Inhibiting effect of phosphorus compounds on model transesterification and direct esterification reactions catalysed by titanium tetrabutylate: 2

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The inhibiting effect of phosphorus compounds on the polymerization to poly(butylene terephthalate) catalysed by titanium tetrabutylate was investigated by making use of model molecules. The inhibition, observed on both transesterification and direct esterification reactions, appears only in the presence of acidic OH groups in the phosphorus compounds, which permit the formation of complexes with the Ti atoms of the catalyst. The occurrence of such complexes was confirmed by infra-red spectroscopy.

(Keywords: phosphorus compounds; transesterification; direct esterification)

INTRODUCTION

It is well known that thermal and hydrolytic degradation reactions can affect saturated polyesters in polycondensation as well as in melt processing[1], and bring about lower molecular weights as well as poorer mechanical properties of the polymers. The species responsible for these thermal and hydrolytic instabilities is generally the residual catalyst, which also exerts its action on the various kinds of exchange reactions that can occur when the polyester is employed in blends, leading to the formation of new copolymers and, as a consequence, to undesired modifications of the blend properties. The prevention of such reactions is therefore an important feature in polyester synthesis and blend technology; for this purpose many patents and technical papers suggest the addition of phosphorus compounds (e.g. organophosphites, phosphonic and phosphorus acids, etc.) in the polymerization or blending[2-9].

In earlier work[10] on the kinetics of polymerization to poly(butylene terephthalate) (PBTP) catalysed by titanium tetrabutylate, studied with the aid of model molecules, we found that small amounts of phosphorus acid or phosphoric acid strongly inhibited the catalysis of the ester interchange reaction; on the contrary, no appreciable inhibiting effect was exerted by some other phosphorus compounds (triphenyl phosphite, triphenyl phosphate, etc.) claimed in the patent literature as polymer 'stabilizers'. The inhibition was explained in terms of the formation of stable adducts between H_3PO_3 (or H_3PO_4) and the catalyst, involving the OH groups of the acid.

In the present paper we describe further research on the effect of the presence of other phosphorus compounds, bearing either two, one or no OH groups per molecule, with the aim of elucidating the mechanism of inhibition of the ester interchange and direct esterification reactions catalysed by $Ti(OBu)_4$.

EXPERIMENTAL

Model molecules and reaction conditions

We made use of monofunctional model molecules, i.e. 4-hydroxybutyl benzoate (HBB) as a model for the hydroxy end-groups in the chain, 1,4-butylene dibenzoate (BDB) as a model for the polymer and benzoic acid (BA) as a model for carboxy end-groups.

The reactions were carried out at 167°C, starting from HBB (or HBB plus BA) with $Ti(OBu)_4$ as catalyst (about 6×10^{-4} mol l^{-1}) and various initial amounts of diphenyl phosphite (DPPI), diphenyl phosphate (DPPA), phenyl phosphinic acid (PPIA), phenyl phosphonic acid (PPOA), phosphoric acid (PIA) or phosphorus acid (POA) up to about 10^{-2} mol l^{-1} for each additive. *Figure 1* shows the structures of these phosphorus compounds.

In the absence of BA, the main reaction occurring, at least initially, is the ester interchange

$$\underset{\text{(HBB)}}{2\,C_6H_5COO(CH_2)_4OH} \rightarrow HO(CH_2)_4OH + \underset{\text{(BDB)}}{C_6H_5COO(CH_2)_4OCOC_6H_5} \quad (1)$$

The direct esterification reaction also occurs if BA is

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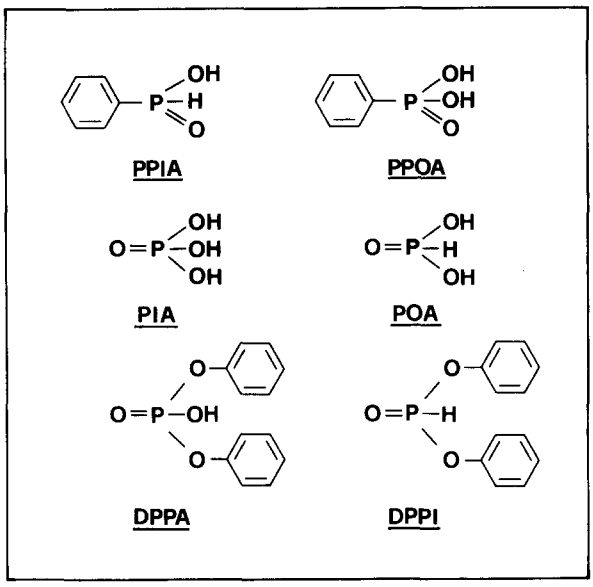

Figure 1 Molecular structures of the investigated phosphorus compounds

added initially

$$C_6H_5COOH + C_6H_5COO(CH_2)_4OH \rightarrow$$
(BA) (HBB)
$$C_6H_5COO(CH_2)_4OCOC_6H_5 + H_2O \quad (2)$$
(BDB)

Products

4-Hydroxybutyl benzoate was synthesized as reported elsewhere[11]. Benzoic acid and tetrabutyl titanate were Merck commercial products, and the latter was twice distilled at reduced pressure before use. DPPI, DPPA, PPIA, PPOA, POA and PIA were Aldrich commercial products and were dried before use.

Reaction apparatus

The reactions took place in a small glass reactor (capacity about 40 ml) equipped with a heating coil and closed with a Teflon cap bearing a thermometer and a hole sealed by a silicon seal. The reaction mixtures were stirred by a magnetic stirrer and the temperature was controlled to within ± 0.5°C. The reactor was loaded at room temperature and closed after bubbling dry nitrigen through for about 10 min, the desired temperature being reached by circulating hot silicon oil. Four minutes were required for the temperature to attain a steady value. At different times, samples were withdrawn from the reactor through the silicon seal with a syringe. The weighed samples, mixed with an acetonitrile solution of naphthalene (as an internal standard), were analysed by high pressure liquid chromatography (h.p.l.c.).

H.p.l.c. analysis

Measurements of the concentration of BDB were carried out as described elsewhere[12] using acetonitrile as the solvent and eluting with methanol/water (63/37% by volume) at a flow rate of 1.0 ml min^{-1}. The column temperature was 55°C.

Infra-red spectroscopy

Infra-red measurements were performed by means of a Bruker IFS 48 Fourier transform infra-red spectrophotometer. All compounds were examined in the pure state as nujol mulls or, whenever possible, in suitable solvents at room temperature.

In order to detect evidence of possible interactions between PIA (or POA) and $Ti(OBu)_4$, thoroughly stirred mixtures of these compounds in different ratios were examined at room temperature, and measurements were repeated on the same samples after a 2 min heating at about 170°C.

RESULTS AND DISCUSSION

Table 1 collects the initial compositions of the reaction system in the absence of BA, together with the initial rates of BDB formation determined from the curves of [BDB] *versus* time shown in *Figures 2* and *3*. From these figures it appears that DPPI has no appreciable inhibiting effect on reaction (1) catalysed by $Ti(OBu)_4$; the lower reaction rate observed in the presence of a large amount of DPPI (run I) is in fact attributable to the lower concentration of the catalyst added in this run. Moreover, the effects of PPIA and DPPA in nearly equal molar concentrations are shown to be similar, a somewhat stronger inhibition being exerted by PPOA.

The absence of an inhibiting effect on the part of DPPI is in accordance with our earlier results[10] regarding the addition of triphenyl phosphite, triphenyl phosphate, triethyl phosphite and triethyl phosphate; nevertheless, it is in contrast with some statements in the literature, where phosphorus compounds not containing OH groups are described as polymer 'stabilizers'[13]. This apparent contrast has been interpreted in rather recent studies[14–17] on blends of polyesters containing residual polymerization catalyst. In these works, the inhibition of the transesterification reactions by phosphorus compounds without OH groups is attributed to OH-bearing species that arise as products of hydrolysis reactions which occur in the presence of even small traces of water.

In order to obtain information on the stoichiometry of the possible adducts between titanium and phosphorus compounds, we rearranged the kinetic data on the grounds of a reasonable approximation, i.e. by supposing that the titanium involved in such species is completely inactive as a catalyst for reaction (1). Under this assumption, the catalytic activity will be exerted only by

Table 1 Initial compositions and experimental reaction rates at 167°C ($[HBB]_0 = 5.15$ mol l^{-1})

Run	10^4 $[Ti(OBu)_4]_0$ (mol l^{-1})	Additive	10^4 [P] (mol l^{-1})	10^4 d[BDB]/dt (mol l^{-1} s^{-1})
A	6.75	–	–	17.0
B	7.15	PPIA	3.11	13.0
C	6.74	PPIA	7.12	8.3
D	6.56	PPIA	12.7	5.0
E	6.47	PPOA	3.29	6.6
F	6.70	PPOA	7.77	1.7
G	6.37	PPOA	13.0	~0
H	8.27	DPPI	7.53	19.5
I	6.12	DPPI	13.9	14.5
J	6.85	DPPA	3.38	12.5
K	7.44	DPPA	6.52	9.7
L	7.02	DPPA	13.3	7.5

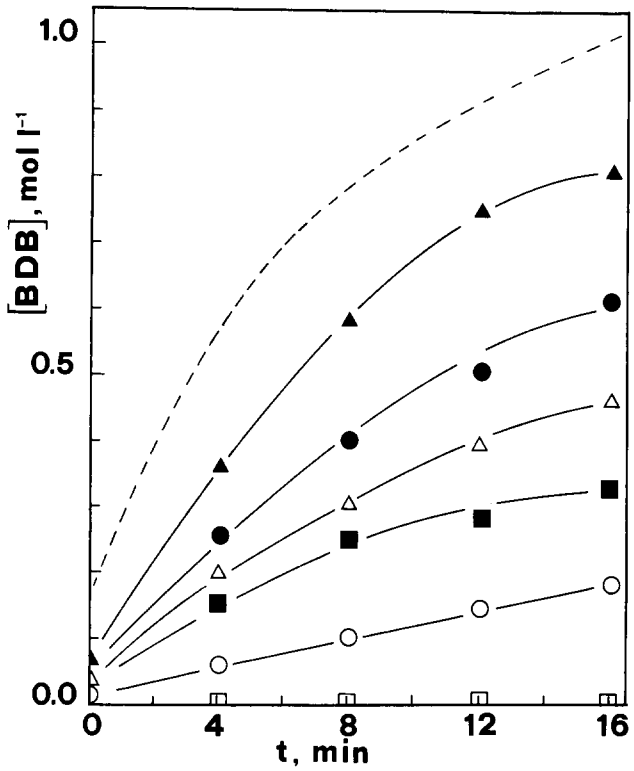

Figure 2 Formation of BDB at 167°C starting from HBB and $Ti(OBu)_4$ (– – –, run A) and in the presence of PPIA (▲, run B; ●, run C; ■, run D) or PPOA (△, run E; ○, run F; □, run G) added initially. For the initial compositions, see *Table 1*

the amount of $Ti(OBu)_4$ that exceeds the stoichiometric ratio with respect to the phosphorus compound. From this view point the initial reaction rates, expressed as rates of BDB formation, were plotted *versus* the concentration of the 'active' catalyst (*Figure 4*). Data pertaining to the reactions carried out in the presence of DPPI (which brings about no appreciable inhibiting effect) were plotted *versus* the effective $Ti(OBu)_4$ initial concentration, whereas for all other compounds, including H_3PO_3 and H_3PO_4, whose data have been taken from the literature[10], appropriate expressions for the concentration of the 'active' catalyst [Ti]* were chosen. *Figure 4* shows that the data obtained in the presence of phosphorus compounds bearing two or more OH groups per molecule (PPOA, PIA and POA) fall near the dashed line, representing the case of the absence of phosphorus compounds if a 1:1 adduct is assumed (i.e. if v_0 is plotted as a function of $[Ti]^* = [Ti(OBu)_4]_0 - [P]$). For phosphorus compounds bearing one OH group (PPIA and DPPA) we are led to suggest the formation of a 1:2 $Ti(OBu)_4$/P complex (i.e. the kinetic data fall near the dashed line if v_0 is plotted *versus* $[Ti]^* = [Ti(OBu)_4]_0 - [P]/2$). It must be noted that the points on the left of the plot do not follow such behaviour, probably because the catalyst involved in the complex is still partly active and/or there is an equilibrium between free $Ti(OBu)_4$ molecules and the adducts formed, so that a small quantity of non-complexed Ti exists even in the presence of a stoichiometric quantity of the phosphorus compound.

Evidence for the formation of complexes involving phosphorus compounds can be obtained by means of infra-red spectroscopy, since the stretching frequencies of some bonds are affected, in particular the P–O bonds[18–20]. To this end, we studied by infra-red spectroscopy some of the most significant cases, examining mixtures of the catalyst with PPOA (a strong inhibitor), PPIA and DPPA (both rather strong inhibitors).

In the infra-red spectrum of PPOA the $\nu_{P=O}$ stretching vibration gives the broad band at 1221 cm^{-1}, whereas the ν_{P-O} in-phase and out-of-phase stretching modes are found at 938 and 1016 cm^{-1}, respectively. This compound was mixed at room temperature with an equimolar amount of $Ti(OBu)_4$, upon which the band at 938 cm^{-1} was found to disappear, whereas the band at 1221 cm^{-1} was remarkably weakened. The spectrum of the same mixture after a 2 min heating at 170°C showed no significant differences.

The spectrum of PPIA shows a strong band at 1198 cm^{-1} which is generally assigned to the $\nu_{P=O}$ stretching vibration, the ν_{P-O} stretching mode being associated with the band at 987 cm^{-1}. The ν_{P-H} stretching vibration gives the band at 2360 cm^{-1}. Upon addition to PPIA of an equivalent amount of $Ti(OBu)_4$ the band at 1198 cm^{-1} was found to disappear; after a 2 min heating at 170°C a new band appeared at 1222 cm^{-1}.

In the spectrum of DPPA the $\nu_{P=O}$ stretching vibration gives a strong band at 1192 cm^{-1}, whereas the ν_{P-O} modes cannot be identified with equal certainty. Upon addition of increasing amounts of $Ti(OBu)_4$ the band at 1192 cm^{-1} was progressively replaced by a new band at 1273 cm^{-1}; for a [Ti]/[P] ratio of 2:1 only the latter is observable.

All these results support our interpretation of the kinetic data, i.e. that at high temperature phosphorus compounds with acidic OH groups interact appreciably with $Ti(OBu)_4$, probably with the formation of chelated titanate species.

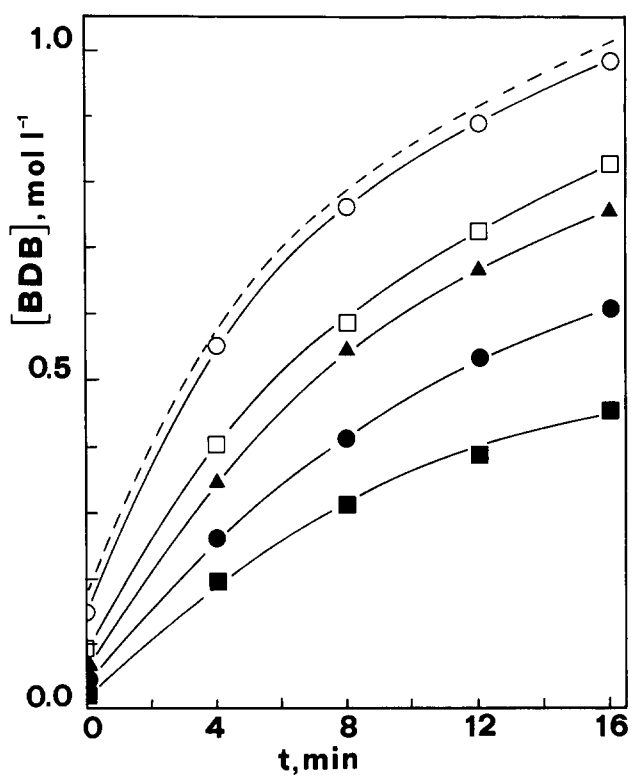

Figure 3 Formation of BDB at 167°C starting from HBB and $Ti(OBu)_4$ (– – –, run A) and in the presence of DPPI (○, run H; □, run I) or DPPA (▲, run J; ●, run K; ■, run L) added initially. For the initial compositions, see *Table 1*

During the polymerization of PBTP appreciable amounts of carboxy end-groups are present in the reaction system, belonging to the acid used as a reagent and/or formed in the process because of degradation reactions. These groups contribute to the formation of polymer molecules through the direct esterification reaction, represented in terms of our model molecules by equation (2). This reaction has been widely studied in the past and the results of our investigations were reported in earlier papers[11,12,21]. In the present work the influence of some phosphorus compounds on reaction (2) was studied. The experiments were carried out starting from HBB and BA in different ratios, with a constant quantity of $Ti(OBu)_4$ as a catalyst, and various concentrations of H_3PO_3 or H_3PO_4, both strong inhibitors of the ester interchange reaction (reaction (1)) catalysed by $Ti(OBu)_4$. The initial compositions of the reaction system, including various initial amounts of BA, are collected in *Table 2* together with the measured initial rates of BDB formation. In *Figure 5* the kinetic results are shown for H_3PO_4; similar behaviour was observed for H_3PO_3. From the different sections of this figure, it appears that for a fixed Ti/P ratio, the rate of BDB formation becomes greater and greater with increasing initial concentration of BA.

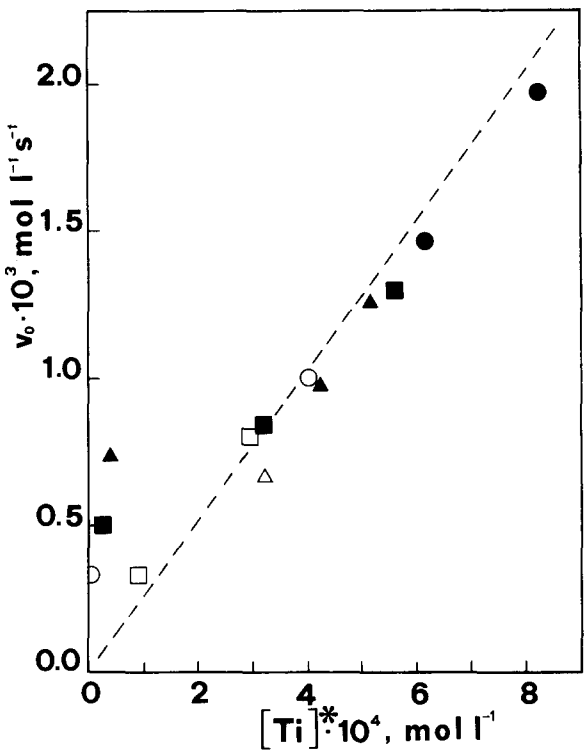

Figure 4 Initial rate of BDB formation at 167°C as a function of the 'active' catalyst concentration [Ti]*. [Ti]* = $[Ti(OBu_4]_0$ for DPPI (●); [Ti]* = $[Ti(OBu)_4]_0 - [P]/2$) for DPPA (▲) and PPIA (■); [Ti]* = $[Ti(OBu)_4]_0 - [P]$ for PPOA (△), H_3PO_3 (○) and H_3PO_4 (□). Data concerning H_3PO_3 and H_3PO_4 are taken from the literature[10]

It should be noted that in the presence of HBB and BA reactions (1) and (2) take place simultaneously, and BA behaves as a catalyst for both reactions[21]; consequently, BDB formation stems from four contributions, two concerning $Ti(OBu)_4$-catalysed reactions and two concerning BA-catalysed reactions. Since other investigations[10] have shown that an amount of H_3PO_4 (or H_3PO_3) corresponding to a $[Ti(OBu)_4]/[P]$ ratio equal to 1:2 is sufficient to inhibit almost completely the ester interchange reaction catalysed by $Ti(OBu)_4$ (reaction (1)), we must infer that in these conditions only the following contributions have to be taken into account: (i) $Ti(OBu)_4$-catalysed reaction (2); (ii) BA-catalysed reaction (2); and (iii) BA-catalysed reaction (1).

Table 2 Inital compositions and experimental reaction rates at 167°C

Run	$[HBB]_0$ (mol l^{-1})	$[BA]_0$ (mol l^{-1})	10^4 $[Ti(OBu)_4]_0$ (mol l^{-1})	Additive	10^4 [P] (mol l^{-1})	10^4 d[BDB]/dt (mol l^{-1} s^{-1})
A1	4.82	0.525	7.25	–	–	2.4
B1	4.83	0.511	7.00	PIA	3.30	1.4
C1	4.85	0.473	6.39	PIA	8.17	0.58
D1	4.82	0.512	7.45	PIA	13.2	0.42
E1	4.40	1.20	6.57	–	–	2.2
F1	4.40	1.19	6.34	PIA	3.15	1.6
G1	4.39	1.20	6.63	PIA	7.96	1.0
H1	4.41	1.17	6.44	PIA	13.6	0.90
I1	3.92	1.95	6.44	–	–	2.5
J1	3.93	1.94	6.56	PIA	3.18	2.3
K1	3.93	1.94	6.34	PIA	8.26	2.0
L1	3.93	1.93	6.36	PIA	12.8	1.9
M1	4.84	0.496	6.85	POA	4.28	1.2
N1	4.82	0.523	6.89	POA	9.10	0.94
O1	4.82	0.527	6.32	POA	15.8	0.57
P1	3.97	1.88	6.92	POA	3.06	2.3
Q1	3.93	1.94	6.70	POA	6.80	2.2
R1	3.95	1.91	6.81	POA	12.5	2.0
S1	4.83	0.510	–	–	–	0.42
T1	4.39	1.20	–	–	–	1.0
V1	3.89	2.00	–	–	–	1.8

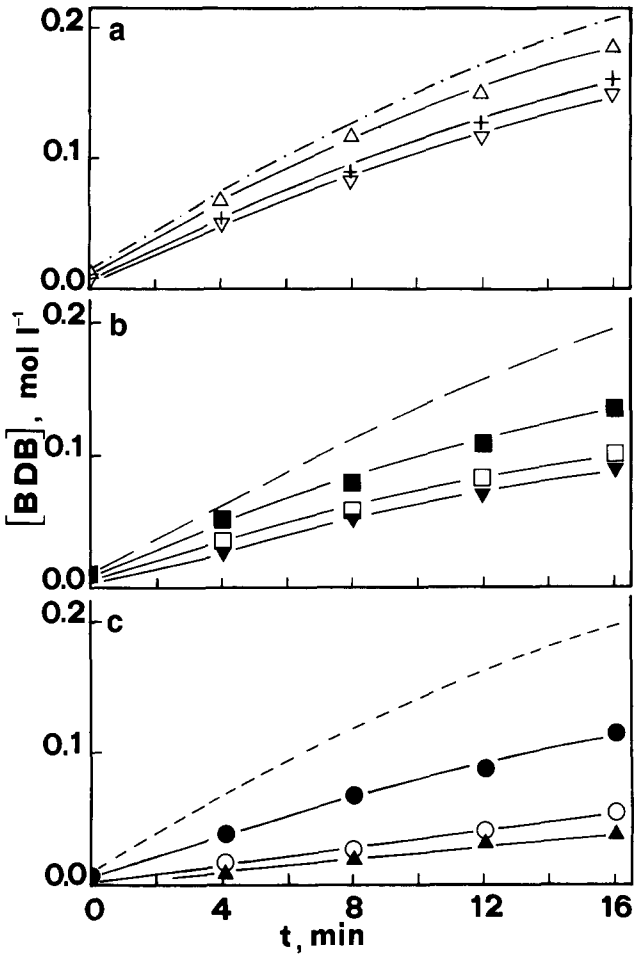

Figure 5 Formation of BDB at 167°C starting from HBB, $Ti(OBu)_4$ and different amounts of BA and in the presence of H_3PO_4. (a) $[BA]_0 \approx 2$ mol l^{-1}: (—·—) run I1; (△) run J1; (+) run K1; (▽) run L1. (b) $[BA]_0 \approx 1.2$ mol l^{-1}: (— —) run E1; (■) run F1; (□) run G1; (▼) run H1. (c) $[BA]_0 \approx 0.5$ mol l^{-1}: (- - -) run A1; (●) run B1; (○) run C1; (▲) run D1. For the initial compositions, see *Table 2*

A comparison of the initial rates of BDB formation in the presence of higher concentrations of H_3PO_3 or H_3PO_4, with the values observed in the cases of similar BA and HBB initial concentrations but in the absence of both $Ti(OBu)_4$ and phosphorus additives (runs S1, T1 and V1), shows that within experimental error BDB formation stems from only contributions (ii) and (iii). This means that H_3PO_4 and H_3PO_3 behave as strong inhibitors of both reactions (1) and (2) catalysed by $Ti(OBu)_4$.

In conclusion, the kinetic data reported in this paper support what had been found earlier[10], i.e. that the inhibition exerted by phosphorus compounds on the transesterification (reaction (1)) catalysed by $Ti(OBu)_4$ is possible only when one or more acidic OH groups are present in the molecule of the phosphorus additive. In fact, the presence of such groups permits the formation of adducts with Ti atoms (probably titanate chelates) which can be considered inactive as catalysts and whose stoichiometry (1:1 or 1:2 Ti/P ratio) depends on the number of OH groups in the additive molecule. The formation of these adducts, confirmed by infra-red spectroscopy, can be considered as the reason for the inhibition of both transesterification and direct esterification reactions catalysed by $Ti(OBu)_4$.

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