

## THE INFLUENCE OF ALKALI METAL HALIDES ON THE BUTADIENE CYCLOTRIMERIZATION CATALYZED BY (BENZENE)TITANIUM(II) COMPLEXES

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Addition of alkali chlorides (MCl) to  $(\eta^6\text{-C}_6\text{H}_6)\text{Ti}(\text{AlCl}_4)_2$  (*Ia*) decreases the catalytic activity of *Ia* while the selectivity of the (*Z,E,E*)-1,5,9-cyclododecatriene formation is improved only when NaCl is used at the optimum molar ratio  $\text{NaCl}/Ia \sim 5$ . The alkali chlorides remove free  $\text{AlCl}_3$ , which is present in the system as an admixture, probably in the form of  $\text{MAlCl}_4$  complexes; however, an excess of MCl brings about the decomposition of catalytic trinuclear Ti(II) complexes during the butadiene cyclotrimerization. In addition to inactive  $\text{TiCl}_2$ , this decomposition yields some  $\text{AlCl}_3$  which induces the formation of cationic byproducts, 1-phenylbut-2-ene and (*E*)-1,4-poly(butadiene), before it is deactivated or quenched with MCl.

The activity and selectivity of the titanium catalysts producing (*Z, E, E*)-1,5,9-cyclododecatriene ((*Z, E, E*)-CDT) from butadiene have been optimized by changing the nature and molar ratio of the titanium and aluminium components in the catalytic system and/or by adding modifiers.<sup>1-3</sup> The (benzene)titanium(II) complex,  $(\eta^6\text{-C}_6\text{H}_6)\text{-Ti}(\text{AlCl}_4)_2$  (*Ia*) was found to be a highly active catalyst; however, it produced a considerable amount of byproducts<sup>4</sup> (polymer 22% and waxy polymer 13%, at 60°C). Their formation was ascribed to the cationic activity of the  $\text{AlCl}_3$  component of the complex which was consistent with the observation that the byproduct formation was suppressed by addition of organic electron donors or alkali halides<sup>4</sup>. We have, however, recently shown that pure complex *Ia* produces a maximum of 2% of low-molecular cationic products and a maximum of 8% of polymer<sup>5</sup> and thus it seems to be highly probable that crude *Ia* was used in the cited work<sup>4</sup>, i.e. containing certain amounts of free aluminium chloride which could be at least partly removed by the modifiers. Since the purification of crude *Ia* consists of repeated precipitation with n-hexane from concentrated benzene solutions<sup>6</sup>, which is difficult to carry out on a large scale, the suppression of the formation of cationic products in the "in situ" prepared systems by adding organic electron donors or alkali halides is the subject of numerous patents, e.g., refs<sup>7-12</sup>.

Here we describe the influence of various alkali halides MX (M = Li, Na, K, Rb; X = Cl, Br) on the kinetics and selectivity of the butadiene cyclotrimerization in-

duced by *Ia* and  $(\eta^6\text{-C}_6\text{H}_6)\text{Ti}(\text{AlBr}_4)_2$  (*Ib*). This study was carried out to establish the mode of interaction of alkali halides with the reacting catalytic systems and to find the limitations of this method for suppression of the cationic activity.

## EXPERIMENTAL

**Chemicals.** The complexes  $\text{C}_6\text{H}_6\cdot\text{Ti}(\text{AlX}_4)_2$  ( $\text{X} = \text{Cl}$  (*Ia*),  $\text{Br}$  (*Ib*)) were prepared as described elsewhere<sup>6</sup>. They were purified by repeated precipitation from benzene solution with hexane.  $\text{Et}_3\text{Al}$  and  $\text{Et}_2\text{AlCl}$  were the same as used previously<sup>13</sup>. Aluminium trichloride was prepared from the reaction of  $\text{CCl}_4$  vapour with powdered aluminium metal (99.999%). A colourless crystalline material was obtained by distillation of the crude product with aluminium powder.  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{RbCl}$  and  $\text{KBr}$  (Lachema, Brno, p.a.) were dried in a vacuum oven at  $200^\circ\text{C}$  and stored over  $\text{P}_2\text{O}_5$ .

**Methods.** The kinetics of the butadiene conversion have been measured in a high-vacuum apparatus at constant butadiene concentration and temperature. Standard experimental conditions were  $[\text{Ti}] = 1.29 \cdot 10^{-3} \text{ mol l}^{-1}$ ,  $[\text{C}_4\text{H}_6] = 6.36 \cdot 10^{-2} \text{ mol l}^{-1}$ , volume of the catalyst solution  $30 \text{ cm}^3$  (at  $20^\circ\text{C}$ ), the reaction temperature  $50^\circ\text{C}$ . The powdered alkali halides were weighed and transferred to the reactor under argon. The reactor was then heated to  $100^\circ\text{C}$  under a vacuum of up to  $10^{-5} \text{ Torr}$  ( $10^{-3} \text{ Pa}$ ) for 1 h. The catalyst solutions were added and stirred with alkali halides at  $35^\circ\text{C}$  for 60 min. The values of butadiene consumption were determined after each 60 s. Descriptions of the apparatus in detail, the measurement procedure; isolation of the products and identification by means of gas chromatography and infrared spectrometry were published earlier<sup>5</sup>.

## RESULTS AND DISCUSSION

The presence of free aluminium chloride decreases the rate of the butadiene cyclotrimerization catalyzed by *Ia* whereas it induces a very rapid butadiene consumption immediately after introduction of butadiene (Fig. 1). The retarding effect of  $\text{AlCl}_3$  on the rate of butadiene cyclotrimerization with *Ia* is analogous to that observed

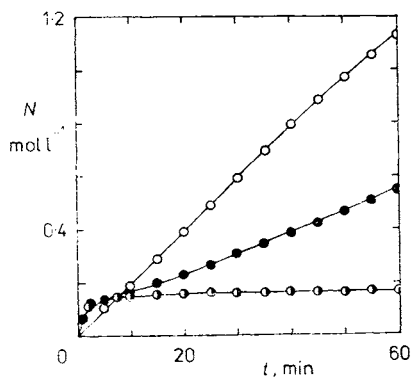


FIG. 1

Kinetics of the butadiene consumption catalyzed by *Ia* ( $\circ$ ), *Ia* +  $1.0 \text{ AlCl}_3$  ( $\bullet$ ), and  $\text{AlCl}_3$  ( $\circ$ ) (standard conditions,  $[\text{AlCl}_3] = 1.29 \cdot 10^{-3} \text{ mol l}^{-1}$ )

in the presence of  $\text{EtAlCl}_2$  (ref.<sup>13</sup>). This effect can be brought about by the solvation of *Ia* with an aluminium Lewis acid thus preventing the access of butadiene to the titanium ion. The initial rapid butadiene consumption is due to the cationic catalysis by  $\text{AlCl}_3$  itself in the rigorously anhydrous medium, which is ensured by the presence of the Ti(II) complex. In the blank experiment with  $\text{AlCl}_3$  alone, however, the butadiene consumption ceased in a later stage (Fig. 1).

The presence of  $\text{AlCl}_3$  in the *Ia* system induces the formation of byproducts arising from the Friedel–Crafts reactions between butadiene and benzene, 1-phenylbut-2-ene dominating; differences in the abundance of higher butadiene–benzene oligomers between the *Ia* +  $\text{AlCl}_3$  and  $\text{AlCl}_3$  systems, although noticeable, were not studied in detail. The presence of  $\text{AlCl}_3$  in the *Ia* system also increases the percentage yield of (*E*)-1,4-poly(butadiene) (PB) which inherently accompanies the (*Z,E,E*)-CDT formation<sup>5</sup> on *Ia* (Table I). This shows that the solvation of *Ia* with  $\text{AlCl}_3$  retards the polymerization to (*E*)-1,4-PB to a lower extent than the cyclotrimerization reaction.

It becomes apparent from results presented in Fig. 1 and Table I that the selective elimination of free  $\text{AlCl}_3$  from the *Ia* system should lead to an increase in its activity and selectivity in the (*Z,E,E*)-CDT formation. The alkali chlorides form complexes with the aluminium chloride, which is present in solution largely as a dimer<sup>14</sup>, to give  $\text{M}^+(\text{AlCl}_4)^-$  or  $\text{M}^+(\text{Al}_2\text{Cl}_7)^-$ . As indicated by spectroscopic studies in molten state, the  $\text{AlCl}_4^-$  anion is generally more stable than  $\text{Al}_2\text{Cl}_7^-$  (ref.<sup>15</sup>). The study of interaction of  $\text{Al}_2\text{Cl}_6$  with  $\text{MCl}$  and the structure of the product(s) in aromatic hydrocarbons, which would be relevant to the above catalytic application, is hampered by the low solubilities of all the components. However, the complexes  $\text{M}^+(\text{AlCl}_3\text{Et})^-$  are readily formed using a weaker Lewis acid<sup>16</sup>,  $\text{EtAlCl}_2$ . The ability of alkali chlorides to remove  $\text{AlCl}_3$  from solution was demonstrated by adding a ten-fold excess of  $\text{MCl}$  to the  $\text{AlCl}_3$  solution in benzene. After stirring for 1 h at 35°C, the system appeared to be practically inactive to the admitted butadiene. On the other hand, no decrease in the concentration of *Ia* was observed by electronic absorption spectroscopy (for the spectrum, see refs.<sup>5,6</sup>) after analogous treatment of the *Ia* solution with any of the alkali chlorides used. The influence of the alkali metal chlorides on the catalytic behaviour of pure *Ia* and in the presence of added  $\text{AlCl}_3$ , as well as an analogous study on the *Ib*–KBr system, are described below.

#### The *Ia* + *n* NaCl Systems (*n* = 1–200)

The kinetic curves for these systems show (Fig. 2) that an increasing amount of NaCl induces faster and stronger deactivation of the catalyst. At *n* = 200 the system turned inactive shortly after admission of butadiene and the product of deactivation formed a fine dark precipitate. The butadiene products display a slight decrease in percentage yields of (*E*)-1,4-PB and 1-phenylbut-2-ene with a minimum at *n* = 5, however, at

TABLE I

Characteristics of the butadiene cyclotrimerization catalyzed by the  $C_6H_6 \cdot Ti(AlCl_4)_2$  (*Ia*) + MCl (M = Li, Na, K, Rb) and  $C_6H_6 \cdot Ti(AlBr_4)_2$  (*Ib*) + KBr systems

Catalytic system <sup>a</sup>	Butadiene conversion after 1 h, mol l <sup>-1</sup>	Reaction rate after 1 h 10 <sup>-5</sup> mol l <sup>-1</sup> s <sup>-1</sup>	Composition of the oligomer fraction <sup>b</sup> , %			Polymer <sup>c</sup> wt. %
			PhB	( <i>Z,E,E</i> )-CDT	( <i>E,E,E</i> )-CDT	
<i>Ia</i>	1.12	23.8	2	98	trace	8
+ 1 AlCl <sub>3</sub>	0.54	13.3	38	62	0	23
1 NaCl	0.96	20.4	2	98	trace	7
5 NaCl	0.80	10.5	1	99	trace	6
20 NaCl	0.62	6.9	1.5	98	0.5	9
40 NaCl	0.43	0.8	4	95	1	13
200 NaCl	0.08	0	—	—	—	—
5 LiCl	0.71	9.8	2	96	2	7
5 KCl	0.61	8.0	4	93.5	2.5	10
5 RbCl	0.52	5.6	6	91	3	12
<i>Ib</i>	0.81	6.9	1	99	trace	5
+ 2 KBr	0.47	3.2	2	96	2	6
3 KBr	0.21	0	5	92	3	8
5 KBr	0.04	0	—	—	—	—

<sup>a</sup> Standard conditions:  $[Ti] = 1.28 \cdot 10^{-3} \text{ mol l}^{-1}$ ,  $[C_4H_6] = 6.36 \cdot 10^{-2} \text{ mol l}^{-1}$ , solvent benzene 30 cm<sup>3</sup>, temperature 50°C. <sup>b</sup> Gas chromatographic analysis (wt. %); figures for PhB (1-phenylbut-2-ene) include the contents of other products of the Friedel-Crafts addition of benzene to butadiene (1,3-diphenylbutane was isolated, the presence of the other components was deduced from GC MS measurements). <sup>c</sup> The polymer was (*E*)-1,4-PB according to infrared spectra; a low amount of cross-linked polymer due to cationic activity of aluminium halides would not be registered by this method.

higher values of  $n$  the percentage yields of the both byproducts as well as that of  $(E, E, E)$ -CDT increase with increasing magnitude of  $n$  (see Table I). These figures prove that the cationic activity of these systems passes through a minimum at  $n = 5$  while the overall activity steadily decreases with increasing magnitude of  $n$ . The systems  $Ia + 5 MCl$  were further selected to compare the effect of different alkali metal cations.

#### The $Ia + 5 MCl$ Systems ( $M = Li, Na, K, Rb$ )

The kinetic curves in Fig. 3 and results in Table I indicate that the higher the extent of the deactivation, the higher is the cationic activity of the system. Both the overall catalytic activity and the selectivity of the  $(Z, E, E)$ -CDT formation decrease in the order of the salts  $NaCl > LiCl > KCl > RbCl$ . All systems with added  $MCl$  thus decrease the catalytic activity of  $Ia$  and only those containing  $NaCl$  at  $n = 1-5$  slightly increase its selectivity.

Since  $Ia$  is virtually stable with respect to alkali chlorides, as also follows from very small differences in the initial reaction rates in the  $Ia$  and  $Ia + 5 MCl$  systems (Fig. 3), the enhanced deactivation of the catalyst during the butadiene cyclotrimerization implies that (at least) one of the catalytic transient complexes<sup>5</sup> is more apt to react with the alkali chlorides. To explain the observed increase of the cationic activity in all of the  $Ia + 5 MCl$  systems except  $NaCl$ , it is necessary to suppose that the affinity for alkali halides ought to be comparable for this transient complex and the aluminium chloride dimer. The decomposition of a trinuclear complex by the reaction with  $MCl$  according to Eq. (A) should produce a binuclear complex, however, with rather low stability. It can be expected to decompose according to Eq. (B) to  $TiCl_2$  and free  $AlCl_3$  which acts as the cationic catalyst till it is deactivated or quenched with  $MCl$ .

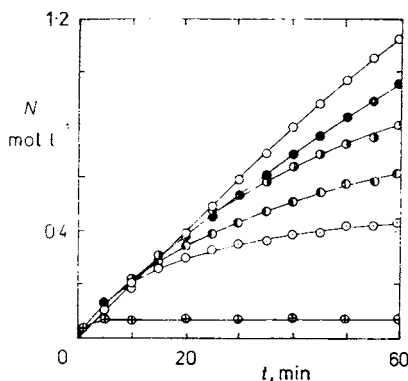
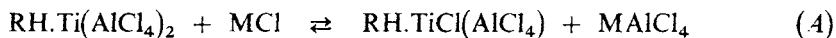


FIG. 2

Kinetics of the butadiene consumption catalyzed by the  $Ia + n NaCl$  systems under standard conditions:  $n = 0$  (○), 1 (●), 5 (⊙), 20 (⊖), 40 (⊗), and 200 (⊕)



(RH — a hydrocarbon ligand associated with Ti during the formation of (Z, E, E)-CDT)

This mode of the catalyst deactivation thus yields a dark precipitate of  $\text{TiCl}_2$ , whereas deactivation in the cyclotrimerization reaction, which is assumed<sup>5,13</sup> to be induced by the electron transfer  $\text{Ti}(\text{II})$ -to-RH, yields a rusty-yellow precipitate<sup>17</sup> of  $\text{TiCl}_3$ .

It can be concluded that NaCl is the most convenient modifier among alkali halides since its presence induces the least deactivation of *Ia* during the catalytic reaction (Fig. 3) while it removes free  $\text{AlCl}_3$  in a relatively low excess ( $n = 5$ ). The efficiency of its use was examined in the systems composed of *Ia* and 0.1 equivalent of  $\text{AlCl}_3$ . This system produced 20% phenylbutene and 11% (*E*)-1,4-PB in addition to (Z, E, E)-CDT while the addition of 1 equivalent of NaCl decreased the content of phenylbutene to 3% and (*E*)-1,4-PB to 9% (after consumption of  $0.6 \text{ mol l}^{-1}$  of butadiene in both experiments). The catalytic activity in the latter experiment was, however, 10% lower. These results indicate that the optimum application of NaCl would be such that all free  $\text{AlCl}_3$  should be consumed prior to the butadiene admission while a minimum amount of NaCl should remain unreacted in the catalytic system.

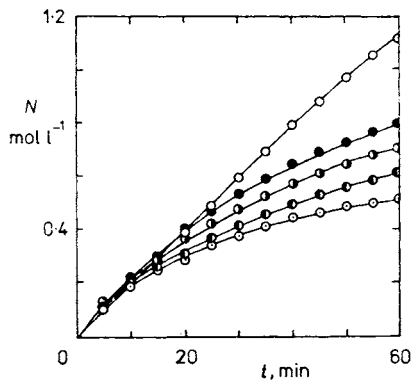


FIG. 3

Kinetics of the butadiene consumption catalyzed by the *Ia* + 5 MCl systems under standard conditions: no MCl (○), NaCl (●), LiCl (◐), KCl (◑), and RbCl (◒)

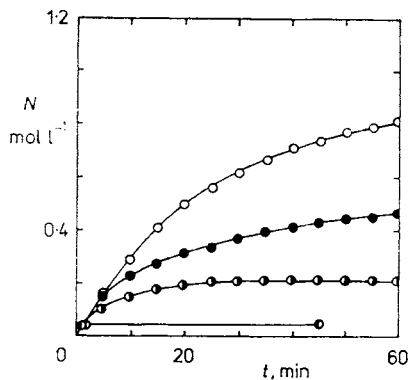


FIG. 4

Kinetics of the butadiene consumption catalyzed by the *Ib* +  $n$  KBr systems under standard conditions:  $n = 0$  (○), 2 (●), 3 (◐), and 5 (◑)

*The Ib + n KBr Systems (n = 1–5)*

In contrast to *Ia*, complex *Ib* displays a higher initial rate of butadiene cyclotrimerization and more rapid deactivation<sup>5,18</sup>. The selectivity for the (*Z,E,E*)-CDT formation is very high (Table I) and a further improvement through addition of alkali bromides could hardly be expected. The experiments with addition of KBr to *Ib* should, however, confirm our conclusions on the deactivation mechanism of *Ia* in the presence of alkali chlorides.

It follows from Fig. 4 and Table I that complex *Ib* is deactivated very rapidly in the presence of a much smaller excess of KBr than in the chloro systems and the deactivation is analogously accompanied by higher percentage yields of the cationic by products. Complete deactivation of *Ib* was observed for  $n = 3$  after 30 min reaction time and for  $n = 5$  nearly immediately (Fig. 4). The deactivation product formed a fine dark precipitate. These systems were reactivated by adding 40 equivalents of EtAlCl<sub>2</sub>, with a reaction order with respect to butadiene of 1.8, which is a value that is typical for catalysis by Ti(II) trinuclear complexes<sup>5,13,17</sup>. Since it is known that, in contrast to TiBr<sub>2</sub>, TiBr<sub>3</sub>, the main deactivation product of *Ib* in the absence of KBr, cannot be reactivated<sup>18</sup> by adding EtAlCl<sub>2</sub>, the above results imply that the KBr-induced deactivation product of *Ib* was mainly TiBr<sub>2</sub>.

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