Investigation on Model Molecules of the Reactions Induced by Triphenyl Phosphite Addition during Polyester Processing

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ABSTRACT: Reactions between model compounds were carried out at high temperatures (150−250 °C) in order to provide a correct simulation of the behavior of hydroxyl and carboxyl polyester chain ends in the presence of triphenyl phosphite (TPP). The reaction between TPP and alcohol (3-phenyl-1-propanol) leads to phenoxy/alkoxy substitutions on the phosphite. The elimination of phenol in open systems is considered as the driving force of this reaction. The occurrence of multisubstitutions between alcohol and phosphite is confirmed. On the other hand, carboxylic acid (4-*tert*-butylbenzoic acid) reacts with triphosphite to produce ester (or phenyl ester) and phosphonate. The driving force is the creation of a stable phosphoryl bond. NMR experiments lead furthermore to conclusive results concerning the higher velocity of the acid reaction with aliphatic phosphite than of the acid reaction with aromatic phosphite. In the reactions involving alcohol, acid, and phosphite, the conditions favoring ester formation are explained: The presence of TPP is seen to greatly promote the ester production.

Introduction

Phosphites are highly reactive substances that have found fairly extensive use in many fields. These trivalent phosphorus compounds are characterized by their unshared pair of electrons that confers a high degree of chemical reactivity. They serve therefore as intermediates for the synthesis of numerous organophosphorus compounds.[1] In addition to this transient utility, the ease of phosphite oxidation favors their use as antioxidants and peroxide deactivators. Different improvements result from their addition as stabilizers during polymer synthesis or processing: they prevent the polymer discoloration by heat or UV light, reduce the loss of intrinsic viscosity, act as antifoaming agents, ...[2−6] The efficiency of phosphites for inhibition of ester-exchange reactions and deactivation of residual catalysts was also studied.[7,8]

Moreover, phosphites can take a major part in different polymerizations. For example, their role in amidation processes is largely described in the literature.[9−13] In 1975, Yamazaki *et al.*[10] demonstrated the direct polycondensation reaction of dicarboxylic acids and aromatic diamines by using di- or triaryl phosphites. This phosphorylation reaction has been proved to constitute a highly useful laboratory method for the preparation of new polyamides.[14]

By comparison with the numerous applications relating the phosphite action in amidation processes, only a few papers discuss its role in esterification reactions. Syntheses of active esters of amino acids were mentioned in the presence of di- or triphenyl phosphite by reactions in solution from room temperature to 40 °C. Coupling between acid and alcohol was proposed to proceed similarly as described in amidation processes, simply by replacing amine by alcohol functions.[9]

The only reference in the literature concerning reactions between hydroxyl and carboxyl groups with phosphite at high temperatures in the absence of solvent is described by the work of Aharoni *et al.*[15] Their investigations on the PET/TPP system were complemented by a study using model molecules in order to support their proposed reaction mechanism.

A similar approach is followed in this paper. Work has been carried out concerning the influence of triphenyl phosphite addition during melt mixing of polyester blends.[16] Torque measurements during polyester processing and corresponding intrinsic viscosity values have confirmed an expected chain extension. Chromatographic results have similarly indicated a molecular weight increase. However, the precise nature of this chain extension mechanism has been questioned: Chromatographic and calorimetric observations have strongly suggested the formation of two different kinds of linkages, ester bonds and bonds including phosphorus atoms.

In order to obtain conclusive confirmation of this suggestion, experiments between phosphite and model compounds representative of the polyester hydroxyl and carboxyl chain ends have thus been carried out. The reactions occurring at high temperatures in alcohol/acid/phosphite systems are now analyzed under different conditions (reaction in mass, in solution). Comparisons between the conclusions of this study and the literature will finally be discussed.

Experimental Conditions and Materials

Products. 3-Phenyl-1-propanol (PPOL) (Janssen, 98%) was distilled twice and kept under an argon atmosphere. 4-*tert*-Butylbenzoic acid (BBA) was recrystallized twice from petroleum ether and carefully dried at room temperature under vacuum to remove the remaining traces of solvent while avoiding sublimation. Triphenyl phosphite (TPP) (Janssen, 99+%) was always used from a freshly opened bottle in order to avoid phosphite hydrolysis by moisture.

Tetraethylene glycol dimethyl ether (TGDE) (Janssen, 99%) was carefully distilled before use. Acetonitrile is a high-

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performance liquid-chromatography solvent (Lab-Scan). Water is demineralized and purified with a Water-I purification system from Gelman Sciences.

Phenol (Aldrich, 99+%), 4-*tert*-butylbenzoyl chloride (Janssen, 98%), trimethyl phosphite (Janssen, p.a.), triphenyl phosphate (Janssen, 99+%), and tributyl phosphite (Janssen, 95%) were used as received. Diphenyl phosphite (DPP) (Janssen) was also used as received. The presence within DPP of large amounts of phenol and TPP impurities was further confirmed by HPLC and ^{31}P NMR analyses.

Reaction Conditions. For the reactions performed in solution, the solvent used must fulfill different requirements. In addition to a high boiling point and an absence of reaction or degradation at high temperatures, the further analysis of the reaction products by chromatographic techniques requires a miscibility of this solvent with acetonitrile/water mixtures and a low UV absorption around 254 nm. Tetraethylene glycol dimethyl ether (TGDE) was chosen as the appropriate solvent after a careful distillation in order to obtain a purity compatible with the UV detector sensitivity. The lack of appreciable degradation after heating for 90 min at 270 °C was confirmed by preliminary HPLC measurements.

To perform the reactions in solution, TGDE was heated to 250 °C in a four-necked round-bottomed 100 mL flask fitted with an argon inlet, temperature probe, reflux condenser, and magnetic stirrer. Stoichiometric ratios of alcohol (PPOL)/acid (BBA) or alcohol/acid/phosphite (TPP) were introduced. Reactions between alcohol and phosphite were also carried out in molar ratios 1/1 and 3/1. Typical concentrations used were 0.5−2 g in 50 mL of solvent. Reactions were followed by sampling about 1 mL after different times: 1, 5, 10, 20, 30, 60, 90, 120, and 150 min.

Experiments were also conducted without solvent in a closed system by weighing stoichiometric ratios of the compounds into small glass tubes before sealing under vacuum. The tubes were then put into a Schwing furnace where the temperature is regulated at ±2 deg. Alcohol/acid and alcohol/acid/phosphite reactions were therefore analyzed after different treatments: 10 min at 150, 210, and 245 °C or 30 min at 245 °C.

Some reactions between alcohol, acid, and phosphite were also carried out in a four-necked round-bottomed 50 mL flask fitted with argon inlet, reflux condenser, and magnetic stirrer. The reactor was heated to the desired temperature in a regulated silicone oil bath. Samples were removed periodically and held under inert atmosphere in order to monitor the progress of the reaction. Some were kept in the freezer (−30 °C) during the time preceding the NMR analysis in order to determine the possible evolution of the reaction at room temperature.

Chromatographic Analysis. The reverse-phase high-performance liquid chromatography (HPLC) system consists of a Millipore-Waters model 510 pump controlled by a Millipore-Waters System Controller, a Gilson sample injector model 231, a Lichrosorb RP-18 column (Merck) (silica grafted with C_{18} hydrocarbons) and a Perkin-Elmer LC55 UV detector used at 254 nm. A gradient elution with acetonitrile (solvent A) and water/acetonitrile 80/20 (v/v) (solvent B) was used at a flow rate of 1 mL min^{-1}. Model compound samples were dissolved in acetonitrile. Toluene was used as the internal standard. The injected volume was about 100 μL. The results were analyzed by a Trivector computer.

In order to follow the disappearance of initial compounds, calibrations between peak area ratios and species concentrations were previously realized for PPOL, BBA, and TPP. Therefore, it was possible to express the results as a remaining percentage of the initial quantities. The presence of water in the composition of the eluent phase did not disturb the analysis of triphenyl phosphite: accurate TPP calibrations were obtained.

For the appearance of new products during the reactions, the measurements were normalized with regard to the initial alcohol concentration. They were therefore expressed in arbitrary units. Due to the difference in extinction coefficients, suitable quantitative comparisons between different chemicals cannot be realized. On the other hand, relative comparisons were possible for the defined chemicals between different experiments.

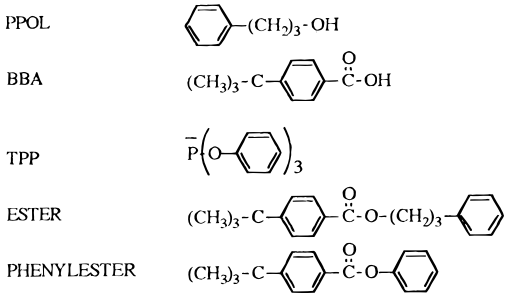


Figure 1. Selected model compounds (BBA, PPOL, TPP) and different esters produced during the reactions ("ester", "phenyl ester").

Table 1. Retention Times Measured in HPLC for the Different Compounds

chemicals	retention time (s)	chemicals	retention time (s)
phenol	366	TPP	2002
PPOL	586	phenyl ester	2002
BBA	1010	ester	2140
DPP	1296	PPOL/TPP	2140
toluene (standard)	1460		

NMR Measurements. ^{31}P nuclear magnetic resonance spectra were recorded on a Bruker AM500 spectrometer at 202.49 MHz in deuteriochloroform as solvent operated in the inverse gate decoupling mode. The experimental setting was as follows: spectral width = 45 000 Hz, pulse width = 5 μs (30°), and relaxation delay = 10 s. ^{31}P chemical shifts are expressed as positive downfield from the external standard (85% H_3PO_4). The samples were prepared with a sufficient concentration in order to accurately carry out quantitative measurements.

Infrared Spectroscopy. Samples were analyzed in NaCl windows. Spectra were recorded in a 580B dispersive Perkin-Elmer spectrometer, controlled by a 3600 Data Station microprocessor. Software from Perkin-Elmer (PE580) is used for data collection, storage, and analysis.

Results

The high boiling point of the selected model compounds allows a correct simulation of high-temperature reactions. Furthermore, the presence of an aromatic ring in their structure ensures the detection by the HPLC UV detector.

The aliphatic alcohol 3-phenyl-1-propanol (PPOL) and the aromatic acid 4-*tert*-butylbenzoic acid (BBA), respectively, simulate the hydroxyl and carboxyl polyester chain ends. Two different esters will be identified as products of the reactions. They will be designated in this work as "ester" and "phenyl ester", respectively (Figure 1).

Chromatographic Study. Peak Assignment. Different experiments were conducted in solution under an inert atmosphere or in sealed tubes under vacuum. Retention times were determined for the used elution program and are displayed in Table 1.

The retention time of diphenyl phosphite (DPP) was determined as 1296 s. However, the closeness of the BBA retention time, combined with the small extinction coefficient of DPP, prevents the observation of its appearance during the high-temperature reactions. Deformations observed in the shape of the BBA peak are caused by fluctuations in the acid protonation; no useful results could be obtained for acid quantification.

In order to identify ester and phenyl ester, their syntheses were first realized by reactions between acid

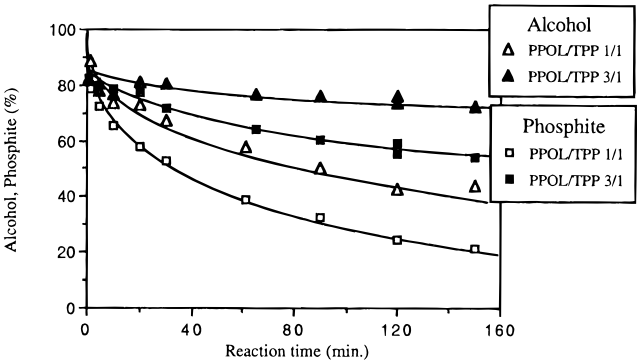


Figure 2. Evolution of the alcohol (△, ▲) and phosphite (□, ■) disappearance (expressed in percentage of the initial amounts) during reactions carried out in solution at 250 °C between alcohol and phosphite with different molar ratios (1/1 and 3/1).

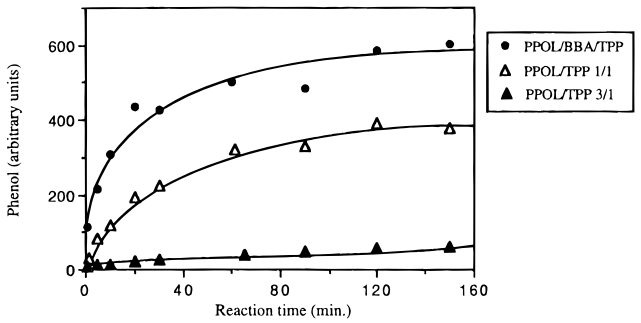


Figure 3. Evolution of the phenol formation during different reactions carried out in solution at 250 °C.

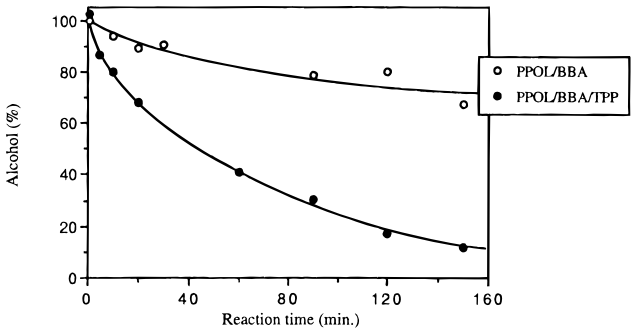


Figure 4. Evolution of the alcohol disappearance (expressed in percentage of the initial amounts) during reactions carried out in solution at 250 °C between equimolar ratios of alcohol and acid with or without the presence of phosphite.

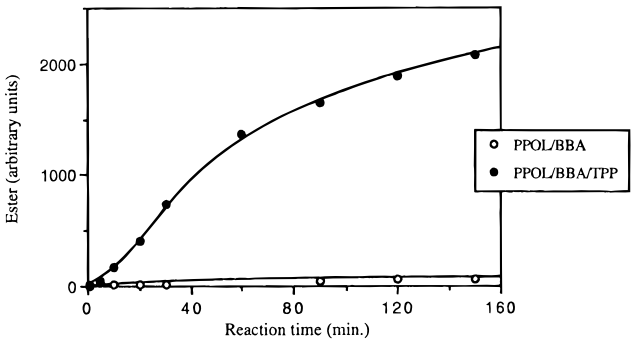


Figure 5. Evolution of the ester formation during reactions carried out in solution at 250 °C between equimolar ratios of alcohol and acid with or without the presence of phosphite.

chloride and alcohol or phenol. Afterward, HPLC analyses confirmed the perfect similarity of the retention times of these pure products with the retention times of products observed after high-temperature reactions, i.e. 2140 and 2002 s, respectively.

Under the chromatographic conditions used, identical retention times are observed for TPP and phenyl ester. This point will be considered for the quantification of the phenyl ester formation (see below). Finally, it is worth remarking that the results expressed in arbitrary units only allow quantitative comparisons for the same compound between different experiments.

Solution Reactions. Alcohol/Phosphite Reactions. The reactions conducted at 250 °C in TGDE solution between TPP and alcohol can be followed by the disappearance of these compounds (Figure 2). Increasing amounts of phenol are also detected (Figure 3). The appearance of a new chemical, most probably resulting from a substitution between alcohol and phosphite, is also observed. Its retention time is identical to the one of the ester (2140 s).

All analyses indicate that the extent of reaction was more important with the PPOL/TPP in equimolar ratio.

Alcohol/Acid/Phosphite Reaction. Reactions conducted in TGDE solution at 250 °C between equimolar amounts of alcohol/acid or alcohol/acid/TPP were also analyzed. Quantification of the remaining alcohol shows clearly that the presence of TPP strongly increases the alcohol consumption rate (Figure 4). Moreover, Figure 5 shows a much larger ester formation.

However, similar retention times (2140 s) were observed for the ester and the compound appearing in PPOL/TPP reactions. This can interfere with the ester quantification realized in the PPOL/BBA/TPP system. The importance of PPOL/TPP reactions can indeed not be neglected a priori, and the peak observed after 2140 s may not therefore fully result from ester formation. In order to determine the importance of this disturbance, quantitative measurements of the concerned peak were realized in all systems.

These comparisons reveal that the compound resulting from PPOL/TPP reactions only concerns small quantities compared to those measured in the PPOL/BBA/TPP system (≈1.3%). Therefore, although the appearance of a different product with identical retention time decreases the calculation precision, the peak observed after 2140 s in the PPOL/BBA/TPP reaction can almost totally be considered as corresponding to ester formation. The conclusions expressed above need not be modified: ester formation is largely favored by the TPP addition.

The formation of phenol and phenyl ester is also observed in alcohol/acid/phosphite systems (Figures 3 and 6). Phenol should most probably be produced by PPOL/TPP substitution reactions.

The peak observed with a retention time of 2002 s can be attributed to the presence of both TPP and phenyl ester. Accurate quantification of the phenyl ester formation can thus not be simply deduced. However, the progressive TPP consumption by reaction with alcohol and/or acid is assumed to be quite rapid and, therefore, greatly reduces its contribution to the considered peak. Consequently, the large increase starting after 20−30 min can be attributed most principally to the formation of large amounts of phenyl ester (Figure 6). The influence of the remaining TPP is then assumed to become negligible. Quantification of the phenyl ester formation was thus realized for reaction times equal to or greater than 20 min. The precise shape of this curve cannot be deduced for lower reaction times, however. Only the absence of phenyl ester for $t = 0$ can be assumed.

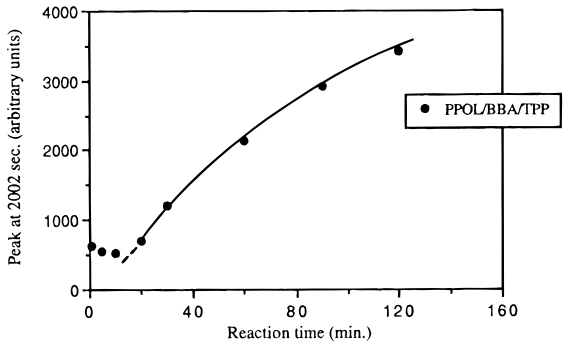


Figure 6. Evolution of the formation of the peak observed with 2002 s retention time during the reaction carried out in solution at 250 °C between equimolar ratios of alcohol, acid, and phosphite. (The curve represents the appearance of phenyl ester during the reaction.)

Table 2. Quantification (Expressed in Arbitrary Units) of the Formation of New Products during Reactions Carried out in a Closed System between Alcohol and Acid, with or without Phosphite[a]

		phenol	ester	phenyl ester
reacn PPOL/BBA	10 min at 150 °C		678	
	10 min at 210 °C		8 996	
	10 min at 245 °C		13 225	
	30 min at 245 °C		18 703	
reacn PPOL/ BBA/TPP	10 min at 150 °C	777	1 749	1 838
	10 min at 210 °C	848	9 692	6 661
	10 min at 245 °C	1338	11 180	23 842
	30 min at 245 °C	1448	13 583	25 958

[a] Nevertheless, due to procedure difference, no quantitative comparisons can be realized with the experiments conducted in solution.

Sealed Tube Reactions. The reaction between alcohol and acid with or without phosphite was also carried out in tubes sealed under vacuum. The results presented in Table 2 allow comparisons between various conditions (10 or 30 min at 150, 210, or 245 °C) concerning the appearance of different chemicals. Imprecisions caused by the possible confusion between ester and another unidentified reaction product (peak at 2140 s retention time, already discussed above) mean that the measured ester values in PPOL/BBA/TPP systems are upper limits for the real amounts present.

In the presence of phosphite, a higher temperature or a longer reaction time increases the quantity of phenol and phenyl ester produced. Ester formation is favored by the phosphite addition for smooth reaction conditions (150 or 210 °C). However, the experiments carried out at a higher temperature (245 °C) reveal that the presence of TPP reduces the esterification process, more probably by allowing the possibility of phenyl ester creation.

These observations realized for closed systems differ from those coming out of reactions conducted in solution. This difference in influence of phosphite concerning the esterification reaction will be discussed later.

^{31}P NMR Experiments. Peak Assignment. Reactions between model compounds were conducted without solvent under an inert atmosphere at 190, 210, or 230 °C. Samples were withdrawn after different times and analyzed by ^{31}P NMR. Reproducibility of this NMR technique was successfully checked.

The assignment of the observed peaks, displayed in Tables 3 and 4, was realized by reference to the literature,[17−19] also considering that atoms or groups distant from those attached directly to the phosphorus atom under investigation exert little or no effect on ^{31}P chemical shifts.[19]

Table 3. ^{31}P NMR Chemical Shifts for the Phosphorus-Containing Reagents and Exchange Products

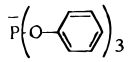
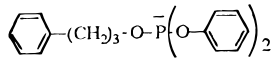
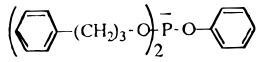
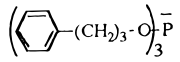
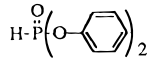
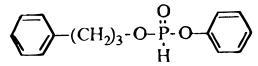
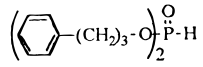
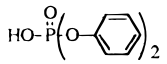
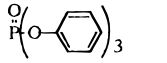
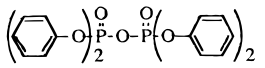
	128.8 ppm
	130.0 ppm
	135.2 ppm
	140.1 ppm
	1.0 ppm
	4.9 ppm
	8.6 ppm

Table 4. ^{31}P NMR Chemical Shifts for the Oxidized Phosphorus-Containing Products

	-10.7 ppm
	-17.3 ppm
	-25.2 ppm

Some peaks were identified by using pure reference compounds: chemical shifts of tributyl phosphite ($P(O\text{-}Bu)_3$), trimethyl phosphite ($P(OMe)_3$), and dibutyl phosphite ($HP(O)(OBu)_2$) were observed at 139.0, 140.7, and 7.7 ppm, respectively.

Triphenyl phosphite coming from a freshly opened bottle shows a single peak at 128.8 ppm, confirming its purity and the anhydrous character of the $CDCl_3$ used. The peak corresponding to diphenyl phosphite (DPP) is observed at 1.0 ppm. Some impurities present in DPP were also identified: DPP contains triphenyl phosphite and small amounts of triphenyl phosphate (chemical shift at −17.3 ppm). After contact with air moisture, TPP is hydrolyzed to DPP. Furthermore, a preliminary experiment confirmed that a prolonged reflux (7 h) of a mixture of TPP and water under air lead to a complete hydrolysis and to formation of phenol and phosphorus and phosphoric acids. However, heating under inert atmosphere for 2 h at 230 °C did not induce any TPP modification.

Alcohol/Phosphite Reactions. After reaction between PPOL and TPP, new ^{31}P NMR peaks appear at 140.1, 135.2, and 130.0 ppm. Neither other important peaks nor further hydrolysis or oxidation was observed, confirming thereby the simplicity of the chemical transformations.

The identification of the new compounds (Table 3) revealed a substitution process between the phenoxy groups of the triphenyl phosphite and the alkoxy groups of the alcohol. Due to the three potential reactive groups present in TPP, experiments carried out with the alcohol/phosphite 3/1 molar ratio lead to extended substitutions (Figure 7). The peak attributed to dialkyl aryl phosphite (135.2 ppm) is often present in smaller

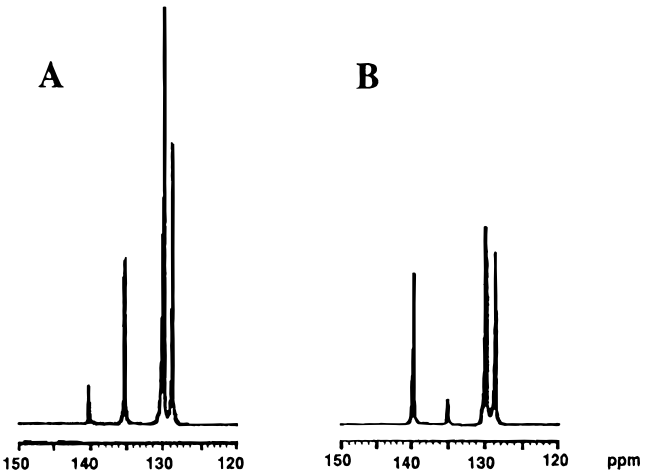


Figure 7. ^{31}P NMR spectra of the reactions carried out for 2 h at 230 °C between PPOL and TPP with different molar ratios: (A) alcohol/phosphite 1/1 (equimolar amounts); (B) alcohol/phosphite 3/1.

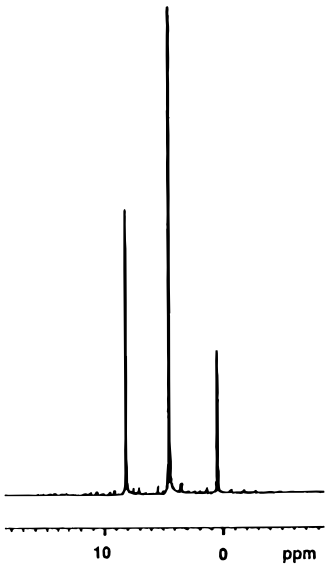


Figure 8. ^{31}P NMR spectrum of the reaction carried out for 30 s at 210 °C between equimolar amounts of alcohol and DPP.

amounts. At room temperature, this reaction (largely reduced) was also observed.

The extent of this substitution reaction is not easily reproducible. While some syntheses show a large transformation from triaryl to trialkyl phosphite, corresponding to an almost complete alcohol consumption, other experiments only lead to limited modifications. In these cases, a reaction time increase does not substantially enhance the substitution process. This discrepancy was observed independently of the alcohol/phosphite molecular ratio used (1/1 and 3/1). A higher reaction temperature (230 °C) seems to favor the substitution process.

The phenoxy/alkoxy substitution is also observed between diphenyl phosphite (DPP) and alcohol with the appearance of peaks at 8.6 and 4.9 ppm. This reaction involving phosphonates was observed to proceed to completion (Figure 8). Moreover, it cannot be neglected at room temperature. It becomes difficult therefore to determine if complete reaction was already realized after 1 min at 210 °C or was continued at room temperature during the time preceding the NMR analysis. Anyway, the substitution between PPOL and phosphonates is conclusively shown to occur rapidly.

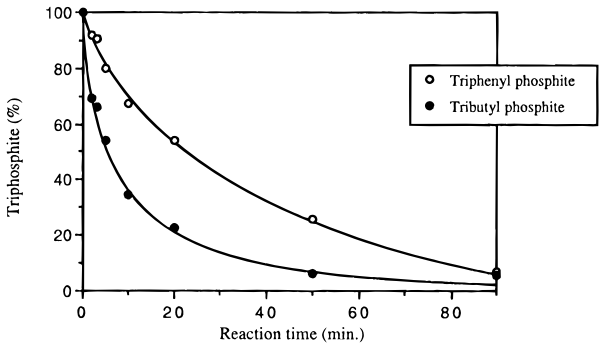


Figure 9. Evolution versus time of the percentage of unreacted triphosphite during reactions carried out at 190 °C between equimolar amounts of acid and triphenyl or tributyl phosphite.

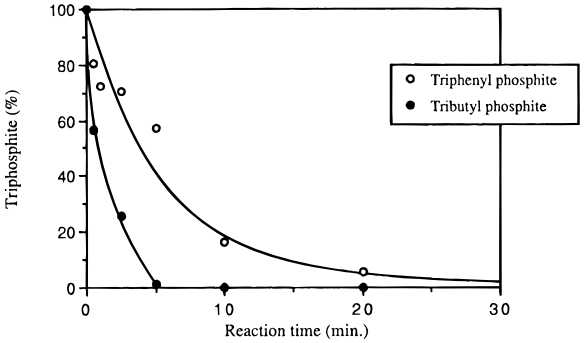


Figure 10. Evolution versus time of the percentage of unreacted triphosphite during reactions carried out at 210 °C between equimolar amounts of acid and triphenyl or tributyl phosphite.

Table 5. Kinetic Constants (Deduced from ^{31}P NMR Measurements) of the Reaction between Acid and Triphenyl or Tributyl Phosphite Carried out at 190 or 210 °C (min^{-1})

	190 °C	210 °C
triphenyl phosphite	0.029	0.146
tributyl phosphite	0.071	0.803

Acid/Phosphite Reactions. The reaction between acid and triphenyl phosphite leads to TPP disappearance and DPP formation (peak at 1.0 ppm). Similarly, dibutyl phosphite appears after reaction between acid and tributyl phosphite. Consequently, the presence of acid results in a transformation of the phosphorus compounds from triphosphite (P^{III}) into phosphonate (P^{V}).

An investigation was carried out at two temperatures (190 and 210 °C) concerning how the kinetics of this acid/triphosphite reaction depends on the nature of the phosphite substituents. The results (Figure 9 and 10) conclusively prove a higher reactivity for the trialkyl phosphite at both temperatures. The first-order character with regard to the triphosphite (1) was verified, and measurements of the kinetics constant are displayed in Table 5.

$$-\frac{\mathrm{d[P]}}{\mathrm{d}t} = k[\mathrm{P}] \qquad (1)$$

where [P] is the triphosphite concentration.

A higher temperature increases the reaction rate but particularly increases the reactivity difference observed between trialkyl and triaryl phosphite.

Beyond this initial reaction between acid and triphosphite, many modifications can occur due to second-

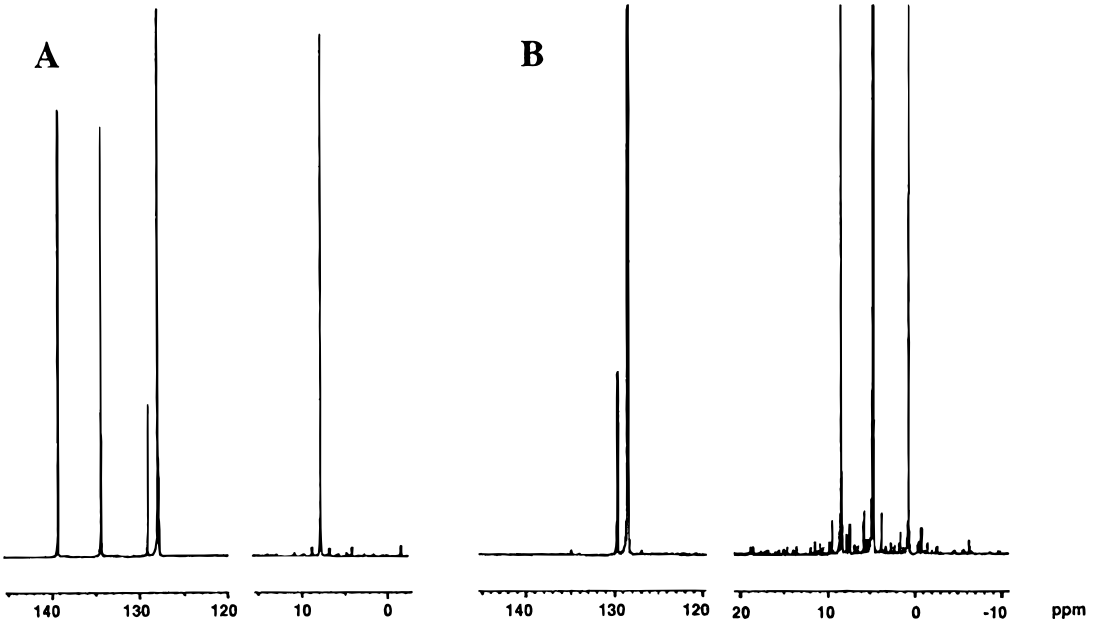


Figure 11. ^{31}P NMR spectra of the reaction carried out at 210 °C between equimolar amounts of PPOL, BBA, and TPP: (A) 10 min reaction; (B) 50 min reaction.

ary processes involving phosphorus compounds. Their importance increases of course with the reaction temperature. An orange-red color and a precipitate sometimes appear, especially during long-time reactions. Some major peaks were observed at −10.7, −17.3, and −25.2 ppm. Their assignment is reported in Table 4.

As a result of a separate analysis of the commercial compound, the peak at −17.3 ppm was undeniably attributed to triphenyl phosphate. In addition to the correspondence with the literature data,[17,18,20] different observations were considered for the assignment of the two other peaks. First, the peak at −10.7 ppm appeared before the one at −25.2 ppm, the latter growing considerably with reaction time. Furthermore, when exposed to air moisture, the samples revealed a large decrease of the peak at −25.2 ppm, counterbalanced by an increase of the other peak. Finally, the peak at −25.2 ppm is very intense after a heating for 2 h at 230 °C of DPP alone.

Those compounds result from secondary reactions observed after prolonged heat exposure at 230 °C and can quite easily be avoided at lower temperatures (190, 210 °C). Extensive investigations concerning the mechanisms of formation and the identification of all secondary byproducts were not realized.

Alcohol/Acid/Phosphite Reactions. ^{31}P NMR analyses of the reactions carried out between the PPOL, BBA, and TPP revealed the appearance of chemical shifts similar to those observed in alcohol/phosphite or acid/phosphite systems. Other peaks with significant intensities were not detected. Secondary reactions, as seen in acid/phosphite systems, appeared reduced. Analysis of reactions carried out at different temperatures revealed many similarities but some differences.

In an experiment at 210 °C, TPP substitutions (peaks at 130.0, 135.2, and 140.1 ppm) and dialiphatic phosphite (peak at 8.6 ppm) were rapidly observed (Figure 11) and increased with reaction time. As the transformation into phosphonates by acid reaction reduces the triphosphite quantity, aromatic−aliphatic diphosphite and DPP successively appear (peaks at 4.9 and 1.0 ppm) and progressively dominate the phosphorus compounds present in the system.

However, another synthesis conducted at 210 °C showed a very limited presence of substituted triphosphites. Nevertheless, dialiphatic phosphite was rapidly observed and other diphosphites (4.9 and 1.0 ppm) successively appeared. For prolonged reaction times (10 to 90 min), the peaks corresponding to the two latter diphosphites increased to a considerable extent while the dialiphatic phosphite amount (peak at 8.6 ppm) decreased. This point could suggest an equilibrium or an exchange process between the three phosphonate species.

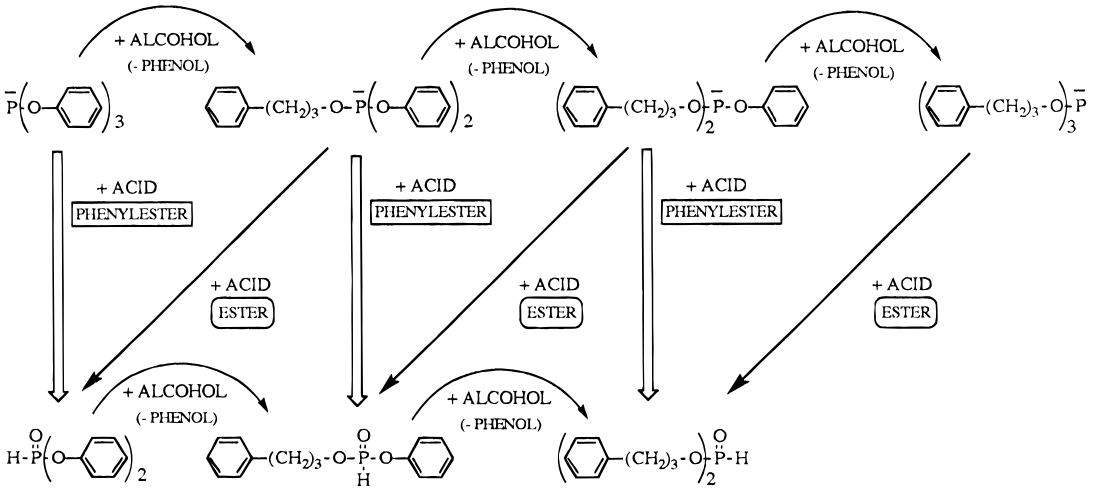
The triphosphite transformations into phosphonate were quantified and a kinetic constant was calculated. The obtained value was $k = 0.046$, strongly reduced by comparison to those measured in acid/triphosphite reactions at 210 °C (Table 5).

Infrared Experiments. Some reactions carried out without solvent at 230 °C were also analyzed by infrared spectroscopy. Chemical modifications were detected by comparisons between spectra of the pure compounds. Assignment of the different absorbance peaks was realized according to the literature.[21−24] It must be first noticed that the 940−1000 cm^{-1} range is not sufficient for diagnostic purposes in IR spectroscopy of phosphorus compounds. The peaks can indeed be attributed to many different bonds (P−OH, P=O, P−O−P, P−O−C). The precise nature of the bond must thus be proved by the presence of another characteristic peak in a different wavelength range, e.g. 2450 cm^{-1} for a P−H bond.

The reaction between alcohol and TPP still shows the maintenance of phosphorus with an unshared pair of electrons (P^{III}−O−Ph bond at 858 cm^{-1}) but suggests substitutions between PPOL and TPP (P−O−C_{alkyl} bond at 1050−970 cm^{-1}). Phenol production is observed (1388 cm^{-1}) and phosphonates are not detected: no peak at 1278 (P=O), 947 (P^{V}−O−Ph) or 2450 cm^{-1} (P−H).

Few modifications can be noticed after DPP reaction with alcohol: phenol, initially present in DPP, is still observed (1367 cm^{-1}). The presence of aromatic phosphonate is also confirmed: P−H and P^{V}−O−Ph bonds at 2441 and 940 cm^{-1}, respectively. Suggestion of aliphatic phosphonate creation is supported by the

Scheme 1. Synthesis of the Possible Pathways Explaining the Formation of the Different Phosphorus Compounds Observed by ^{31}P NMR in the Reactions Involving Alcohol, Acid, and Phosphite



peaks at 993 cm^{-1} (P—O—C_{alkyl} bond) and at 1244 cm^{-1} (P═O bond in P—O—C_{alkyl} compounds).

Reactions between acid and triphosphites were also investigated. The disappearance of COOH (1691 cm^{-1}) is confirmed. In the BBA/tributyl phosphite system, aromatic/aliphatic ester is produced (1720 cm^{-1}), as well as aliphatic phosphonate (P—H, P═O, and P—O—C_{alkyl} bonds at 2424, 1278, and 980 cm^{-1}, respectively). Similarly, in the BBA/triphenyl phosphite reaction, aromatic/aromatic ester (1735 cm^{-1}) and aromatic phosphonate (P—H and P^{v}—O—Ph bonds at 2441 and 945 cm^{-1}, respectively) appear.

Similar consequences of an extended heating were observed in pure DPP or BBA/TPP systems: the P—H bond (2450 cm^{-1}) disappears and peaks at 1296 and 969 cm^{-1} are observed. They could respectively be attributed to P═O and P—O—P bonds in $(PhO)_2$—P(O)—O—P(O)—$(OPh)_2$. The creation of tetraphenyl pyrophosphate is thus not rejected by the infrared analysis.

Useful information can also be deduced from analysis of alcohols/acid/TPP systems: peaks corresponding to P^{III} (862 cm^{-1}) and carboxyl function (1691 cm^{-1}) disappear. Two different kinds of ester bonds were produced: aromatic—aromatic (1736 cm^{-1}) and aromatic—aliphatic (1718 cm^{-1}). More information cannot be extracted from the infrared spectrum, due to the large number of peaks resulting from the presence of many different chemicals.

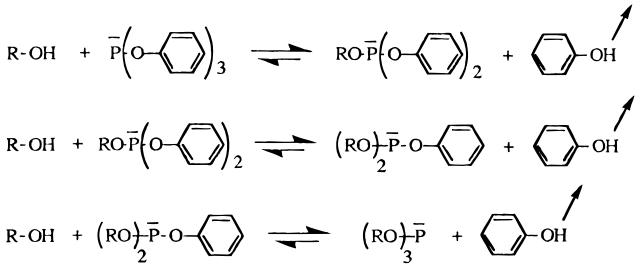
In brief, infrared spectroscopy observations realized on the investigated reactions are fully in accordance with measurements obtained by other techniques and support particularly well the ^{31}P NMR results.

Discussion

NMR Measurements. ^{31}P NMR allows the identification of the phosphorus compounds produced during the main reactions involving triphenyl phosphite, alcohol, and acid (Table 3). Scheme 1 displays the possible reaction pathways between them.

Triphosphites are represented in the upper line. Diphosphites (lower line) are not usually present as trivalent pyramidal derivatives ($(RO)_2POH$) but exist substantially in the stable tetrahedral phosphonate form ($(RO)_2P(O)H$).[25,26] Absorption bands characteristic of P═O and P—H bonds are present in IR spectroscopy[21] and ^{31}P NMR measurements show more than 95% of the molecules with the hydrogen directly attached to the phosphorus atom.[19] This verifies the very large displacement of the tautomeric equilibrium in favor of the phosphonate form. This explains for example the lack of oxidizability of these compounds.

Scheme 2. Reaction Mechanisms between Phosphite and Alcohol (R- as Ph—$(CH_2)_3$—)



Transformation of one compound to another is indicated in different ways: curve lines for alcohol reaction and vertical or oblique arrows for acid reaction on a phenoxy or alkoxy site of the triphosphite, respectively.

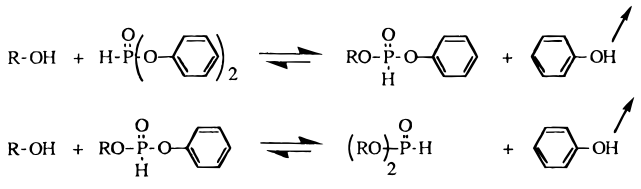
In addition to these reactions, triphosphites are subject to hydrolysis.[1,5−6,27,28] Contact between triphenyl phosphite and air moisture indeed induces its transformation into phosphonate. However, care was taken to avoid such modifications during our experiments and hydrolysis will not be considered during this discussion.

The reactions between alcohol and TPP lead to triphosphite substitutions (Scheme 2). The redox level of the P atom is not modified: phosphorus keeps its unshared pair of electrons. Secondary reactions, such as isomerization of the phosphite,[29] were not observed in our experiments. According to the literature,[30] our measurements show that the displacements occur rapidly. We even observe a small reaction at room temperature.

Such reactions totally confirm the previous results described in the literature: phenoxy/alkoxy interchanges were indeed observed between TPP and bis(2-hydroxyethyl)terephthalate after 5 min at 275 °C.[15] A rapid but incomplete exchange was also noticed between TPP and *p*-chlorophenol in solution at 100 °C.[13] Furthermore, some phosphite species are prepared by this transesterification process.[28,31]

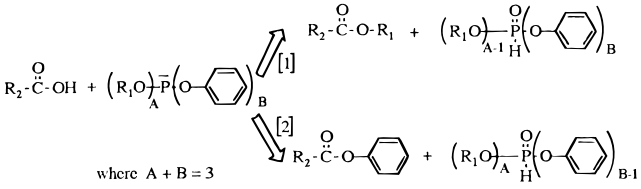
Our observations support the hypothesis of a fast equilibrated reaction. Phenol elimination can be considered as the driving force for the substitution process.

Scheme 3. Reaction Mechanisms between Phosphonate and Alcohol (R- as Ph−$(CH_2)_3$−)



Scheme 4. Substitution Reaction between Different Phosphonate Species

Scheme 5. Reaction Mechanism between Phosphite and Acid (R_1−, R_2− as Ph−$(CH_2)_3$− and $(CH_3)_3$−C−Ph−, respectively)



Differences between experiments can lie in the fact that our synthesis conditions cannot really be considered as representing a totally open system and that parameters favoring the phenol elimination can thus not totally be controlled. However, it can readily be assumed that an increased reaction temperature promotes the equilibrium displacement. Should this be total, complete substitution could logically be observed.

The reaction between alcohol and diphenyl phosphite (Scheme 3) occurs similarly.[15,32,33] The substitution velocity was also observed: holding for 1 min at 210 °C is enough to induce important displacements on the phosphonate, and reaction was even observed at room temperature. Easy phenol elimination is also proposed as a driving force for an extended substitution process.

Besides this reaction involving alcohol, analysis at extended reaction times shows the progressive decrease of the dialiphatic phosphite and the corresponding increase of other phosphonates. This observation could be attributed to exchange reactions between the different phosphonate species (Scheme 4).

Reactions between carboxylic acid and triphosphite lead to ester (or phenyl ester) and phosphonate formation[13,15,34] (Scheme 5). Such modification from a phosphite with an unshared pair of electrons to a phosphorus atom tetrahedrally connected corresponds to a transition from the upper to the lower line in Scheme 1. The creation of a very stable phosphoryl (P═O) linkages constitutes the driving force of this evolution.[27] Carboxylic acid solvents must therefore be avoided in analyses.

Depending on whether the acid reacts on an alkoxy or phenoxy substituent on the phosphite, ester or phenyl ester is produced. Our investigations clearly showed a faster reaction with tributyl than triphenyl phosphite. The reactivity difference observed is furthermore emphasized by a temperature increase. The presence of aryloxy substituents, more electron-attracting than alkoxy groups,[35] and the following weaker nucleophile action of the phenoxy groups, can explain the triphenyl phosphite lower reactivity.

Therefore, although complementary measurements with other phosphites would be useful, it can be proposed that higher acid reactivity appears on the phosphite alkoxy site in comparison with the phenoxy site. This means that, in Scheme 1, oblique arrows correspond to the highest reactivity.

Beyond the triphosphite transformation to phosphonate, additional reactions were observed. Appearance of triphenyl and diphenyl phosphates (chemical shifts at −17.3 and −10.7 ppm) results from triphenyl and diphenyl phosphite oxidation processes, respectively. Production of tetraphenyl pyrophosphate (−25.2 ppm) occurs afterward. In the presence of moisture, hydrolysis changes it to diphenyl phosphate. Anyway, those reactions can be avoided or at least largely reduced, e.g. by lowering the temperature. This point confirms that they only constitute supplementary modifications and that the nature of the main reaction between acid and triphosphite is not questioned.

In alcohol/acid/TPP systems, the almost immediate formation of dialkyl phosphonate, considered as an end product of the main reactions, is a sign of rapid evolution (Scheme 1). Several pathways can be considered concerning modifications from triphenyl phosphite to dialkyl phosphonate. However, they can be summarized in two distinct options.

The first possibility consists of significant substitutions between triphenyl phosphite and alcohol, followed by an acid reaction on the alkoxy site of the triphosphite and ester formation (as suggested by Figure 11). Different elements favor this option: an easy phenol elimination, especially at high temperatures, largely displaces the equilibrium and leads to rapid and extensive exchanges on the triphosphite. Moreover, a higher acid reactivity is also exerted toward trialkyl phosphite, especially at higher temperatures.

The alternative scheme presents a reverse reaction order: triphenyl phosphite and acid directly produce phenyl ester and further phosphonate substitutions with alcohol lead to dialkyl phosphite appearance. This less favored mechanism can nevertheless prevail if reduced alcohol/triphosphite reactions occur, due to a limited equilibrium displacement.

In brief, two distinct mechanisms are possible. The ease of phenol elimination rules the extent of triphosphite substitution and will determine the predominant reaction scheme. In short, a high temperature in an open system favors twice the pathway involving ester formation.

Chromatographic Experiments. The HPLC experiments throw a different light on the reactions carried out between model compounds. Those observations afford a complementary point of view toward the mechanisms deduced from NMR measurements.

In alcohol/phosphite systems, PPOL and TPP consumption throughout the reaction (Figure 2), phenol production (Figure 3), and appearance of a new compound (2140 s retention time), assigned as a result of the substitution process, constitute different illustrations of the exchange mechanisms described in Scheme 2. Furthermore, HPLC results corroborate the existence of an equilibrium-controlled reaction. The variations observed between PPOL/TPP experiments carried out in solution with different molar ratios (Figure 2) can be explained by the absence of fully open conditions in the reaction system (and the lack of control for parameters leading the displacement equilibrium).

The presence of phosphite in alcohol/acid reactions opens different pathways in addition to the direct esterification process: alcohol/phosphite substitutions

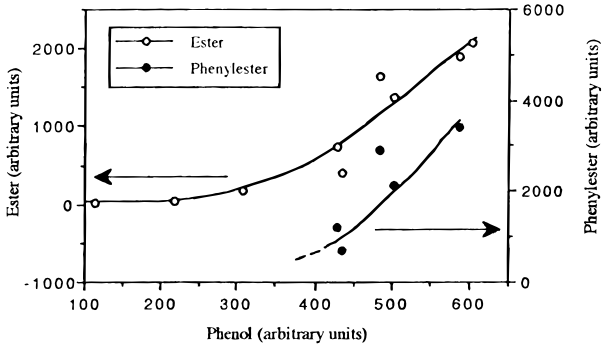


Figure 12. Correlation between phenol, ester, and phenyl ester formation during a reaction carried out in solution at 250 °C between equimolar ratios of alcohol, acid, and phosphite.

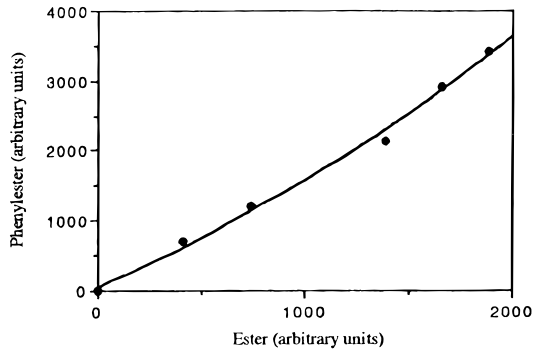


Figure 13. Correlation between ester and phenyl ester formation during a reaction carried out in solution at 250 °C between equimolar ratios of alcohol, acid, and phosphite.

are characterized by phenol liberation (Figure 3) and by a largely increased alcohol consumption rate in the presence of phosphite (Figure 4). Reactions between acid and triphosphite lead to ester and phenyl ester production with phosphonate release. The ester amounts produced during the experiments conducted in solution are enhanced greatly by the phosphite action (Figure 5).

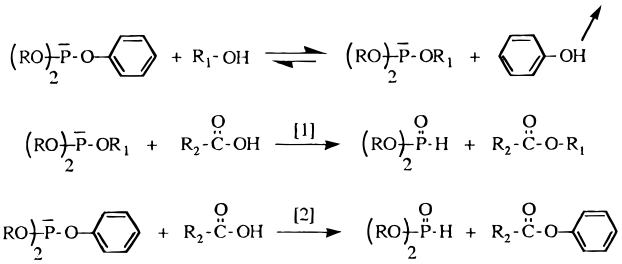
Different observations confirm the described mechanism and eliminate other suggestions. The kinetic constants concerning the triphosphite transformation into phosphonate are greatly different when measured in acid/phosphite or acid/phosphite/alcohol systems. The large reduction observed with the three components can thus be interpreted as a modification of the acid/phosphite reaction mechanism in the presence of an alcohol. This point corroborates the occurrence of different pathways, as described in Scheme 1.

Comparisons between the production of phenol and ester or phenyl ester (presented in Figure 12) highlight the successive character of the reactions: phenol appears first, ester and phenyl ester are produced afterward. This point supports the rapidity of phosphite/alcohol substitutions and the subsequent occurrence of acid reaction.

Moreover, a decrease of the phenol amounts was not observed during the phenyl ester production. Phenyl ester formation by direct esterification between phenol and acid, disfavored due to the phenol acidity, appears unlikely.

Finally, the simultaneous production of ester and phenyl ester (Figure 13) is consistent with the reaction mechanism deduced from NMR observations (Scheme 1). Similarly, this correlation refutes any hypothesis considering phenyl ester as an intermediate in ester formation.

Scheme 6. General Reaction Mechanism Leading to Ester [1] or Phenyl Ester [2] Production in PPOL/BBA/TPP Systems (R_1– as Ph–$(CH_2)_3$–; as $(CH_3)_3$–C–Ph–; R– as R_1– or Ph–)



For closed systems (sealed tubes experiments), phenol cannot be eliminated and the equilibrium point in alcohol/phosphite substitutions is fixed by different parameters, such as amounts of the reactants and tube volume. The limitation of the exchanges in such conditions thermodynamically favors the subsequent acid reaction with a phenoxy substituent of the triphosphite, although the kinetics is faster on the alkoxy site. The occurrence of large phenyl ester production interfers so much with the ester formation (by consumption of the acid) that the amounts of ester appearing at 245 °C are higher with the direct esterification process than in the presence of phosphite (Table 2).

In brief, the conclusions deduced from the chromatographic experiments not only fully support the described reaction mechanisms but also clearly confirm the importance of a large initial alcohol/phosphite exchange process in order to take full advantage of the ester production enhancement expected from the TPP addition.

Conclusion

Reactions between model compounds were carried out at high temperatures in order to provide a correct simulation of the behavior of hydroxyl and carboxyl polyester chain ends in the presence of triphenyl phosphite. Different investigation methods were used: HPLC and ^{31}P NMR and IR spectroscopy. A detailed reaction scheme for the alcohol/acid/triphosphite systems was deduced from all observations. It can be summarized as presented in Scheme 6.

The reaction between TPP and alcohol leads to phenoxy/alkoxy substitutions on the phosphite. The high reactivity of the triphosphite is maintained. The elimination of phenol in open systems greatly increases the substitution rate between PPOL and TPP and is considered as the driving force of this reaction.

On the other hand, acid reacts with triphosphite to produce ester (or phenyl ester) and phosphonate. The driving force is here the creation of a stable phosphoryl (P=O) bond. NMR experiments lead furthermore to conclusive results concerning the higher velocity of the acid reaction with aliphatic phosphite than of the acid reaction with aromatic phosphite. A temperature increase emphasizes this reactivity difference.

In the reactions involving alcohol, acid, and phosphite, different pathways lead to ester or phenyl ester formation. The conditions favoring ester formation are explained: a large substitution between alcohol and phosphite promoted by an easy phenol elimination, coupled with the higher acid reactivity on the generated alkoxy site of the substituted TPP, allows the formation of much larger ester amounts in comparison with the

direct esterification process. The presence of TPP is thus seen to greatly promote the ester production.

However, the occurrence of an acid reaction on a phenoxy site of the phosphite leads concurrently to the creation of phenyl ester. This formation occurs competitively. In the case of an initial limited phosphite/alcohol reaction, the presence of a majority of phenoxy-substituted triphosphite leads to a predominant formation of phenyl ester. For example, closed systems avoid the phenol elimination and reduce therefore the ester creation by favoring the phenyl ester production.

These conclusions are in excellent agreement with the observations realized by Aharoni and co-workers on model molecules of PET. Moreover, the deduced mechanisms confirm the occurrence of multisubstitutions between alcohol and phosphite. An extension of this process to polymers should lead to the creation between different chains of links including phosphorus atoms. These new phosphorus-containing bonds should thus contribute to the polyester melt viscosity, intrinsic viscosity, and molecular weight increases. The suggestions previously expressed in order to explain the polyester behavior after phosphite addition[16] are thus supported by this study on model compounds. However, confirmation of this mechanism must of course be found from direct measurements realized on polymers. This point will be the subject of a following paper.[36]

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