

DEACTIVATION OF ARENETITANIUM(II) BROMOALANE COMPLEXES IN THE CYCLOTRIMERIZATION OF BUTADIENE

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The $C_6H_6 \cdot Ti(II)(AlBr_4)_2$ (*Ib*) catalyst deactivates during the butadiene cyclotrimerization to give a solid containing all titanium (mostly as $TiBr_3$) and a mixture of $AlBr_3$ and $RAI\text{Br}_2$ compounds dissolved in benzene. The residual cationic catalytic activity of the deactivated *Ib* system is due to presence of $AlBr_3$. In contrast to $TiCl_3$, the deactivated *Ib* system and the model system $TiBr_3 + AlBr_3$ are not activated by the addition of $EtAlCl_2$ in the presence of butadiene: the highly active benzenetitanium(II) system is re-constituted only after reduction of $TiBr_3$ with Et_3Al followed by the addition of $EtAlCl_2$. The addition of Et_2AlBr to *Ib* accelerates the deactivation of the system. Deactivation products of this system contain mainly Ti(II) species which forms benzenetitanium(II) catalytic system after addition of $EtAlCl_2$. All the $EtAlCl_2$ reactivated systems produce (*Z, E, E*)-1,5,9-cyclododecatriene with high catalytic stability and considerable selectivity (>90%). This behaviour points to the catalysis by benzenetitanium(II) chloroalane complexes containing only low amount of bromine atoms and ethyl groups.

Arenetitanium(II) complexes $C_6H_6 \cdot Ti(AlCl_4)_2$ (*Ia*) and $C_6H_6 \cdot Ti(AlBr_4)_2$ (*Ib*) catalyze the butadiene cyclotrimerization to (*Z, E, E*)-1,5,9-cyclododecatriene (CDT) with selectivity as high as 92% and 95%, respectively¹. The *Ia* system deactivates negligibly in course of the catalytic reaction, the *Ib* system, which displays considerably higher initial reaction rate than the former one, is, however, rapidly deactivated. Products of the catalyst deactivation were found to separate into a dark red precipitate, which contains all the titanium present in the system, and an aluminium product soluble in benzene. The solid products were not specified precisely by analytical methods due to low quantity of the material which could be obtained in the laboratory scale experiment (≤ 0.04 mmol *Ib*) and its reactivity to dioxygen and humidity. The analysis of bromoaluminium compound presumably present in the reaction solution was not attempted because of the simultaneous presence of CDT, higher oligomers and a polymer.

In this paper we extend our previous study¹ since better characterization of the deactivation products may aid to understand the mechanism of the deactivation process and to design the optimum catalyst. The deactivated *Ib* system is studied by checking its residual catalytic activity and by comparing this activity with that of the reference system $TiBr_3 + AlBr_3$ and $AlBr_3$ alone. The previous analysis

of solid deactivation products is complemented by analysis of the soluble deactivation products by using the ESR method. The influence of the addition of Et_2AlBr on the catalytic behaviour of the *Ib* system is also described. The nature of deactivation products of both *Ib* and $\text{Et}_2\text{AlBr} + \text{Ib}$ systems is further characterized by their catalytic behaviour after the addition of excess of EtAlCl_2 , the addition of which is known to reactivate analogous chlorine-containing systems in the presence of butadiene².

EXPERIMENTAL

Chemicals. The complex $\text{C}_6\text{H}_6\cdot\text{Ti}(\text{AlBr}_4)_2$ (*Ib*) was prepared and purified as described elsewhere³. Et_2AlBr was prepared from ethylaluminium sesquibromide by heating with NaBr ⁴. EtAlCl_2 was prepared by the reaction of ethylaluminium sesquichloride with AlCl_3 and purified by distillation and crystallization⁵. Et_3Al (Fluka) was handled under argon and purified by distillation *in vacuo*. TiBr_4 and AlBr_3 were prepared by reacting bromine with the metals under argon. Crude products were distilled *in vacuo*. AlBr_3 was further purified by heating with the aluminium powder to 200° until the colourless product was obtained. $(\text{Cp}_2\text{TiBr})_2$ was prepared by the reduction of Cp_2TiBr_2 with Al powder in THF; AlBr_3 was washed out with ethyl ether. Butadiene (Fluka, puriss.) and benzene were purified as described previously¹.

Methods. Kinetics of the butadiene conversion was measured in the high-vacuum apparatus at constant butadiene concentration and constant temperature. Experimental details of the measurement, product isolation, and identification of products were described recently¹. Dosing of further components (Et_2AlBr 0.1M, Et_3Al 0.1M, and EtAlCl_2 1.0M, all in benzene) was carried out by opening break-seals attached to the reactor with a magnetic breaker.

ESR spectra were measured on an ERS-220 spectrometer (German Acad. Sci., Berlin, G.D.R.) at room temperature in the X-band. Electronic absorption spectra were taken on a Varian Cary 17 D spectrometer with the reaction mixtures being analyzed in sealed quartz cells (Hellma).

RESULTS AND DISCUSSION

The Residual Catalytic Activity of the Deactivated

$\text{C}_6\text{H}_6\cdot\text{Ti}(\text{AlBr}_4)_2$ System

Recently we have found¹ that the initial rate of the butadiene cyclotrimerization for the $\text{C}_6\text{H}_6\cdot\text{Ti}(\text{AlBr}_4)_2$ (*Ib*) system ($k_{\text{app}}(\text{Ib}) = 210 \text{ l}^{1.5} \text{ mol}^{-1.5} \text{ s}^{-1}$) was higher than that for the $\text{C}_6\text{H}_6\cdot\text{Ti}(\text{AlCl}_4)_2$ (*Ia*) system ($k_{\text{app}}(\text{Ia}) = 75 \text{ l}^{1.9} \text{ mol}^{-1.9} \text{ s}^{-1}$) and that the rapid deactivation of the arenetitanium(II) catalyst occurred in the former system. Since in both systems the butadiene cyclotrimerization was assumed to proceed by the same mechanism on active species preserving the trinuclear structure of the original arenetitanium(II) complex, the difference in the reaction order with respect to butadiene concentration might be due to the difference in deactivation of both systems. The complex *Ib* decomposed during the butadiene cyclotrimerization as was evidenced by electronic absorption spectra of the reaction mix-

tures, and its concentration along with the reaction rate decreased with the amount of the consumed butadiene (turnover about 1 800 molecules of butadiene per one molecule of *Ib*).

Presently, we have prolonged the measurement of kinetics of the butadiene consumption to as far as the complex *Ib* is completely decomposed. This occurred, as seen from the electronic absorption spectra, after 150 min of the reaction when a slow and constant reaction rate was achieved (see Fig. 1*a*, curve 1). The five-fold increase of the butadiene concentration after 90 min, which accelerated the deactivation of residual traces of *Ib*, showed that the reaction order in butadiene was lower than 0.5.

The composition of products obtained after 1 h of the reaction (CDT 95%, (*E*)-1,4-polybutadiene 4%, 1-phenylbut-2-ene 1%, traces of (*E, E, E*)-CDT, diphenylbutanes and higher products of benzene alkylation with butadiene¹) changed in the prolonged experiments so that the content of all the butadiene-benzene adducts, including oligomers and a butadiene polymer containing phenyl groups, increased with the amount of butadiene consumed at the low reaction rate. The latter products are characteristic of the cationically catalyzed reaction between benzene and butadiene and also the kinetics of butadiene consumption with the deactivated *Ib* system showed features of cationic catalysis by Lewis acids⁶ (AlCl_3 , AlBr_3).

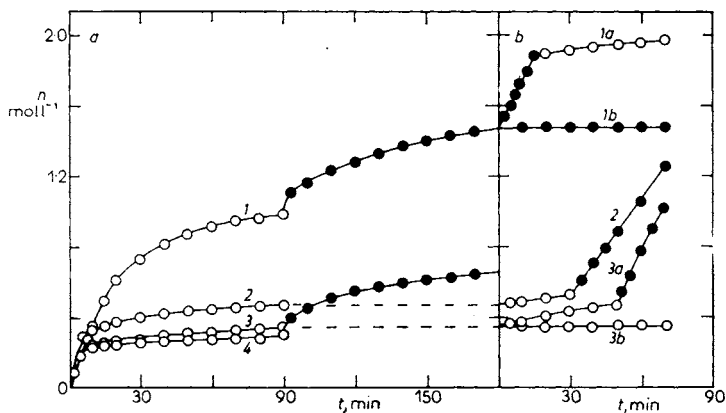


FIG. 1

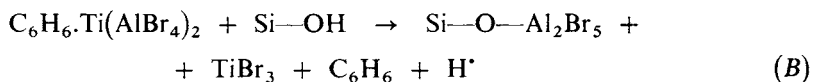
Kinetics of the butadiene conversion catalyzed by systems containing *Ib* and model systems at the butadiene concentration 63.6 mmol l^{-1} —○— and 318 mmol l^{-1} —●—. *a* Catalytic systems: *Ib* 1, $4\text{Et}_2\text{AlBr} + \text{Ib}$ 2, $\text{TiBr}_3 + \text{AlBr}_3$ 3 (in all systems $[\text{Ti}] = 1.28 \text{ mmol l}^{-1}$, $[\text{Al}] = 2.56 \text{ mmol l}^{-1}$). *b* The catalytic systems from the part *a* after addition of 40 equivalents of EtAlCl_2 (with respect to Ti): curves 1*b*, 2, 3*b* or after the addition of 4 equivalents of Et_3Al followed after 5 min by 40 equivalents of EtAlCl_2 : curves 1*a*, 3*a*

The analogous kinetics was actually found and the same and very similar products of cationic catalytic activity were obtained with the AlBr_3 catalyst and with the $\text{TiBr}_3 + \text{AlBr}_3$ system prepared according to equation (A).



The kinetics of the butadiene consumption was characterized by high initial rates after admission of butadiene or after increase of the butadiene concentration during the reaction (see Fig. 1a, curve 3, 4). In the later stage of nearly constant reaction rate the reaction order with respect to butadiene concentration was lower than 0.5. In both systems the similar mixtures of low-molecular alkylation products containing butadiene and benzene units in various ratios were obtained while CDT and high-molecular (*E*)-1,4-polybutadiene were absent. Low amount of the powdery, probably highly cross-linked polymer possessed low content of (*E*)-1,4- bonds and contained some phenyl groups.

The comparison of catalytic activities of the deactivated *Ib* system, $\text{TiBr}_3 + \text{AlBr}_3$ system, and AlBr_3 leads to the conclusion that the residual activity of the *Ib* system is due to AlBr_3 present in the solution, while TiBr_3 or other solid products of the *Ib* deactivation have no observable catalytic effect. Minor differences (*e.g.*, higher abundance of low-molecular products) in the catalytic activity of the AlBr_3 catalyst and the systems containing initially *Ib* may arise from elimination of OH groups from the reactor glass walls ($\text{Si}-\text{OH}$) by arenetitanium(II) complex according to Eq. (B).



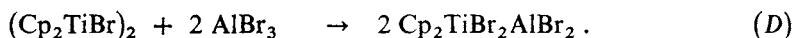
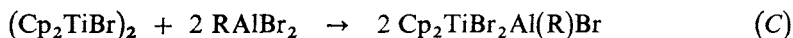
The similar nature of the deactivated *Ib* system and the $\text{TiBr}_3 + \text{AlBr}_3$ system was also indicated by the electronic absorption spectra. The agitated reaction mixture of the deactivated *Ib* system displayed the absorption bands at 500 nm and at 300 to 350 nm. The bands at 300, 345 and 500 nm belonged to TiBr_3 which sedimented on standing. The yellow supernatant solution exhibited an intense band at 332 nm which was ascribed to the interaction of AlBr_3 with products of the butadiene conversion¹. The system $\text{TiBr}_3 + \text{AlBr}_3$ gave virtually the same spectrum of TiBr_3 and the solution showed a band at 350 nm shifting in time to 370 nm. The interaction of AlBr_3 with butadiene yielded the absorption band at 370 nm which could be tentatively assigned to protonized hydrocarbon cations⁷.

Deactivation Products of *Ib*

The previous examination of the solid deactivation products of *Ib* gave mostly semiquantitative results which indicated that a complex mixture of compounds was

formed¹. The chemical analysis yielded Br : Ti ratio in the range 2.4–2.7. Mass spectra revealed the presence of the compound $C_{12}H_{19}TiBr_2$ in addition to $TiBr_3$. The amount of hydrogen which was evolved in the reaction of the solid material with water corresponded to less than 10% of the total titanium content. All the above results pointed mainly to the presence of Ti(III), a substantial part of which was present in the form of $TiBr_3$, and hence, the complementary aluminium products of the composition $RAiBr_2$ (R – derived from butadiene or its oligomers) should be found in the reaction solution in addition to $AlBr_3$.

The evidence for the presence of the $RAiBr_2$ compounds and $AlBr_3$ in the reaction solution is now obtained by the ESR detection of complexes formed upon addition of $(Cp_2TiBr)_2$ to the reaction solution of the deactivated *Ib* system. Stable Ti–Al binuclear complexes displaying different ESR spectra are formed according to equations⁸ (C) and (D).



The unpaired electron density on the aluminium nucleus ($I_{Al} = 5/2$) results in the appearance of the six-line ESR spectrum of $Cp_2TiAlBr_4$ (Fig. 2, curve 1). The alkyl substituent in the complex $Cp_2TiAlBr_3Et$ reduces this electron density and as a result a single-line ESR spectrum is obtained⁸ (Fig. 2, curve 3). The reaction solution containing the added $(Cp_2TiBr)_2$ (to give Ti : Al = 1) gave an ESR spectrum which was a composite of both the above spectra (Fig. 2, curve 2). Since the nature of the substituent R has no influence on the ESR spectra of the binuclear Ti–Al complexes⁸,

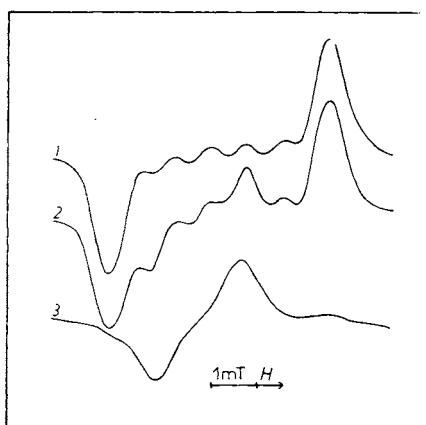
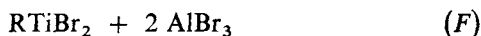
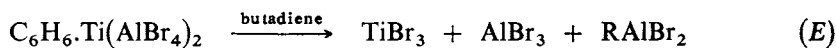


FIG. 2

ESR spectra of benzene solutions of binuclear Ti–Al complexes: 1 $Cp_2TiAlBr_4$ ($g = 1.985$, $a_{Al} = 0.78$ mT), 2 $(Cp_2TiBr)_2$ (0.8 ml of 0.1M solution) added to the reaction solution which was separated from the precipitate after 150 min of the butadiene cyclotrimerization with *Ib* (0.04 mmol in 30 ml) (cf. Fig. 1a, curve 1), 3 $Cp_2TiAlBr_3Et$ ($g = 1.987$, $\Delta H = 1.8$ mT) containing a trace of $Cp_2TiAlBr_4$; all spectra taken at room temperature

the ESR spectrum of the reaction solution was simulated by measuring mixtures containing $\text{Cp}_2\text{TiAlBr}_4$ and $\text{Cp}_2\text{TiAlBr}_3\text{Et}$ in various ratios. The best agreement was obtained for the ratio $\text{Cp}_2\text{TiAlBr}_4 : \text{Cp}_2\text{TiAlBr}_3\text{Et}$ equal to $4(\pm 0.5) : 1$ which implied that about 20% of AlBr_3 was alkylated during the deactivation of the *Ib* system.

The deactivation of *Ib* in the presence of butadiene may proceed according to equations (E)–(G).



As the decomposition of *Ib* according to Eq. (E) suggests 50% formation of AlBr_3 , the 20% yield of RAlBr_2 found in the deactivated *Ib* system indicates that about 40% of *Ib* decomposed in this way. This value roughly corresponds to the value of Br : Ti (2.4–2.7) found by chemical analysis of the solid material. The rest of Ti(III) has to be assigned to the poorly characterized RTiBr_2 , where R is $\text{C}_{12}\text{H}_{19}$, or a polymeric radical¹. The low quantity of the Ti(II) product, probably TiBr_2 , took origin in the thermal decomposition or disproportionation of RTiBr_2 ^{9,10} since a dilution of the benzene solution of *Ib* with butadiene or products of its oligomerization should hardly result in the *Ib* dissociation according to Eq. (G). We assume that TiBr_2 is trapped in the insoluble Ti(III) products and cannot react with the soluble bromoaluminium components.

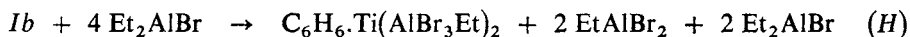
All these results allow us to make a conclusion that the deactivation of the *Ib* system lies in the irreversible electron transfer from the Ti(II) species to butadiene or to the unsaturated hydrocarbon product. The oxidation of Ti(II) to Ti(III) always leads to the decomposition of the trinuclear Al—Ti—Al structure as has been shown by oxidation of *Ia* with Hg(I) or Ti(IV) chlorides² (see Eq. (A)). The mechanism of the deactivating electron transfer is not known. It should occur in that stage of the catalytic cycle of the butadiene cyclotrimerization which involves reversible changes of formal titanium valency $\text{Ti(II)} \rightleftharpoons \text{Ti(IV)}$ and partially reversible changes of π -allyl to σ -alkenyl bonding as proposed in the preceding paper¹.

The System $\text{Et}_2\text{AlBr} + \text{Ib}$

We have attempted to prevent the oxidative decomposition of *Ib* in course of the butadiene cyclotrimerization by the addition of 4 equivalents of Et_2AlBr to *Ib*, however, no stabilizing effect on the arenetitanium(II) complex was observed. The kinetic curve of the butadiene consumption showed even accelerated deactivation of the catalyst (Fig. 1a, curve 2). The partially deactivated catalyst induced slow butadiene consumption at constant rate which, in contrast to the *Ib* system, showed

the reaction order with respect to butadiene concentration approximately equal to 1.0 and did not yield products of the cationic catalysis. The reaction products contained CDT 94%, (*E, E, E*)-CDT 2%, a mixture of (*E*)- and (*Z*)-1,4-polybutadiene and a trace of 1,5-cyclooctadiene. We suppose that byproduct oligomers and (*Z*)-1,4-polybutadiene were formed mainly with the low active catalyst.

The kinetic behaviour of the $\text{Et}_2\text{AlBr} + \text{Ib}$ system can be qualitatively explained by the electron donating effect of ethyl groups introduced into the outer positions⁸ of *Ib*. This effect accelerates both the cyclotrimerization reaction and the electron transfer which is followed by immediate decomposition of the trinuclear Ti(III) species. Since the stability of arenetitanium(II) complexes decreases with increasing number of ethyl groups in the complex⁸, the mixture of EtAlBr_2 and Et_2AlBr formed according to Eq. (H) is not able to re-constitute the arenetitanium(II) complex, though in the presence of butadiene it reduces the Ti(III) formed to Ti(II) species (see below).



The catalytic system, showing low and constant activity, formed brown, mostly homogeneous system from which, however, a small amount of dark precipitate settled out after several hours. Owing to this behaviour, the deactivation products were not accessible to analytical methods applied to the deactivated *Ib* system. The only information on the nature of this low active system was obtained from changes in its catalytical properties induced by the addition of EtAlCl_2 in large excess (see below).

Reversible Activation of the Deactivated Ib Systems by the Addition of EtAlCl₂ in Excess

We have recently shown that arenetitanium(II) complexes are formed *in situ* after addition of a large excess of EtAlCl_2 to TiCl_2 or to TiCl_3 in the presence of butadiene^{2,11,12}. The catalysis by arenetitanium(II) complexes was indicated by the reaction order of butadiene consumption with respect to butadiene concentration higher or equal to 1.5. Since the analogous application of EtAlBr_2 would in the present case lead again to low-active systems¹², both the *Ib* and $\text{Et}_2\text{AlBr} + \text{Ib}$ deactivated systems were subjected to the reactivation with EtAlCl_2 in an effort to find out the oxidation state of titanium in them and to get information on the *in situ* formation of benzenetitanium(II) complexes containing chloro, bromo and ethyl ligands and on their catalytic behaviour in the cyclotrimerization of butadiene.

The additions of 40 equivalents of EtAlCl_2 with respect to titanium influenced the deactivated *Ib* system and the $\text{TiBr}_3 + \text{AlBr}_3$ system on one side, and the low-active $\text{Et}_2\text{AlBr} + \text{Ib}$ system on the other side, in different ways (see Fig. 1b). The

former systems lost even the weak cationic catalytic activity (Fig. 1*b*, curves 1*b*, 3*b*) but the latter one became immediately more active and showed the approximate reaction order in butadiene about 1.6 (Fig. 1*b*, curve 2). The former two systems turned active only when the addition of 4 equivalents of Et_3Al preceded the addition of EtAlCl_2 (Fig. 1*b*, curves 1*a*, 3*a*). The reaction order with respect to butadiene concentration was found also about 1.5–1.6. These values of the reaction order indicated the catalysis by the benzenetitanium(II) complexes, producing CDT with high selectivity (>90%). High catalytic stability of all the reactivated systems showed that bromine atoms in the benzenetitanium(II) complexes were largely substituted with chlorine atoms from EtAlCl_2 and the content of ethyl groups in the complexes was low¹². The comparison with the catalytic activity of the 40 $\text{EtAlCl}_2 + 1a$ system¹² indicates that the titanium deactivated products were mostly transformed into the benzenetitanium(II) species.

In contrast to TiCl_3 ^{2,11,12}, the deactivated 1*b* system and the $\text{TiBr}_3 + \text{AlBr}_3$ system were not activated by EtAlCl_2 in the presence of butadiene and thus it must be anticipated that TiBr_3 does not exchange bromine for chlorine atoms and ethyl group of EtAlCl_2 . This is compatible with the higher affinity of Ti(III) to heavier halogen atoms as it follows from the reduction of TiCl_2I_2 with R_2AlI , yielding 99% TiI_3 ¹³. The above TiBr_3 containing systems require the action of a strong reducing agent (Et_3Al) which reduces TiBr_3 to Ti(II) products which, analogously to products of the $\text{Et}_2\text{AlBr} + 1b$ system, form the benzenetitanium(II) system after the addition of EtAlCl_2 . The interaction of different modifications of solid TiCl_3 with R_3Al and R_2AlCl compounds has been proven and formation of surface lower valent titanium compounds with coordinated organoaluminium compounds deduced from infrared spectra and analysis of gaseous products¹⁴.

In the present case, we suggest that the ethylation of the TiBr_3 surface may lead to formation of either finely dispersed TiBr_2 or soluble allyltitanium(III) compounds formed by the insertion of butadiene into the Ti—ethyl bond. Both the products can enter the cyclotrimerization catalytic cycle: TiBr_2 or other Ti(II) species are solvated with EtAlCl_2 and give the benzenetitanium(II) complex, while the allyltitanium(III) bromide may disproportionate into TiBr_2 and bis(allyl)titanium(IV) species^{9,10} which is intermediate in the catalytic cycle¹.

The more detailed investigation of the products of the TiBr_3 reaction with Et_3Al and of the deactivation products in the $\text{Et}_2\text{AlBr} + 1b$ system is precluded by instability and great complexity of the systems. Nevertheless, the finding that they form highly active benzenetitanium(II) systems by the action of EtAlCl_2 opens the possibility to exploit bromine-containing Ziegler catalysts¹⁵ for the butadiene cyclotrimerization.

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