mixed phosphoric ester. Decrease in the concentration of diethyl chlorophosphate cannot be followed, only the increase in the relative quantity of the diethyl phenylphosphate. The decreasing absorption of $(EtO)_2P(O)Cl$ at 1023 cm^{-1} is suppressed by the increasing band of $(EtO)_2P(O)(OPh)$ at around the same frequency. Formation of the hydrolyzed

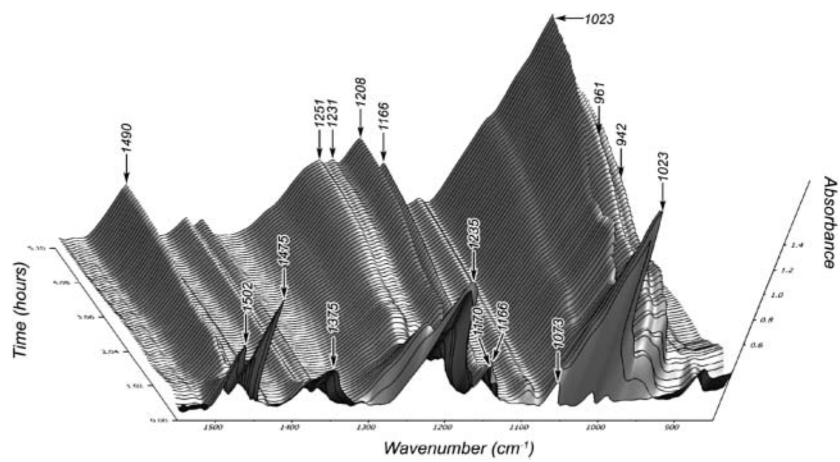


Figure 2 A segment of the time-dependent IR spectrum for the phosphorylation of phenol with diethyl chlorophosphate in water in the presence of sodium hydroxide at 26°C.

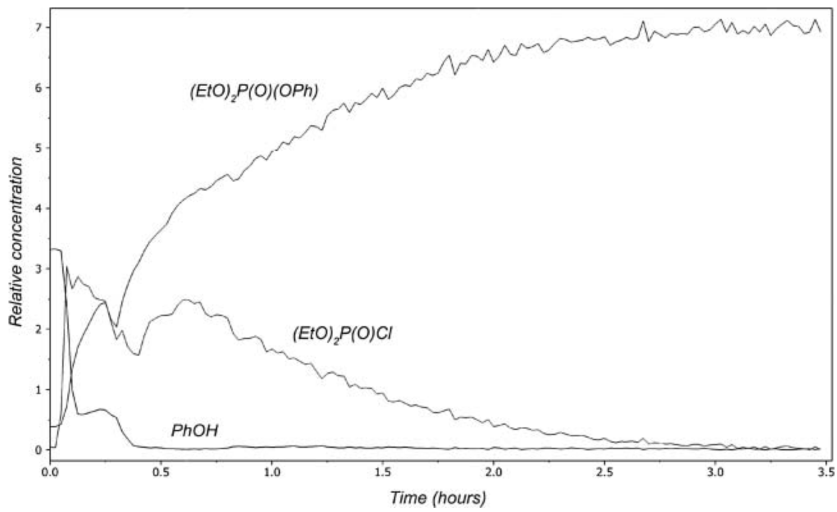


Figure 3 Concentration profile for the reaction of phenol with diethyl chlorophosphate.

byproduct, $(EtO)_2P(O)OH$, formed only in 10% could not be identified in the 3D diagram. The phosphorylation was complete after 3.5 h. The absorbance–time diagram obtained after deconvolution, which is the separation of the overlapping absorption bands of the reaction components, is shown in Figure 3.

It was also possible to reproduce the IR spectra of the reaction components, such as phenol, diethyl chlorophosphate, and diethyl phenylphosphate by deconvolution (Figure 4 and Table II). It can be seen that the real IR spectra of the components are quite similar to those obtained by deconvolution (Figure 1 vs. Figure 4).

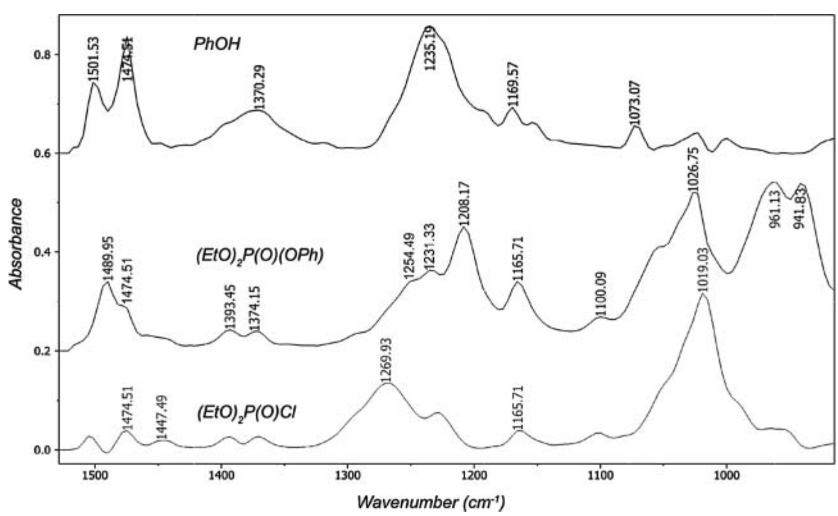


Figure 4 IR spectra for the reaction components obtained from the 3D diagram after deconvolution.

Table II IR absorptions measured and obtained from the 3D diagram after deconvolution (in cm^{-1})

$(EtO)_2P(O)Cl$			PhOH			$(EtO)_2P(O)(OPh)$		
	Obtained after deconv.	Measured		Obtained after deconv.	Measured		Obtained after deconv.	Measured
				1502	1502		1490	1490
				1475	1475		1475	1475
				1371	1378			
$\nu_{P=O}$	1270	1282	$\nu_{P=O}$	1235	1235	$\nu_{P=O}$	1255	1255
						$\nu_{P=O}$	1231	1231
							1208	1208
	1166	1166		1170	1170		1166	1166
$\nu_{P\text{–}O\text{–}C}$	1019	1023		1073	1073	$\nu_{P\text{–}O\text{–}C}$	1027	1023
		1007					961	961
							942	942

In summary, the heterogeneous phase Schotten–Baumann phosphorylation of phenol by diethyl chlorophosphate was monitored by in situ FTIR spectroscopy. The reaction path could be analyzed by a 3D IR spectrum and an absorbance–time diagram.

EXPERIMENTAL

Equipment

In situ Fourier transform IR measurements were carried out using a ReactIR 1000 spectrometer. The ATR measuring head was placed in a 100-mL four-necked flask equipped with a dropping funnel, a condenser, a thermometer, and a magnetic stirrer. The temperature was maintained by using an appropriately adjusted water bath.

Procedure

To phenol (10.8 g, 115.0 mmol) in water (30 mL), diethyl chlorophosphate (18.3 mL, 126.5 mmol) was added dropwise over 5 min with intensive stirring at $\leq 5°C$. Then a solution of sodium hydroxide (4.83 g, 120.75 mmol) in water (43.5 mL) was added dropwise over 20 min so that the temperature did not rise above 5°C. After that, the mixture was allowed to warm up to 26°C. The phosphorylation was complete after a stirring period of 3.5 h.

In the preparative experiment, the mixed ester was extracted with chloroform (2 × 20 mL). The combined extracts were dried (Na_2SO_4) and purified by column chromatography (silica gel, 3% methanol in chloroform) to give 18.0 g (68%) of the diethyl phenylphosphate in a pure form. ^{31}P NMR ($CDCl_3$) δ –6.2; δ_P[ref. 12] ($CDCl_3$) –5.6.

In the monitoring experiment, the ATR measuring head was placed into the flask.

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