

**EFFECT OF TRIPHENYLPHOSPHINE ON THE CYCLOTRIMERIZATION OF BUTADIENE CATALYZED BY THE  $\text{TiCl}_4$ - $\text{EtAlCl}_2$  SYSTEM**

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Addition of  $\text{PPh}_3$  to the  $\text{TiCl}_4 + n \text{EtAlCl}_2$  ( $n = 4-10$ ) systems, which normally exhibit mostly Friedel-Crafts and polymerization activity towards butadiene, turns these systems into highly specific catalysts for the cyclotrimerization of butadiene to (*Z, E, E*)-1,5,9-cyclododecatriene. The effect of  $\text{PPh}_3$  lies in removal of  $\text{AlCl}_3$ , which is formed in the reduction of  $\text{TiCl}_4$  with  $\text{EtAlCl}_2$  and in the disproportionation of  $\text{EtAlCl}_2$ , for the  $\text{AlCl}_3 \cdot \text{PPh}_3$  complex displays higher stability in comparison with the analogous complexes with ethylaluminium chlorides. The composition of the ( $\eta^6$ -benzene)Ti(II) complexes, which are the catalytically active species, was determined by electronic absorption spectroscopy in the post-reaction mixtures.

The conversion of butadiene into (*Z, E, E*)-1,5,9-cyclododecatriene ((*Z, E, E*)-CDT) induced by the catalysts composed of the Ti(IV) compound and dialkylaluminium halide was first described by Wilke<sup>1</sup> in 1956. Since that time, Ti(IV)-based catalysts have been modified in various ways, the presence of alkylaluminium cocatalysts was, however, found to be essential. It has been recently recognized<sup>2</sup> that, in addition to its reduction function, the aluminium compound takes part in the formation of a trinuclear catalytic complex, in which two aluminium atoms are bound to the central Ti(II) ion through chlorine bridges. This complex is in equilibrium with the analogous ( $\eta^6$ -benzene)Ti(II)( $\text{AlX}_4$ )<sub>2</sub> ( $\text{X} = \text{Cl}$ , partly Et) complex in a benzene-butadiene mixture, and after consumption of butadiene the (benzene)Ti(II) complex can be detected in the electronic absorption spectrum of the reaction mixture.

Since the reduction and solvation powers of the aluminium compounds are polarized to the edge members of the series of the  $\text{Et}_x\text{AlCl}_{3-x}$  ( $x = 0-3$ ) compounds, a two-phase method was developed for the preparation of highly active and selective catalysts:  $\text{TiCl}_4$  was first reduced with  $\text{Et}_3\text{Al}$  to give  $\text{TiCl}_2$  and this was then solubilized by adding  $\text{AlCl}_3$  (ref.<sup>3</sup>) or  $\text{EtAlCl}_2$  (ref.<sup>4</sup>) to give the (benzene)Ti(II) complex. This type of Ti(II) complex is also formed "in situ" in  $\text{TiCl}_4$ - $\text{Et}_x\text{AlCl}_{3-x}$  ( $x = 1-1.5$ ) systems in presence of butadiene<sup>5</sup>. In the absence of butadiene, however, reduction only to Ti(III) can be carried out. The optimum system for the formation of (*Z, E, E*)-CDT requires combination of  $\text{TiCl}_4$  with a 6-fold molar excess

of a 1 : 1 mixture of  $\text{EtAlCl}_2$  and  $\text{Et}_2\text{AlCl}$ . The  $\text{TiCl}_4$ - $\text{EtAlCl}_2$  system yields (*Z,E,E*)-CDT as the main product only at an Al/Ti ratio equal to 10 or greater and although the activity and selectivity of (*Z,E,E*)-CDT formation increases with a further increase in the Al/Ti ratio, the yield of the by-product, (*E*)-1,4-poly(butadiene) ((*E*)-1,4-PB), remains high ( $\sim 40\%$ ). At Al/Ti ratios of less than 10, products of the Friedel-Crafts addition of butadiene to benzene (mainly 1-phenylbut-2-ene) are formed in addition to (*E*)-1,4-PB (ref.<sup>5</sup>). However, Wittenberg and Müller<sup>6</sup> claimed that addition of electron donors, such as ethers, sulfides, amines or phosphines, to the  $\text{TiCl}_4 + n \text{EtAlCl}_2$  ( $n < 10$ ) systems substantially improved their activity in (*Z,E,E*)-CDT formation.

Since the co-catalytic effects of phosphines in many transition metal catalysts are well-known and additions of various phosphines are often used to change the catalyst selectivity<sup>7</sup>, we have undertaken a detailed investigation of the effect of the triphenylphosphine ( $\text{PPh}_3$ ) on the  $\text{TiCl}_4$ - $\text{EtAlCl}_2$  system in order to elucidate the mechanism of the  $\text{PPh}_3$  action.

## EXPERIMENTAL

*Chemicals.*  $\text{TiCl}_4$  (Internat. Enzymes) was refluxed with copper turnings and distilled in vacuo. Benzene, butadiene and  $\text{EtAlCl}_2$  were obtained and purified as described elsewhere<sup>2</sup>. Triphenylphosphine (Lachema, Brno) was recrystallized from a hexane-benzene mixture and dried in a high vacuum.

*Methods.* The kinetics of the butadiene consumption were measured in a high-vacuum apparatus at constant temperature and constant butadiene concentration. Standard experimental conditions were:  $[\text{Ti}] = 1.29 \cdot 10^{-3}$  mol/l,  $[\text{C}_4\text{H}_6] = 1.27-3.18 \cdot 10^{-1}$  mol/l, initial reaction volume 30 ml (at 20°C), reaction temperature 50°C.  $\text{PPh}_3$  was weighed into the reactor which was then sealed to the apparatus and evacuated. Other components were added as benzene solutions from ampoules attached to the reactor through breakable seals. The description of the apparatus, the measuring procedure, product isolation and identification were published earlier<sup>8</sup>.

The electronic absorption spectra of the reaction mixtures were recorded on a Varian Cary 17 D spectrometer in the 270–1000 nm region. After the kinetic experiment, the reactor with an attached all-sealed quartz cell (Hellma) ( $d = 0.5$  cm) was cooled with liquid nitrogen and sealed off from the apparatus. After warming and standing for several hours, the reaction solution was poured into the cell and the whole device was inserted into the measuring space of the spectrometer which was then covered with a spacious housing.

## RESULTS AND DISCUSSION

Two series of the kinetic experiments were carried out with the  $\text{TiCl}_4 + m \text{EtAlCl}_2 + n \text{PPh}_3$  systems to demonstrate the influence of each of the components on the catalytic activity and selectivity of the (*Z,E,E*)-CDT formation. The properties of the  $\text{TiCl}_4 + m \text{EtAlCl}_2 + 2 \text{PPh}_3$  ( $m = 4-10$ ) systems were compared with those

of the same systems without  $\text{PPh}_3$ ; the reaction rates in the linear part of the kinetic curves and yields of products are summarized in Table I and examples of the kinetic

TABLE I

Characteristics of the butadiene oligomerization catalyzed by the  $\text{TiCl}_4 + m \text{EtAlCl}_2$  system in the absence of  $\text{PPh}_3$  and in the presence of 2 equiv. of  $\text{PPh}_3$

$m^a$	$n(\text{PPh}_3)$	$v \cdot 10^5{}^b$ $\text{mol l}^{-1} \text{s}^{-1}$	Yield of polymer, %	Amount in the oligomer fraction, % <sup>c</sup>			
				PhB	1,5-COD	( <i>E,E,E</i> )-CDT	( <i>Z,E,E</i> )-CDT
4	0	1.14	49	90	0	0	10
4	2	5.65	8	0	1.5	2	96.5
5	0	4.62	45	84	0	0	16
5	2	7.42	8	0	0.5	2	97.5
6	0	4.91	50	57	0	0	43
6	2	9.84	12	0	trace	1.5	98.5
7	0	5.70	55	50	0	0	50
7	2	8.34	14	0	0	1	99
10	0	8.30	59	15	0	0	85
10	2	8.42	20	0	0	0	100

<sup>a</sup> Standard experimental conditions:  $[\text{Ti}] = 1.29 \cdot 10^{-3} \text{ mol l}^{-1}$ ,  $[\text{C}_4\text{H}_6] = 3.18 \cdot 10^{-1} \text{ mol} \cdot \text{l}^{-1}$ , benzene solution 30 ml, temperature  $50^\circ\text{C}$ ; <sup>b</sup>  $v$  reaction rate in the linear part of the conversion curve (cf. Fig. 1); <sup>c</sup> PhB 1-phenylbut-2-ene and a mixture of diphenylbutanes; 1,5-COD 1,5-cyclooctadiene; (*E,E,E*)-CDT and (*Z,E,E*)-CDT isomers of 1,5,9-cyclododecatriene; % weight percentage.

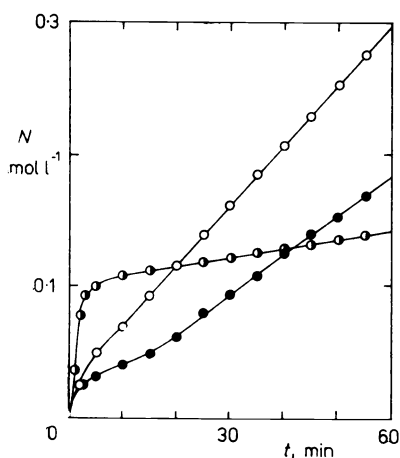


FIG. 1

Kinetics of the butadiene consumption ( $N$ ) catalyzed by the  $\text{TiCl}_4 + 4 \text{EtAlCl}_2$  (○),  $\text{TiCl}_4 + 4 \text{EtAlCl}_2 + 2 \text{PPh}_3$  (●) and  $\text{TiCl}_4 + 2 \text{Et}_2\text{AlCl}$  (○) systems under standard experimental conditions (cf. Table I)

curves are shown in Fig. 1. In the absence of  $\text{PPh}_3$ , the dominating Friedel–Crafts activity of the systems yielded mainly 1-phenylbut-2-ene (PhB) and other products of the benzene alkylation by butadiene, especially at low values of  $m$ . This activity is gradually suppressed by an increase in the value of  $m$ . Simultaneously, an increase in  $m$  leads to an increase in the (Z,E,E)-CDT yield and an increase in the rate of butadiene consumption. The yield of (E)-1,4-PB, however, remains practically constant, about 50% (cf. ref.<sup>5</sup>). The presence of 2 equiv. of  $\text{PPh}_3$  changed these catalytic systems so that they produced a high percentage of (Z,E,E)-CDT, low yield of (E)-1,4-PB and no products of the Friedel–Crafts activity.

The influence of varying amounts of  $\text{PPh}_3$  on the properties of the  $\text{TiCl}_4 + 5 \text{EtAlCl}_2$  system is demonstrated by the results given in Table II. A sharp decrease in the yields of PhB and (E)-1,4-PB occurred in the presence of only one equiv. of  $\text{PPh}_3$ , whereas nearly pure (Z,E,E)-CDT was produced. On the other hand, the presence of 2.5 or 3 equiv. of  $\text{PPh}_3$  led to a considerable decrease in the reaction rate and to lower selectivity of the (Z,E,E)-CDT formation. The presence of 4 equiv. of  $\text{PPh}_3$  deactivated the catalyst.

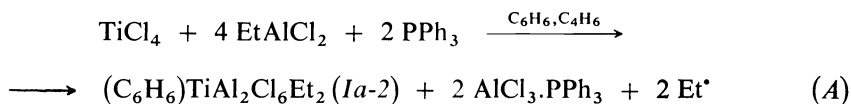
The results obtained when  $\text{PPh}_3$  was added to the  $\text{TiCl}_4$ – $\text{EtAlCl}_2$  systems are based on several well established facts: a) The cyclotrimerization of butadiene to (Z,E,E)-CDT is catalyzed by  $(\eta^6\text{-benzene})\text{Ti}(\text{II})$  complexes,  $(\text{C}_6\text{H}_6)\text{TiAl}_2\text{Cl}_8$  (Ia),  $(\text{C}_6\text{H}_6)\text{TiAl}_2\text{Cl}_7\text{Et}$  (Ia-1) or  $(\text{C}_6\text{H}_6)\text{TiAl}_2\text{Cl}_6\text{Et}_2$  (Ia-2) – their presence in the  $\text{TiCl}_4 + n \text{Et}_x\text{AlCl}_{3-x}$  ( $x = 1, n \geq 40$ ;  $x = 1.5, n \geq 4$ ) systems was recently demonstrated by electronic absorption spectroscopy in the post-reaction cyclotrimerization mixtures<sup>5</sup>. b)  $\text{PPh}_3$  forms stable 1 : 1 complexes with all  $\text{Et}_x\text{AlCl}_{3-x}$  ( $x = 0-3$ ) compounds; more chlorinated (more acid) aluminium compounds are bonded preferably<sup>9</sup>. c)  $\text{PPh}_3$  decomposes the  $(\eta^6\text{-benzene})\text{Ti}(\text{II})$  complexes by abstracting the aluminium component in the absence of a free aluminium compound<sup>9</sup>.

TABLE II

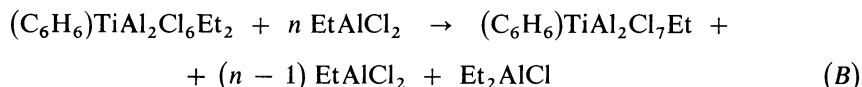
Characteristics of the butadiene oligomerization catalyzed by the  $\text{TiCl}_4 + 5 \text{EtAlCl}_2 + n\text{PPh}_3$  system (experimental conditions and abbreviations as in Table I)

n	$\nu \cdot 10^5$ $\text{mol l}^{-1} \text{s}^{-1}$	Yield of polymer, %	Amount in the oligomer fraction, %			
			PhB	1,5-COD	(E,E,E)-CDT	(Z,E,E)-CDT
0	4.62	45	84	0	0	16
1	6.64	12	1	trace	1	98
2	7.42	8	0	0.5	2	97.5
2.5	3.86	9	0	1	3.5	95.5
3	3.63	9	0	1.5	5	93.5
4	inactive					

These facts indicate that the  $\text{AlCl}_3\cdot\text{PPh}_3$  complex is formed in all the investigated  $\text{TiCl}_4 + m \text{EtAlCl}_2 + 2 \text{PPh}_3$  ( $m \geq 4$ ) systems, e.g., according to Eq. (A).

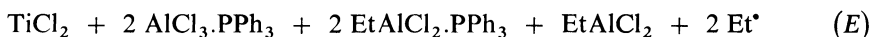
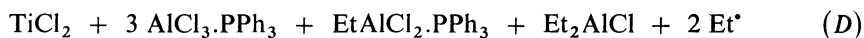
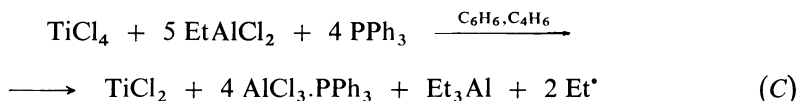


The yields of byproducts, 1,5-cyclooctadiene (1,5-COD) and (*E,E,E*)-1,5,9-cyclododecatriene ((*E,E,E*)-CDT), correspond roughly to catalysis by *Ia-2* if there is no large excess of free  $\text{EtAlCl}_2$  in the resulting system (cf. Table I and ref.<sup>2</sup>). However, an increase in the amount of free  $\text{EtAlCl}_2$  in these systems decreases the number of Et groups in the ( $\eta^6$ -benzene)Ti(II) complex due to the pronounced tendency of these complexes to bind the more chlorinated aluminium component in the system. Thus, in the presence of an excess of  $\text{EtAlCl}_2$ , disproportionation reaction (B) occurs, yielding *Ia-1* which produces 100% (*Z,E,E*)-CDT.



A somewhat higher yield of (*E*)-1,4-PB is typical for all the titanium catalysts containing an excess of  $\text{EtAlCl}_2$  (cf. Table I and refs<sup>2,5</sup>).

Conditions in the  $\text{TiCl}_4 + 5 \text{EtAlCl}_2 + n \text{PPh}_3$  systems are different for  $n > 2$ . Higher yields of 1,5-COD and (*E,E,E*)-CDT and lower reaction rates indicate that more strongly ethylated systems were gradually formed with increasing value of  $n$ . The behaviour of these systems resembles the behaviour of the *Ia-2*- $\text{Et}_2\text{AlCl}$  systems after partial deactivation in a rapid initial cyclotrimerization reaction<sup>2</sup>. This observation and the inactivity of the system for  $n = 4$  indicate that  $\text{EtAlCl}_2$  is disproportionated in the presence of  $\text{PPh}_3$  to give a more ethylated ethylaluminium compound, e.g. according to Eqs (C) or (D). On the other hand, the absence of the  $\text{EtAlCl}_2$  disproportionation (Eq. (E)) would suggest the formation of half the amount of *Ia-2* (from  $\text{TiCl}_2$  and  $\text{EtAlCl}_2$ ) and, hence, the observable catalytic activity of the system with  $n = 4$ .



The actual degree of  $\text{EtAlCl}_2$  disproportionation is not known; systems of this type cannot be studied by the method using the reaction with pentamethylcyclopentadiene ( $\text{Cp}^*\text{H}$ ) and the spectroscopic determination of the structure of the  $\text{Cp}^*\text{TiAl}_2\text{Cl}_{8-x}\text{Et}_x$  ( $x = 0-4$ ) complexes formed, as these systems contain less free aluminium component than required for the stoichiometric formation of these complexes<sup>9</sup>.

The above conclusions concerning the formation of the catalytically active  $\text{Ti(II)}$  species were qualitatively confirmed by the electronic absorption spectra of the reaction solutions after all the butadiene was consumed. The presence of  $\text{PPh}_3$  in the  $\text{TiCl}_4$ - $\text{EtAlCl}_2$  systems allowed us to observe the charge transfer band of the ( $\eta^6$ -benzene) $\text{Ti(II)}$  complexes (*Ia* 397 nm, *Ia-1* 404 nm, *Ia-2* 411 nm,  $\epsilon \sim 2000 \text{ cm}^2 \cdot \text{mmol}^{-1}$ ) (ref.<sup>2</sup>) which was otherwise obscured by the much more intense absorption of the cationic species<sup>5</sup>. In the  $\text{TiCl}_4 + m \text{ EtAlCl}_2 + 2 \text{ PPh}_3$  systems, a charge transfer band was found at 402 nm (corresponding mostly to *Ia-1*) for the system with  $m = 10$  and at 410 nm (corresponding mostly to *Ia-2*) for the system with  $m = 4$ . In the  $\text{TiCl}_4 + 5 \text{ EtAlCl}_2 + n \text{ PPh}_3$  systems, charge transfer was observed at 402 nm for  $n = 1$  and at 410 nm for  $n = 2$ . In all these systems, the product of the catalyst deactivation formed a fine precipitate, mostly  $\text{TiCl}_3$  (refs<sup>2,5</sup>) which, when dispersed in solution, absorbed in the 440–450 nm region; the measurements on the soluble (benzene) $\text{Ti(II)}$  complexes were carried out after its sedimentation. The identity and position of the charge transfer band was checked by the measurement after addition of 4 equiv. of hexamethylbenzene (HMB) which specifically shifts the band position by 10 nm to shorter wavelengths<sup>2</sup>. The spectra of the systems with  $n = 2.5$  and 3 were dominated by the band at 450 nm corresponding to a soluble product of the catalyst deactivation<sup>5</sup>; in the former system, a weak charge transfer band indicating the presence of *Ia-2* was observed only after addition of HMB.

The kinetics and spectroscopic results allow us to conclude that the formation of the trinuclear  $\text{Al-Ti(II)-Al}$  catalytic complexes in the  $\text{TiCl}_4$ - $\text{EtAlCl}_2$  systems, which proceeds in the presence of butadiene<sup>5,10</sup>, is strongly enhanced by addition of  $\text{PPh}_3$ . This component increases the reduction power of ethylaluminium compounds through a disproportionation reaction (Eq. (C) or (D)) and binds  $\text{AlCl}_3$  which has been released in the reduction of  $\text{TiCl}_4$  to  $\text{Ti(II)}$  (see Eq. (A)). Thus, additions of  $\text{PPh}_3$  replace the use of more ethylated aluminium components in the systems, preventing the formation of  $\text{AlCl}_3$  with its Friedel-Crafts catalytic activity. However, comparison of the reaction rates in the  $\text{TiCl}_4 + 4 \text{ EtAlCl}_2 + 2 \text{ PPh}_3$  and the  $\text{TiCl}_4 + 2 \text{ Et}_2\text{AlCl}$  systems, as illustrated in Fig. 1, shows that the latter system is more active. Nevertheless, the suggestion that the disproportionating effect of  $\text{PPh}_3$  can be replaced by using  $\text{Et}_2\text{AlCl}$  (so that the effective  $\text{Et/Cl}$  ratio is kept the same) seems to be valid as follows from the composition of the products which is practically the same in both the systems (for the former system, see Table I). The difference in the activities of the two systems can be due e.g., to a lower degree of the  $\text{EtAlCl}_2$  disproportionation and/or a retarding effect of the  $\text{AlCl}_3 \cdot \text{PPh}_3$  complex;

study of the reasons for this difference is beyond the scope of this work. The problem of whether  $\text{EtAlCl}_2$  itself is disproportionated by the action of  $\text{PPh}_3$  is being studied using  $^{27}\text{Al}$  NMR spectroscopy (for the method, see ref.<sup>11</sup>).

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