Models for the formation of poly(butylene terephthalate): Kinetics of the titanium tetrabutylate-catalysed reactions: 2.

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In order to investigate the mechanism of catalysis of titanium tetrabutoxide on the polycondensation of poly(butylene terephthalate), this reaction has been studied with the aid of model molecules. The catalytic and retarding effects of benzoic acid have also been taken into account. Appropriate kinetic equations are derived and discussed and the results compared with experimental data obtained at different temperatures and molar ratios of reactants.

Keywords Poly(butylene terephthalate); formation; models; kinetics; titanium tetrabutylate; catalysis

INTRODUCTION

In our previous work[1-3] some of the reactions taking place during the formation of poly (butylene terephthalate) have been investigated with the aid of monofunctional model molecules. 4-Hydroxybutyl benzoate (HBB) was chosen as a model for hydroxyl end-groups, 1,4-butylene dibenzoate (BDB) as a model for the polymer, and benzoic acid (BA) as a model for the carboxyl end-groups. Titanium tetrabutylate, $Ti(OBu)_4$, was used as catalyst.

Among the reactions examined, particular attention was devoted to those leading to polymer growth by ester interchange and direct esterification:

$$\underset{\text{(HBB)}}{2\,C_6H_5COO(CH_2)_4OH} \rightleftharpoons \underset{\text{(BD)}}{HO(CH_2)_4OH} + \underset{\text{(BDB)}}{C_6H_5COO(CH_2)_4OCOC_6H_5} \quad \text{(A)}$$

$$\underset{\text{(HBB)}}{C_6H_5COO(CH_2)_4OH} + \underset{\text{(BA)}}{C_6H_5COOH} \rightleftharpoons H_2O + \underset{\text{(BDB)}}{C_6H_5COO(CH_2)_4OCOC_6H_5} \quad \text{(B)}$$

It appeared that reactions (A) and (B), in the temperature range 150°–200°C, are both catalysed by $Ti(OBu)_4$: however, it was also found that the activity of $Ti(OBu)_4$ is partially inhibited by benzoic acid. It was tentatively concluded that the catalyst acts by a coordinative mechanism.

The present study is devoted to a better understanding of the mechanism of these reactions.

Experiments were carried out on HBB in the presence of different amounts of BA with or without $Ti(OBu)_4$ at temperatures of 150° and 167°C and without solvents. Under these conditions and for low conversions side and reverse reactions can be neglected[1-3].

EXPERIMENTAL

Products

4-Hydroxybutyl benzoate and 1,4-butylene dibenzoate were synthesized as previously reported[2].

Reagent-grade anhydrous benzoic acid (BA) was used as supplied by Merck; 1,4-butanediol (BD) and titanium tetrabutylate were commercial products and they were distilled at reduced pressure before use.

For kinetic experiments homogeneous samples were introduced into glass tubes (6 mm internal diameter) in a dry box. They were weighed and sealed under a reduced pressure of nitrogen, and then placed in a constant-temperature (±0.1°C) oil bath.

After appropriate time intervals, the tubes were removed and quenched in an ice bath. They were broken and the mixtures dissolved in a suitable solvent.

High-pressure liquid chromatography analysis

Measurements of HBB and BDB concentrations were carried out on a Perkin–Elmer Series 2 h.p.l.c. instrument, equipped with an LC-65T u.v. detector fixed at 254 nm. An ODS-HC SIL-X-1 0.26×25 cm column was employed. Samples were dissolved in weighed amounts of an acetonitrile/naphthalene solution and eluted with a mixture of acetonitrile and water (40/60 by vol) at $1.0\ \text{ml min}^{-1}$ flow rate; the temperature of the column was kept at 45°C. Under such conditions benzoic acid, 4-hydroxybutyl benzoate, naphthalene (used as internal standard) and butanediol dibenzoate were eluted in about 10 min. The amounts of 4-hydroxybutyl benzoate and butanediol dibenzoate were measured by the internal standard calibration method.

Titrations

Benzoic acid content could not be evaluated by h.p.l.c. because of unsatisfactory analytical reproducibility. It was determined by titration with an alcoholic solution of NaOH.

RESULTS AND DISCUSSION

The results pertaining to the formation of BDB are shown in *Figures 1* and *2*; the disappearance of BA for different

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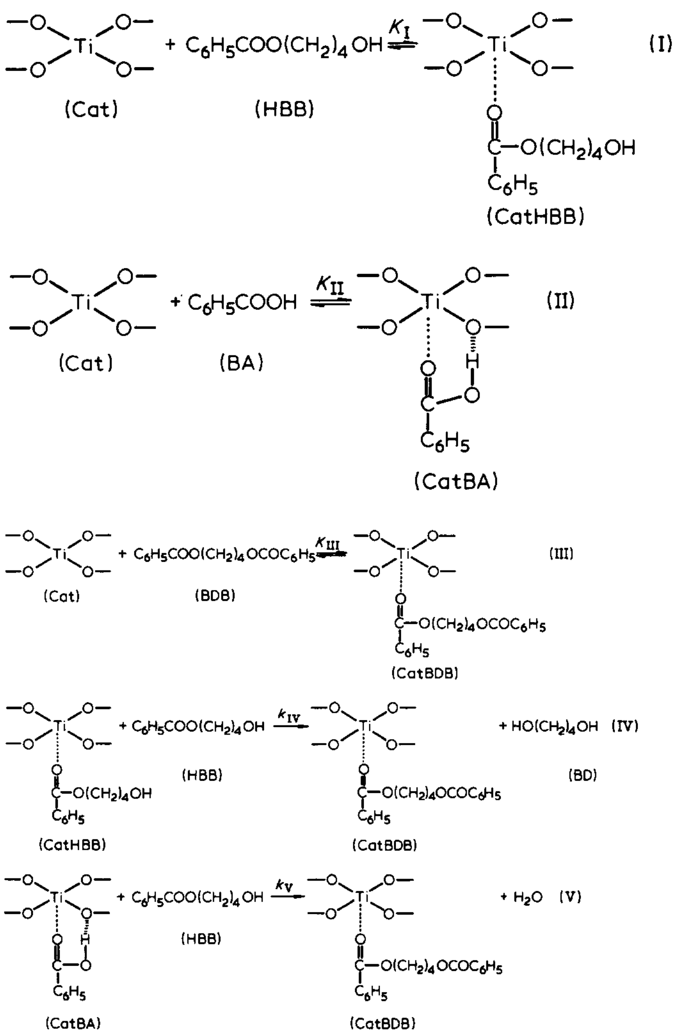
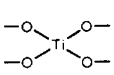
initial ratios (HBB/BA) in the absence of solvents appears in *Figures 3* and *4*. These data confirm that benzoic acid acts as a retarder when it is present in addition to $Ti(OBu)_4$, but it acts as a catalyst in the absence of $Ti(OBu)_4$. In a previous paper[2] we suggested for the reaction (A) catalysed by $Ti(OBu)_4$ a coordinative mechanism involving the formation of an adduct between a carbonyl group and the Ti atom. It is reasonable to suppose that the retarding effect of BA may be due to the formation of another adduct, between BA itself and the Ti atom, more stable than those formed by HBB and BDB. This leads us to propose the following kinetic scheme.



In these two mechanisms we suppose, according to the properties of the alcoxytitanium compounds[4], that the catalyst (indicated as



and 'Cat') is not autoassociated in our reaction conditions, and that all or some of its initial butoxy groups have been replaced by $-O(CH_2)_4OCOC_6H_5$ or $-OCOC_6H_5$ groups. Furthermore, although in the above scheme CatHBB and CatBA are indicated as intermolecular adducts, it is implicit that they can also be intramolecular as suggested by Fradet[5,6].

Steps (I) to (III) can be assumed to be fast equilibrium reactions (with $K_{II} >> K_{III} \simeq K_I$ according to the above assumptions) whereas the other steps can be taken as the slower ones, being shifted to the right under our experimental conditions (high HBB concentration, initial absence of BD, BDB and H_2O, low conversions).

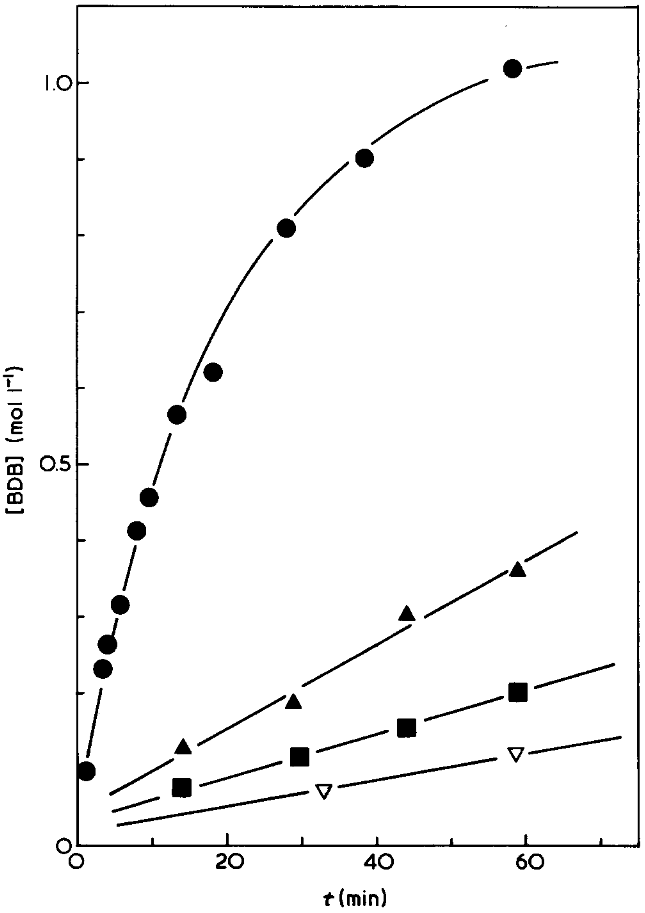


Figure 1 BDB formation at 150°C at different initial BA and HBB concentrations: with $Ti(OBu)_4$ (6.68×10^{-4} mol l^{-1}) – ●, $[BA]_0=0$; ▲, $[BA]_0=0.097$ mol l^{-1}; ■, $[BA]_0=0.346$ mol l^{-1}; and without catalyst – ▽, $[BA]_0=1.25$ mol l^{-1}. For HBB initial concentrations see tables

If $[Cat]_0$ represents the initial concentration of $Ti(OBu)_4$, the material balance for the catalyst is

$$[Cat]_0=[Cat]+[CatHBB]+[CatBA]+[CatBDB] \quad (1)$$

Likewise, the material balance for HBB, BA and BDB is:

$$[HBB]_0+2[BDB]_0+[BA]_0=[HBB]+2[BDB]+[BA] \quad (2)$$

$$[BDB]_0=[BDB]-[BD]-[H_2O] \quad (3)$$

$$[BA]_0=[BA]+[H_2O] \quad (4)$$

where [CatHBB], [CatBA], [CatBDB] are not considered since, under our conditions, they are negligible.

It follows that:

$$\frac{d[BDB]}{dt}=\frac{d[BD]}{dt}+\frac{d[H_2O]}{dt} \quad (5)$$

$$\frac{-d[BA]}{dt}=\frac{d[H_2O]}{dt} \quad (6)$$

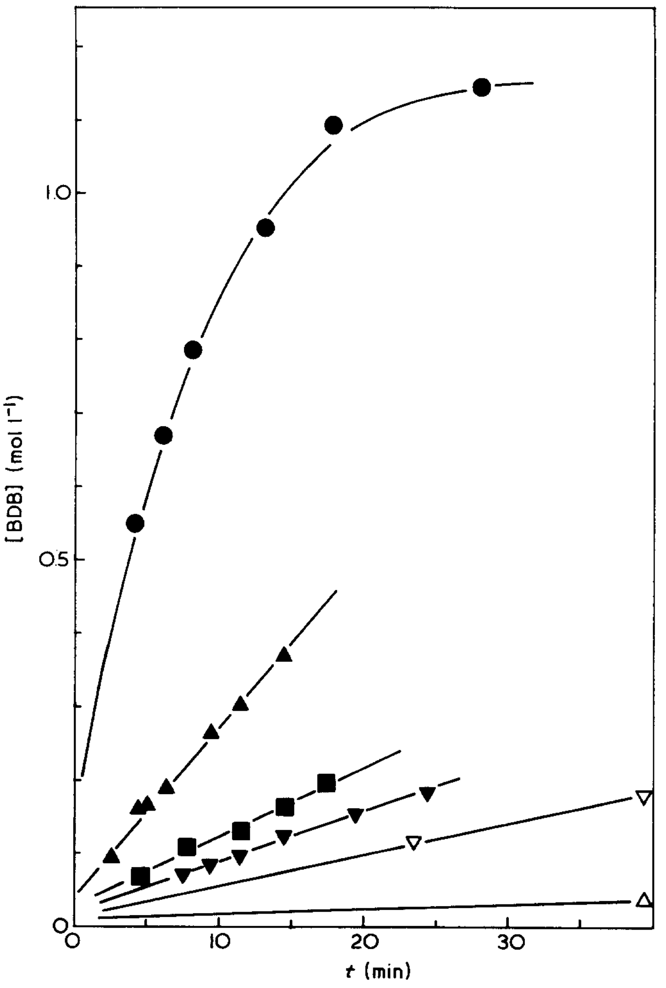


Figure 2 BDB formation at 167°C at different initial BA and HBB concentrations: with Ti(OBu)$_4$ (6.61 × 10^{-4} mol l^{-1}) – ●, $[BA]_0=0$; ▲, $[BA]_0=0.102$ mol l^{-1}; ■, $[BA]_0=0.437$ mol l^{-1}; ▼, $[BA]_0=1.26$ mol l^{-1}; and without catalyst – ▽, $[BA]_0=1.24$ mol l^{-1}; △, $[BA]_0=0.078$ mol l^{-1}. For HBB initial concentrations see tables

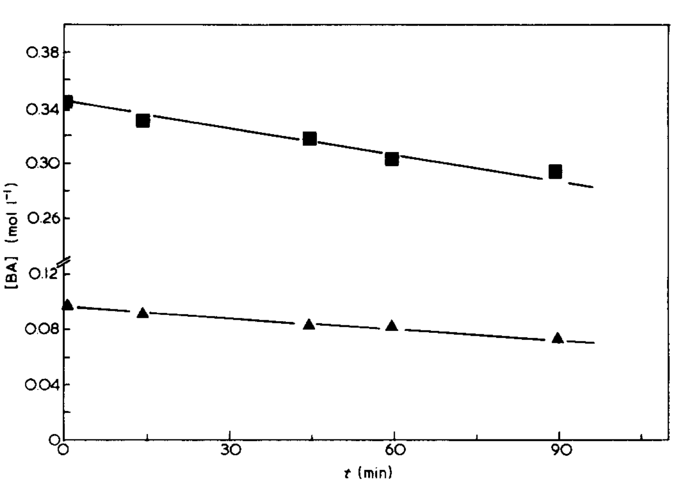


Figure 3 BA disappearance at 150°C with catalyst (Ti(OBu)$_4$, 6.68 × 10^{-4} mol l^{-1}), at different initial BA and HBB concentrations: ▲, $[BA]_0=0.097$ mol l^{-1}; ■, $[BA]_0=0.346$ mol l^{-1}. For HBB initial concentrations see tables

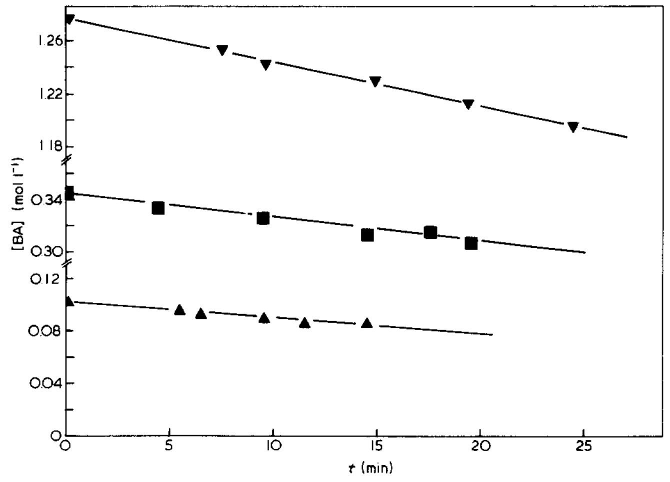


Figure 4 BA disappearance at 167°C with catalyst (Ti(OBu)$_4$, 6.61 × 10^{-4} mol l^{-1}), at different initial BA and HBB concentrations: ▲, $[BA]_0=0.102$ mol l^{-1}; ■, $[BA]_0=0.347$ mol l^{-1}; ▼, $[BA]_0=1.26$ mol l^{-1}. For HBB initial concentrations see tables

Moreover, from the kinetic scheme

$$\frac{\mathrm{d}[\mathrm{BDB}]}{\mathrm{d}t}=k_{\mathrm{IV}}[\mathrm{HBB}][\mathrm{CatHBB}] \tag{7}$$

$$\frac{-\mathrm{d}[\mathrm{BA}]}{\mathrm{d}t}=k_{\mathrm{V}}[\mathrm{HBB}][\mathrm{CatBA}] \tag{8}$$

From equations (1) to (8) and from the equilibrium constants for steps (I), (II) and (III), we obtain:

$$\frac{\mathrm{d}[\mathrm{BDB}]}{\mathrm{d}t}=\frac{[\mathrm{Cat}]_0(K_{\mathrm{I}}k_{\mathrm{IV}}[\mathrm{HBB}]^2+K_{\mathrm{II}}k_{\mathrm{V}}[\mathrm{BA}][\mathrm{HBB}])}{1+K_{\mathrm{I}}[\mathrm{HBB}]+K_{\mathrm{II}}[\mathrm{BA}]+K_{\mathrm{III}}[\mathrm{BDB}]} \tag{9}$$

$$\frac{-\mathrm{d}[\mathrm{BA}]}{\mathrm{d}t}=\frac{[\mathrm{Cat}]_0K_{\mathrm{II}}k_{\mathrm{V}}[\mathrm{BA}][\mathrm{HBB}]}{1+K_{\mathrm{I}}[\mathrm{HBB}]+K_{\mathrm{II}}[\mathrm{BA}]+K_{\mathrm{III}}[\mathrm{BDB}]} \tag{10}$$

As is shown in *Figures 1* to *4*, when BA is added with HBB, and Ti(OBu)$_4$ is not present, both reactions (A) and (B) can lead to the formation of BDB with appreciable rates. As equations (9) and (10) are derived for the initial rates of the Ti(OBu)$_4$-catalysed reactions only, they must be modified to take into account the contributions of the uncatalysed reactions.

Although esterification is probably one of the most studied reactions, a kinetic equation is far from being definitively established[7] and this is even more true for ester interchange reactions. We choose for the uncatalysed reaction (A) an order of 2 for HBB and of 1 for BA, whereas for the uncatalysed reaction (B) kinetic orders of 1 and 2 for HBB and BA respectively seemed to be a better choice, in accordance with other authors[7]. These assumptions lead to equations (11) and (12):

$$\frac{\mathrm{d}[\mathrm{BDB}]}{\mathrm{d}t}=\frac{[\mathrm{Cat}]_0(K_{\mathrm{I}}k_{\mathrm{IV}}[\mathrm{HBB}]^2+K_{\mathrm{II}}k_{\mathrm{V}}[\mathrm{HBB}][\mathrm{BA}])}{1+K_{\mathrm{I}}[\mathrm{HBB}]+K_{\mathrm{II}}[\mathrm{BA}]+K_{\mathrm{III}}[\mathrm{BDB}]}+k_{0,\mathrm{A}}[\mathrm{HBB}]^2[\mathrm{BA}]+k_{0,\mathrm{B}}[\mathrm{HBB}][\mathrm{BA}]^2 \tag{11}$$

$$\frac{-\mathrm{d}[\mathrm{BA}]}{\mathrm{d}t}=\frac{[\mathrm{Cat}]_0 K_{\mathrm{II}} k_{\mathrm{V}}[\mathrm{BA}][\mathrm{HBB}]}{1+K_{\mathrm{I}}[\mathrm{HBB}]+K_{\mathrm{II}}[\mathrm{BA}]+K_{\mathrm{III}}[\mathrm{BDB}]}+k_{0,\mathrm{B}}[\mathrm{HBB}][\mathrm{BA}]^2 \qquad (12)$$

From the experimental data of initial rates at different initial ratios (HBB/BA), we were able to calculate the six constants that appear in equations (11) and (12), assuming that under our experimental conditions the term $K_{\mathrm{III}}[\mathrm{BDB}]$ is negligible. The values are reported in *Table 1*. In *Tables 2* and *3* the experimental initial rates (slopes of curves of *Figures 1* to *4*) are compared with the values calculated by introducing the data of *Table 1* into equations (11) and (12): quite good agreement is found. From equation (11) it appears that at low conversions, in the absence of benzoic acid, the order for reaction (A) turns out to be 1 with respect to the catalyst $\mathrm{Ti(OBu)_4}$, whereas the order with respect to HBB might range between 1 and 2, but actually approaches the latter value even at the highest concentrations of HBB because of the low value of K_{I}. All this is supported by our previous experimental data[2]. In the Ti-catalysed system, the presence of BA brings about retardation of BDB formation: this result can be accounted for by the relatively high value of the equilibrium constant K_{II} (see *Table 1*).

The stability of the adduct between BA and Ti strongly decreases when temperature increases from 150° to 167°C (see *Table 1*); therefore the retarding effect of BA decreases as temperature increases.

The orders assumed for BA and HBB in the reactions catalysed by BA only lead to kinetic constants $k_{0,\mathrm{A}}$ and $k_{0,\mathrm{B}}$ of the same order of magnitude for both reactions (A) and (B). In view of the low values of $k_{0,\mathrm{A}}$ and $k_{0,\mathrm{B}}$ with respect to k_{IV} and k_{V} the contributions of the uncatalysed reactions (A) and (B) to the overall rate of BDB formation become important only at high BA concentration.

For the disappearance of BA it results from equation (12) that the apparent order with respect to the catalyst is between 1 and 0, depending on the relative weight of the terms on the right-hand side. In the same way the apparent orders with respect to the reactants can assume many different values and this fact can account for the variations of the overall order when conversion increases, and can explain many uncertainties in the literature data[7].

The interactions taking place between carbonyl groups and Ti has been evidenced by i.r. spectroscopy. We were able to observe the formation of a stable adduct between BA and $\mathrm{Ti(OBu)_4}$ at room temperature in chloroform solution: this is in accordance with several authors[6,8,9]. Indeed the strong absorption band of BA at about 1710 $\mathrm{cm^{-1}}$, corresponding to the free carbonyl stretching mode, was completely absent for (BA/Ti) molar ratios up to 1. At the same time a broad absorption appeared at about 1550 $\mathrm{cm^{-1}}$, which can be reasonably assigned to the C=O bond vibration.

For higher (BA/Ti) ratios, the free carbonyl band appears again: from its intensity one can deduce that a weaker 2/1 adduct is also possible. Actually, it has been found that such an adduct is practically the only one present for (BA/Ti) molar ratios higher than 4.

Table 2 Experimental and calculated initial rates of BDB formation and BA disappearance at 167°C with different initial BA and HBB concentrations

	d[BDB]/d*t* × 10^4 (mol $\mathrm{l^{-1}\,s^{-1}}$)		−d[BA]/d*t* × 10^5 (mol $\mathrm{l^{-1}\,s^{-1}}$)	
Conc. (mol $\mathrm{l^{-1}}$)	Exp.	Calc.	Exp.	Calc.
With $\mathrm{Ti(OBu)_4}$				
$[\mathrm{BA}]_0$ = 0 $[\mathrm{HBB}]_0$ = 5.10	16	16	–	–
$[\mathrm{BA}]_0$ = 0.102 $[\mathrm{HBB}]_0$ = 5.04	3.9	3.9	2.2	2.4
$[\mathrm{BA}]_0$ = 0.347 $[\mathrm{HBB}]_0$ = 4.90	1.7	1.6	3.1	3.1
$[\mathrm{BA}]_0$ = 1.26 $[\mathrm{HBB}]_0$ = 4.33	1.1	1.2	5.5	5.8
Without $\mathrm{Ti(OBu)_4}$				
$[\mathrm{BA}]_0$ = 1.24 $[\mathrm{HBB}]_0$ = 4.35	0.70	0.70	N.D.	3.0

N.D. = not determined

Table 3 Experimental and calculated initial rates of BDB formation and BA disappearance at 150°C with different initial BA and HBB concentrations

	$\mathrm{d[BDB]_0}$/d*t* × 10^4 (mol $\mathrm{l^{-1}\,s^{-1}}$)		−d[BA]/d*t* × 10^5 (mol $\mathrm{l^{-1}\,s^{-1}}$)	
Conc. (mol $\mathrm{l^{-1}}$)	Exp.	Calc.	Exp.	Calc.
With $\mathrm{Ti(OBu)_4}$				
$[\mathrm{BA}]_0$ = 0 $[\mathrm{HBB}]_0$ = 5.14	9.3	9.4	–	–
$[\mathrm{BA}]_0$ = 0.097 $[\mathrm{HBB}]_0$ = 5.08	0.92	0.94	0.50	0.78
$[\mathrm{BA}]_0$ = 0.346 $[\mathrm{HBB}]_0$ = 4.94	0.45	0.40	1.1	0.92
Without $\mathrm{Ti(OBu)_4}$				
$[\mathrm{BA}]_0$ = 1.25 $[\mathrm{HBB}]_0$ = 4.39	0.32	0.33	N.D.	1.4

N.D. = not determined

However, it is logical to suppose that at higher temperatures the adduct is mainly of the 1/1 type.

On the contrary, no convincing spectroscopic evidence has been found for the adduct between HBB and Ti under the same conditions: this in any case confirms our previous suggestions about a weaker adduct.

Table 1 Values of the kinetic and equilibrium constants at different temperatures

T (°C)	K_{I} (l $\mathrm{mol^{-1}}$)	K_{II} (l $\mathrm{mol^{-1}}$)	k_{IV} (l $\mathrm{mol^{-1}\,s^{-1}}$)	k_{V} (l $\mathrm{mol^{-1}\,s^{-1}}$)	$k_{0,\mathrm{A}}$ ($\mathrm{l^2\,mol^{-2}\,s^{-1}}$)	$k_{0,\mathrm{B}}$ ($\mathrm{l^2\,mol^{-2}\,s^{-1}}$)
150	0.13	170	0.68	2.5×10^{-3}	0.8×10^{-6}	2.0×10^{-6}
167	0.10	50	1.40	9.5×10^{-3}	1.7×10^{-6}	4.5×10^{-6}

CONCLUSIONS

We have studied the reactions between HBB and BA at 150° and 167°C, with the aim of attaining better knowledge of the catalytic activity of the titanium compounds.

Equations derived by a mechanism assuming that HBB and BA are activated through the formation of adducts with titanium enable us to explain most of the experimental evidence. In particular, by these equations we can:

(i) rationalise the retarding effect of BA on BDB formation;

(ii) calculate the initial slopes for the disappearance of BDB and BA for different initial ratios (HBB/BA) and for different temperatures; and

(iii) propose a qualitative interpretation for most of the literature data about the apparent orders of reaction, in spite of their remarkable scatter due to different reaction conditions.

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