

EFFECT OF MERCURY CHLORIDES ON THE ACTIVITY OF COMPLEX TITANIUM-BASED CATALYSTS FOR THE CYCLOTIMERIZATION OF BUTADIENE

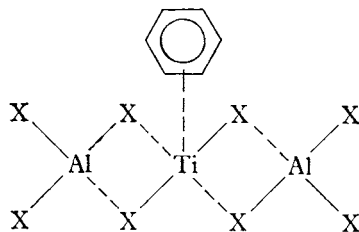
Jindřich POLÁČEK, Karel MACH and Lidmila PETRUSOVÁ

*J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2*

Received November 22nd, 1984

Mercury chlorides decompose arenetitanium(II) complexes by redox reactions, e.g. $Ti^{2+} + Hg^+ \rightarrow Ti^{3+} + Hg^0$, and thus inhibit their catalytic activity in the cyclotrimerization of butadiene. The effect of mercury chlorides added to the $TiCl_4$ - Et_3Al catalytic system depends on their ratio to organoaluminium compound. The cyclotrimerization activity is preserved when a sufficient excess of the latter is present, ensuring the reverse reduction of Ti(III) to Ti(II). A high cyclotrimerization activity and selectivity of the catalysts are achieved if Ti(II) is converted to trinuclear Al-Ti-Al complex under the effect of ethylaluminium dichloride.

The catalytic activity of titanium-based Ziegler catalysts for the cyclotrimerization of butadiene to 1,5,9-cyclododecatriene was discovered by Wilke¹ in the late 1950s. In the early 1960s, Müller and coworkers² and Vohwinkel³ found that this reaction is also catalyzed by arenetitanium(II) complexes, prepared by Natta and coworkers⁴ in 1959. The structure of these crystalline, well-defined substances,



I (Ia for X = Cl)

was determined by chemical methods^{5,6}, by the ESR study of their redox reaction with cyclopentadiene⁷, and by X-ray diffraction analysis⁸. It has been suggested^{3,9} that the cyclotrimerization process on them involves displacement of the coordinated arene molecule by three molecules of butadiene, and this concept has recently been borne out¹⁰ by the experimental results of a kinetic study of the cyclotrimerization of butadiene catalyzed by chloro, bromo, and mixed chloro-bromo arenetitanium(II) complexes.

Since cyclic trimers of dienes are valuable intermediates in a number of organic syntheses, the results of examination of the cyclotrimerization activity of titanium-based catalysts have

largely been included in the patent literature while only scarce reports, following up the corresponding patents or aimed at the elucidation of the cyclotrimerization mechanism, have appeared in scientific journals⁹⁻¹⁶.

In the patent literature, the use of a wide variety of co-catalytic components improving the activity or selectivity of the cyclotrimerization reaction is claimed. Among these components are also chlorides of mercury¹⁷. In a US patent¹⁸ mercury(II) chloride is even proposed as a substitute for AlCl_3 in the $\text{TiCl}_4\text{-Et}_3\text{Al-AlCl}_3$ catalytic system. In the present work, the interaction of mercury chlorides with $(\eta^6\text{-benzene})\text{bis}(\text{dichloro}(\mu\text{-chloro})\text{titanium(II)})$, (*Ia*), and with the $\text{TiCl}_4\text{-Et}_3\text{Al}$ catalytic system is studied with a view to elucidating the role of mercury chlorides in the formation of the catalytically active species.

EXPERIMENTAL

Chemicals. The preparation and purification of $\text{C}_6\text{H}_6\cdot\text{TiAl}_2\text{Cl}_8$ complex has been described¹⁹. TiCl_4 (Internat. Enzymes) was refluxed with copper chips and vacuum distilled. $(\text{C}_2\text{H}_5)_3\text{Al}$ was prepared by boiling $(\text{C}_2\text{H}_5)_2\text{AlCl}$ with sodium metal followed by vacuum distillation. $\text{C}_2\text{H}_5\text{AlCl}_2$ was obtained as colourless crystals, m.p. above 25°C , by vacuum distillation from a mixture of ethylaluminium sesquichloride with aluminium chloride. HgCl_2 and Hg_2Cl_2 were chemicals of reagent grade purity (Lachema) and they were used with no additional purification. Butadiene of technical purity (Fluka) and benzene of reagent grade purity (Lachema) were purified as described previously¹⁰.

Apparatus. The vacuum apparatus and the procedure for monitoring the butadiene conversion, including the isolation and analysis of the products, have been described previously¹⁰. The $\text{TiCl}_4\text{-Et}_3\text{Al}$ catalytic system was obtained by mixing benzene solutions of the components in the reactor before starting the reaction with butadiene. Hg_2Cl_2 was added either directly to the reactor before sealing the latter to the vacuum equipment, or stepwise during the reaction with the aid of a magnetically controlled dosing device. HgCl_2 was weighed into an ampoule with a break seal. The ampoule was evacuated, sealed up, and then attached by sealing to the reactor. Finally, HgCl_2 was sublimed in vacuum into the reactor space.

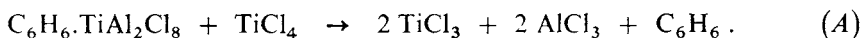
Measurement of the electronic absorption spectra of catalytic systems. The electronic absorption spectra were measured in sealed quartz cells on a Varian Cary 17 D instrument.

RESULTS AND DISCUSSION

Interaction of Hg_2Cl_2 with $\text{C}_6\text{H}_6\cdot\text{TiAl}_2\text{Cl}_8$

The conversion curves in Fig. 1a and the data in Table I show that the cyclotrimerization activity of $\text{C}_6\text{H}_6\cdot\text{TiAl}_2\text{Cl}_8$ complex decreases with increasing Hg_2Cl_2 additions and ultimately it is inhibited completely as the mercury(I)-to-titanium(II) ratio reaches the value of one. The latter systems exhibit a low polymerization or alkylation activity giving highly crosslinked *trans*-1,4-poly(butadiene), phenylbutene and its homologues. Since aluminium chloride is known to promote cationic polymerization of butadiene to *trans*-1,4-poly(butadiene), particularly in the presence of Ti(III)

or Ti(IV) halides^{3,20,21}, polymerizations of butadiene were carried out under analogous reaction conditions both with aluminium chloride and with the $\text{TiCl}_3 + \text{AlCl}_3$ catalytic system prepared by the reaction²²



The resulting conversion curves exhibit a course (Fig. 1*b*) closely similar to those found for the interaction of butadiene with $\text{C}_6\text{H}_6 \cdot \text{TiAl}_2\text{Cl}_8 + \text{Hg}_2\text{Cl}_2$ systems at ratios $\text{Hg}^+/\text{Ti}^{2+} \geq 1$, the reaction products being identical, too (Table I). The benzenetitanium(II) complex- Hg_2Cl_2 systems differed from those formed according to Eq. (A) only in a grey turbidity which deposited on the bottom of the reactor after stopping the experiment and gave microscopic droplets of mercury on trituration.

Occurring also in the absence of butadiene, the reaction between $\text{C}_6\text{H}_6 \cdot \text{TiAl}_2\text{Cl}_8$ and Hg_2Cl_2 at $\text{Hg}^+/\text{Ti}^{2+} = 1$ was monitored spectrophotometrically. The absorption bands of the arene-titanium(II) complex¹⁰ decreased and that at 450 nm caused by the forming russet-yellow suspension increased during the reaction with the surface of Hg_2Cl_2 . The suspension emerging from reaction according to Eq. (A) gave rise to an absorption band at the same wavelength, and so this band was attributed to titanium trichloride. The formation of mercury is probably quantitative, as indicated by the value of 0.72 mmol of mercury obtained in the form of droplets per mmol Ti(II); the small fraction of mercury remaining in the suspension was not determined. All these results agree with the oxidative decomposition of the Ti(II)

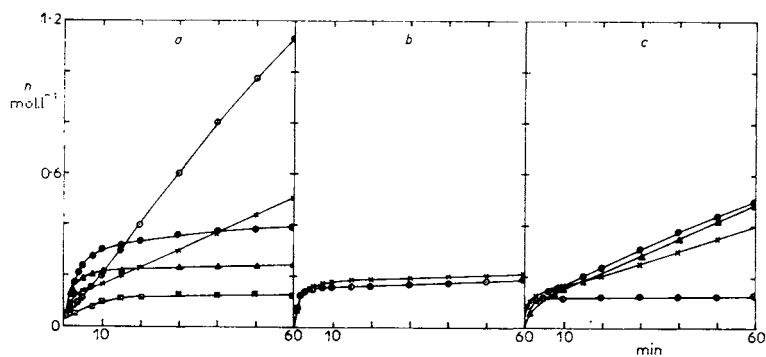


FIG. 1

Kinetics of butadiene conversion with the catalytic systems studied (see Table I). Systems: *a* —○— A, —×— B, —△— C, —●— D, —□— E; *b* —○— F, —×— G; *c* —○— H, —×— I, —●— J, —●— K

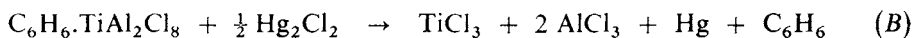
TABLE I

Characteristics of the catalytic systems (concentration of the titanium component 1.28 mmol l^{-1} , reaction temperature 50°)

System	Component ratio	Reaction rate ^a $10^{-5} \text{ mol l}^{-1} \text{ s}^{-1}$		Reaction order ^c	Amount in the oligomer fraction ^d %			PB ^e %
		A ^b	B ^b		FB	(Z,E,E)-CDT	(E,E,E)-CDT	
$\text{C}_6\text{H}_6 \cdot \text{TiAl}_2\text{Cl}_8$								
A	—	33.2	—	1.9 ^f	2	97–98	1	8
$\text{C}_6\text{H}_6 \cdot \text{TiAl}_2\text{Cl}_8 + \text{Hg}_2\text{Cl}_2$								
B	1:0.2	11.5	—	—	7	93	0	15
C	1:0.5	0.8	—	—	100	0	0	36
C' ^g	1:0.5	4.2	69.0	1.7	0	99	1	31
D	1:1	1.7	—	—	100	0	0	23
D' ^g	1:1	8.2	128.0	1.7	0	100	0	17
E	1:10	0.5	—	—	—	—	—	—
AlCl_3								
F	—	1.1	—	—	100	0	0	31
$\text{TiCl}_3 + \text{AlCl}_3$								
G	1:1	1.1	—	—	100	0	0	30
G' ^g	1:1	5.2	82.0	1.7	0	99	1	31
$\text{TiCl}_4 + \text{Et}_3\text{Al} + \text{HgCl}_2$								
H	1:1:25:1:12	—	0.6	—	—	—	—	—
H' ^g	1:1:25:1:12	10.0	154.0	1.7	0	100	0	28
I	1:2:1:12	—	7.9	—	0	98	1	14
$\text{TiCl}_4 + \text{Et}_3\text{Al}$								
J	1:1	—	11.3	—	0	97	1	16
K	1:2	—	11.8	—	0	58	24	36

^a Rate of the butadiene conversion in the linear part of the conversion curve (for experiments C', D', G', H' only after the cyclotrimerization has started). ^b Butadiene concentration: A = 64 mmol l^{-1} , B = 320 mmol l^{-1} . ^c Reaction order with respect to the butadiene concentration (for experiments C', D', G', H' after the cyclotrimerization has started). ^d FB is a mixture of 1-phenyl-2-butene and diphenylbutanes, (Z,E,E)-CDT and (E,E,E)-CDT are two isomers of 1,5,9-cyclododecatriene; oligomer products in experiments I–K contained also 1,5-cyclooctadiene (balance to 100%). ^e *cis*-1,4-Poly(butadiene) in experiment K, a mixture of *cis* and *trans* form in experiments I and J, *trans*-1,4-poly(butadiene) in all other experiments. ^f Ref.¹⁰. ^g Cyclotrimerization activity obtained by addition of $\text{C}_2\text{H}_5\text{AlCl}_2$ (mol. ratio to Ti = 40) after 30 min of reaction; butadiene concentration was increased from 64 to 320 mmol l^{-1} after 90 min of reaction.

complex according to the equation (B)



giving rise to TiCl_3 , which is incapable of catalyzing the cyclotrimerization process²², and to AlCl_3 responsible for the observed cation-type catalytic activity. One molar equivalent of Hg_2Cl_2 added to arenititanium(II) complex can be replaced by one molar equivalent of HgCl_2 without affecting the catalytic activity of this system.

The identical nature of systems obtained according to equations (A) and (B) also reflects in their analogous behaviour during their activation with the excess of EtAlCl_2 . We have shown²² that an inactive system containing TiCl_3 can be reactivated in the presence of butadiene by adding $\text{C}_2\text{H}_5\text{AlCl}_2$ in a sufficient excess ($\text{Al}/\text{Ti} > 30$). As indicated by the kinetic measurements (Fig. 2, Table I), reverse reduction of Ti(III) to Ti(II) occurs in the presence of $\text{C}_2\text{H}_5\text{AlCl}_2$, and a trinuclear complex of type *Ia*, containing probably one ethyl group in the outer position²³, is consecutively formed. The cyclotrimerization process thus sets in with a short induction period and the reaction order with respect to the butadiene concentration approaches 2, a value characteristic for the catalysis by the $\text{C}_6\text{H}_6 \cdot \text{TiAl}_2\text{Cl}_8$ complex¹⁰. The systems $\text{C}_6\text{H}_6 \cdot \text{TiAl}_2\text{Cl}_8 + \text{Hg}_2\text{Cl}_2$ at $\text{Hg}^+/\text{Ti}^{2+} \geq 1$ could be activated in this manner, too (Fig. 2, Table I). When Hg_2Cl_2 was present in an excess with

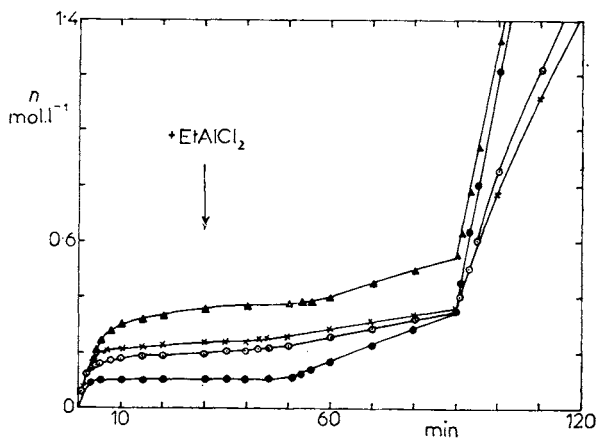


FIG. 2

Kinetics of butadiene cyclotrimerization in systems C, D, G, H (Table I) activated by the addition of $\text{C}_2\text{H}_5\text{AlCl}_2$ (mol. ratio to Ti = 40) after 30 min of reaction, butadiene concentration was increased from 64 to 320 mmol l^{-1} after 90 min of reaction. Activated systems: $-\times-$ C', $-\triangle-$ D', $-\odot-$ G', $-\bullet-$ H'

respect to the stoichiometry of the redox reaction (B), the induction period extended until all Hg^+ was consumed. The active system thus formed showed, however, somewhat improved catalytic properties (a higher reaction rate and a lower polymer yield). Additional portions of Hg_2Cl_2 , delivered in the course of the restored cyclotrimerization, had no observable effect (provided that the molar ratio $\text{C}_2\text{H}_5\text{AlCl}_2/\text{Hg}_2\text{Cl}_2$ was $\gg 1$).

Interaction of HgCl_2 with $\text{TiCl}_4-(\text{C}_2\text{H}_5)_3\text{Al}$ Systems

In the patent mentioned¹⁸, Munley and Wiese propose, for the $\text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al} + \text{AlCl}_3$ catalytic system with the component ratio 1 : 1.25 : 1.12, to replace aluminium chloride with mercury(II) chloride. The occurrence of reaction (B), however, indicates that even if the reduction capacity of the organo aluminium compound were fully exploited, *i.e.*, if the compound were transformed completely to AlCl_3 , this system could afford titanium in a valence state not lower than Ti(III) due to the oxidative effect of HgCl_2 . Kinetic measurements showed that this system is actually inactive (Fig. 1c, Table I). The $\text{TiCl}_4 : \text{Et}_3\text{Al} : \text{HgCl}_2 = 1 : 2 : 1.2$ system, with an enhanced amount of the reducing component, exhibited a cyclotrimerization activity which was only slightly lower than that of the system free of HgCl_2 . The addition of HgCl_2 makes this system similar to the $\text{TiCl}_4 : \text{Et}_3\text{Al} = 1 : 1$ system, as documented by the low polymer yield in both cases (Fig. 1c, Table I).

In order to demonstrate that our interpretation of the interaction mechanism of mercury chlorides with titanium-based complex catalysts is of general validity, we activated the above mentioned and fully inactive system $\text{TiCl}_4 + \text{Et}_3\text{Al} + \text{HgCl}_2$ with component ratios 1 : 1.25 : 1.12 by adding an excess of ethylaluminium dichloride. The induction period was followed by the cyclotrimerization reaction whose reaction order with respect to the butadiene concentration approached the value of 2 and whose products had a composition similar to that obtained with analogously activated $\text{C}_6\text{H}_6 \cdot \text{TiAl}_2\text{Cl}_8 + \text{Hg}_2\text{Cl}_2$ systems at $\text{Hg}^+/\text{Ti}^{2+} \geq 1$ (Fig. 2, Table I).

The results of this work thus indicate that the positive effect of mercury chlorides on the activity of complex titanium-based catalysts, reported in the patent literature, is dubious. This effect can only appear if the reducing organoaluminium component is present in a suitable excess, and it is probably due to the increasing density of chlorine atoms in the neighbourhood of the central titanium atom, for the Ti(III)-compound formed in the redox reaction between Hg^+ or Hg^{2+} and Ti^{2+} is again reduced by the organoaluminium component, and this process is accompanied by an ethyl-chlorine exchange reaction on the aluminium centre. As a consequence, more suitable conditions may occur for the formation of Ti(II) complexes which are carriers of the cyclotrimerization activity²². This explanation is supported by the enhanced activity and lower polymer yield observed in those catalytic systems, where the used amount of mercury chlorides makes such a mechanism possible (Table I).

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Translated by P. Adámek.